

Foreword

Dr. Ramachandra Rao of Mineral Processing group at McGill University, has been the principal driving force behind a series of International Symposia on Waste Processing and Recycling in the Minerals and Metals Industries and has been Editor-in-Chief of the Proceedings for the last three Symposia. The proceeding for all five International Symposia held since 1992 have been published by the Metallurgical Society of the Canadian Institute of Mining and Metallurgy and have been an important reference and stimulus to environmental improvement by the metallurgical and minerals industries.

This experience coupled with many years in the academic world in the mineral-processing field has provided the background for this current undertaking in which key information from a host of publications has been assembled under a single cover for ready reference by all interested organizations and individuals.

This new text focuses on documenting the large number and diversity of processes that have been devised for recovering minerals and metals from industrial by-products, manufacturing and post consumer wastes and outlining the technical and scientific principles underlying these processes.

Each of the twelve chapters has an introduction to help put the contents of the chapter into industrial content. The evaluation of the technical and economic merits of the many processes and techniques described is left to the reader since in many cases these are sensitive to current and local conditions even when the information for specific cases is available.

The text is intended to help those in industry and academia seeking improved technology in this field to see where others have gone and to build on the innovative efforts of previous investigators. Some of these processes are widely used and accepted, others have yet to leave the researchers bench. Both embody techniques and principles that may provide the basis for new and important industrial processes to greatly increase the proportion of secondary resources that are recovered and used beneficially.

The technical world is indebted to Dr Rao for undertaking this monumental task.

Mike Sudbury
Oakville, Ontario, Canada

Preface

The mineral and metallurgical industry has resumed expansion of primary production after an extended period in which it was plagued with excess capacity. The mineral and metal recycling industry has over the same period continued to grow and improve collection, upgrading and purification techniques. The purified metal and alloys provided by the recycling industry is still a small proportion of primary production, with the possible exception of lead. This proportion is increasing over time. The quantity of industrial minerals recycled or reused in some way is still minor compared to the total global consumption of industrial minerals obtained by mining and quarrying. Again the proportion is increasing but there is still great scope for further improvement and all too often potentially useful materials end up in landfill or other forms of stockpile.

The challenges associated with increasing recovery of useful metals from solid and liquid waste streams and beneficially using industrial minerals from mining and demolition wastes have been addressed by many talented people in both a laboratory and a commercial setting, new processes investigated and results reported to the technical community at large. Almost every conference of mining and metallurgical professional engineering societies includes papers, often several sessions for presenting papers on the subject. Even more, international symposia exclusively devoted to the subject are sponsored frequently in North American or European countries.

Since 1992, once every three years, I was editor-in-chief of a series of international symposium on waste processing and recycling in mineral and metallurgical industries, sponsored by the Canadian Institute of Mining, Metallurgy and Petroleum. The experience of editing papers in a wide range of topics and also studying similar symposia each focusing on specific theme connected with the subject made me think it would be useful to systematically organize the material under appropriate topical titles leading to a comprehensive presentation of the subject. This will bring together, under each topic, the major work done by different groups of researchers and engineers, often from different countries and originally presented at conferences held at different places and times. Secondly, it will present the common objective, which connects the various topics and in many instances brings common or similar techniques used for resource recovery from sources of widely differing origins.

When I put these thoughts and intention of writing a book to my good friend and professional colleague, Michael (Mike) Sudbury, he enthusiastically supported the project. Mike is now an independent consultant in the Metallurgical and Environmental field, after many years with Falconbridge Ltd. in research, marketing and environmental affairs, and an internationally recognized Canadian leader in the area of environment and recycling in mining and metallurgical industry. He made a major contribution by reviewing several of the draft chapters and identifying many sources of information to add more useful material. I am deeply grateful for his expert advice and significant contribution of time and knowledge to the venture. I believe, this input has helped greatly to enhance the quality of this publication.

The principal focus in the book is on resource recovery and recycling. The subject is presented with technical details of the chemistry, descriptions of processes and comments on the environmental impact. Examples of ecological engineering and waste minimization are also discussed.

An introductory chapter is followed by a chapter devoted to techniques of waste characterization. The next four chapters of the book describe the principles of various techniques and processes used in recycling and resource recovery. The next five chapters discuss the subject under specific topics each focusing on recycling and resource recovery from specific class of metallurgical wastes. The last chapter discusses some of the newly developed and currently developing technologies, some of which may be successfully adopted for industrial use in future years.

It is intended that Chapters 3-6 will serve as a basic introduction to assist an understanding of fundamentals of the various processes. This should help the students specializing in a specific branch of metallurgy to appreciate the techniques and processes developed in other branches of the subject as many times it is found beneficial to employ more than one type of process to achieve best results in resource recovery and recycling. A basic knowledge of various principal techniques developed in different branches of metallurgy should also help in choosing and assessing the applicability of different techniques and processes to achieve specific objectives.

I want to thank many of my colleagues at McGill University and in industries who in various ways helped during the course of this project. First, I thank Professor Jim Finch, NSERC Industry Professor of Mineral Processing for his strong moral support and some useful suggestions. I thank Prof. Robin Drew, Department Chairman for his encouragement and for making available excellent department facilities. Dr. Cesar Gomez, my friend and colleague in the office helped in many different ways. Dr. Gerry Bolton, Dynatec Corporation, Fort Saskatchewan, Alberta and Dr. Rolando Lastra, CANMET, Ottawa sent me useful technical material. I should also acknowledge with thanks, the support of several Canadian mineral industries and research consortia, notably, Inco, Falconbridge, Teck Cominco, SGS Lakefield and COREM, and the Natural Sciences and Engineering Research Council of Canada (NSERC) for the ongoing mineral processing and environment research and education program of McGill University.

Several graduate students and associates of the department helped me in gathering and organizing technical material from various sources. Special thanks go to Dr. Luis Calzado, Dr. Mitra Mirnezami, Kevin Robertson, Mustafa Tarkan, Claudio Acuna and Fariba Azgomi. Computer assistance of Ray Langlois, mineral processing technician is greatly appreciated. Ray's daughter Stephanie did a good part of the artistic work. Graphic work was done by Armando Navaratte, E-Graph, Montreal. The secretarial help of Barbara Hanley is gratefully acknowledged.

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Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Quebec, Canada (abbreviated as CIM in the bibliography).

Chapter 2

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Chapter 1

INTRODUCTION

1.1. General Concepts

Recycling, resource recovery, waste management and environmental protection have been among the major concerns in almost all extraction and process industries. The three areas are closely integrated with each other and the importance of each has been steadily growing in the last half century. It started with awareness of environmental pollution caused by almost all major industries, both by the waste products generated, which have to be disposed off as well as by the side effects resulting from the use of a number of industrial products.

A complete waste management system today must comprise waste reduction, reuse and recycling components and byproducts, commonly referred to as 4 Rs, in addition to disposal methods such as landfill and incineration.

Reduction refers to actions that lessen the quantity of waste generated and eventually needs to be managed. It is also called waste minimization and requires adopting existing technologies in such a way as to maximize the efficiency of production and collect the byproducts and 'waste' generated and explore using them for beneficial purpose.

Reuse identifies actions based upon using something over again in its original form for the same purpose or some new one until such time as it becomes waste and needs to be managed. By these definitions, minimization has to be achieved before something becomes waste.

Once a waste is eventually generated, there are two basic options recycling and disposal. **Recycling** represents actions that manage in a way that results in using the materials making the waste as feed stocks for some product or an application distinct from disposal. This is done by segregating waste at source or by extracting materials from it by various techniques, physical, chemical, thermal or biological.

Disposal options include meeting regulatory guidelines by containment that may include solidification or encapsulation methods.

Often, the 'waste' generated in the process still contains material of potential value. With development of new technologies it is becoming possible to further process and recover the material of value. **Resource recovery**, as will be further explained serves the dual purpose of reducing the volume of the waste to be discharged and generating an economic spin-off. By-product synergy is another concept in use building on the precept that 'one man's meat is another man's poison' that is, one companies waste may be good feedstock for another operation. This is a sophisticated extension of the waste exchange concept where surplus products are listed and the list circulated to possible users of the products listed.

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1.2. Waste Minimization

Intensive waste minimization initiatives in response to the 3 R actions are steadily growing. Industrial customers can include iron and steel, utilities, nonferrous metal mining, smelting, casting, plating, chemical processing, automotive, pulp and paper, electronic enterprises and entrepreneurs to develop new products from reuse.

Waste minimization initiatives will have many significant benefits to industry and community. Some of them are:

- protecting workers, local communities and environment leading to better image and lower liability;
- substantial savings by more efficient use of raw materials leading to conservation of resources;
- lower pollution control costs and greater economic incentive;
- providing options for innovative product development by recycling;
- developing a 'sustainable' business operation.

The following factors seriously influence the development of waste minimization industry:

- stricter environmental regulations and enforcement;
- economic advantage realized by eliminating or reducing the use of landfills.
- lower liability costs by preventing or minimizing pollution;
- developing a sustainable business without environmental liability.

1.3. Waste Recycling

Metals and their alloys (steel, aluminum, copper, nickel, etc.) are traditionally recycled whereas minerals and products derived from them (e.g., fertilizer, cement) are not recycled. There is growing concern to efficiently manage minerals and the products generated in recovering them from ore bodies. These include waste rock, tailings, and slag, fly ash and dross. Most metals are not consumed (though some of them are subject to corrosion) and recycling has great environmental and economic pay off. Concentrated scraps, diluted streams and effluents, spent catalysts, arc furnace dust, plating solutions, and process water are some of the examples.

A list of recovered and recycled commodities and a comparison of capital and operating costs for producing metals from ores and scrap are shown in Tables 1.1. A comparison on the present status of recycling of various materials is shown in Table 1.2. Municipal waste estimated at 180 million tons (see Figure 1.1) is estimated to contain about 8.7 % metals, 1.6 % inorganic wastes and 8.2 % glass.

1.4. Economic Incentives for Recycling and Resource Recovery

Economics of resources recovery is determined by several factors, including availability of the raw material, costs associated with mining the ore, transportation, processing and extraction of the metals. Each one of these components is energy intensive. Energy consumption in the production of metals is therefore pervasive. In some cases such as aluminum, it is the most important item. Table 1.3 shows energy requirements of some of the major industries. Further, as will be discussed further in the chapters on specific systems of recycling (Chapters 7-10), one of the principal economic incentives is that the values of the products recovered or recycled, even if it is small relative to the overall industrial output helps to offset the cost of environmental reclamation (discussed in Section 1.5).

Table 1.1. Recovered and Recycled Commodities

Commodity	Annual amount. millions	Percent annual growth	Revenue, \$ x 10 ⁶	Added value \$ x 10 ⁶
Steel	30-40 tons	2.0	9-12,000	6-8,000
Gold	2.6-3.0 troy oz	9.0	1,200	200
Aluminum	1.5-2.0 tons	2.5	1,200	200
Copper	1.4-1.5 tons	1.5	700	150
Silver	55-65 troy oz	5.0	670	100
Superalloy	20-25 lb	15.0	200	30
Germanium	0.19-0.20 lb	6.0	96	10
Titanium	20-22 lb	10.0	55	10
Gallium	0.018-0.020 lb	50.0	6	3

Source: Charles River Associates

Table 1.2. Comparison on the Status of Various Materials

Material	Annual discards*, million ton	Post-consumer recovery, million tons	Recovery rate, %
Aluminum	2.1	0.6	28.6
Paper, paperboard	62.3	12.9	20.7
Glass	13.9	1.0	7.2
Rubber and leather	3.4	0.1	3.0
Iron and steel	11.3	0.3	2.7
Plastics	9.7	0.1	1.0
Total	100.6	14.4	14.3

*Municipal solid waste for 1984.

Source: Franklin Associates Ltd., Prairie Village, KS. (from Lakshmanan and Sridhar, 2002)

The critical efficiency of energy use in most processes range from less than 5% to 50%. The remaining exit the plants as sensible heat in combustion gases leaving the process, sensible heat on the recovered latent heat in cooling water, heat losses from process vessels and piping, and discarded chemical or latent heat in waste streams. Energy consumption can be reduced to some extent resulting in lower pollution by decreasing the quantity of off gases, cooling water and waste solids. This will require an integrated approach to plant design.

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Table 1.3. Energy Consumption in Principal Industries (from Charles River Associates, 1996; from Lakshmanan and Sridhar, 2002)).

Industry	Energy Requirement* million Btu/ton
Copper	80-100
Nickel (from sulfide ore)	200
Zinc	60
Lead	30
Steel	27-30
Nickel (from laterite ore)	600
Aluminum	280
Glass	7.4
Lime	6-8
Cement	7.6

* Includes electrical energy at 10,600 Btu/kWh

1 Btu = 1.055 kjoule

Integrated waste management source reduction and reuse receive priority; however, recycling is emphasized as it potentially prevents useful material from being combusted or land filled, thus reducing the cost of waste disposal and reducing land fills and tailing ponds. In the metals industry, recycling is one of the most effective ways of reducing energy requirement. As metal recycling is done by treating the metal or engineered material ore, the energy associated with mining the ore is eliminated. There would be some cost of collecting the scrap from various sources, but this can be minimized with a planned strategy of collection from the consuming partners, including metallurgical and engineering industries, domestic households and educational and research establishments. By these strategies, very high energy savings can be achieved; for example, it is 95% in the case of aluminum. This has still greater significance when local cost of energy is much higher compared to global cost, which provides an incentive for global competitiveness. In 1996, scrap recovery amounted to 63% for steel and almost 50% for aluminum and copper. New scrap is still continuously produced, which indicates need for performance improvement in production processes.

Similar cost savings by lower energy requirements are achieved by recovering metal values from effluents, mine tailings and sludges (discussed in Chapter 10). In this case, the major energy saving is related to the availability of the raw material in a state of ready to process. Processing of most natural ores requires the ore to be crushed and ground to a degree of fineness to ensure liberation of individual mineral species for physical methods of processing (Chapter 3) or satisfactory rate of reaction in the case of chemical processes (Chapter 4). Both crushing and grinding are energy intensive unit operations. It will not be required to process materials from the secondary sources as it is already in the required state of fineness.

A comparison of the capital costs for production of metals from virgin ores and from scrap is shown in Table 1.4. Table 1.5 records the extent of non-ferrous metal recycling. It is clear, except lead and to a lesser extent copper, there is still great scope for the growth of metal recycle industry. The rapid growth in the use of computers and cell

phones and many such devices for scientific work, communication and entertainment, has given added impetus as all these gadgets use various metals some of which are not abundantly available and have to be recovered from the used gadgets and recycled.

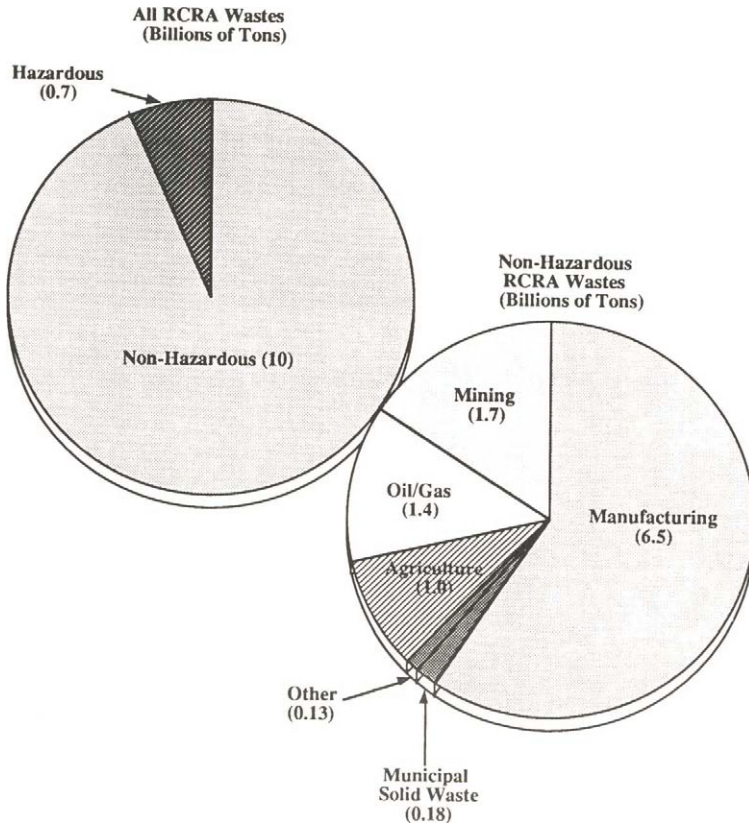


Figure 1.1. Solid Wastes from Various Sources

Note: In Figure 1.1, RCRA stands for the Resource Conservation and Recycling Act (U.S.A.) of 1976. The Act gave authority to the U.S. Environmental Protection Agency (EPA) to control hazardous waste generated from any source, including metal industries, transportation, treatment, storage and disposal. It also set forth framework of non-hazardous wastes.

Table 1.4. Capital Cost in \$/lb for Producing Metal from Scrap and Virgin Ores (from Charles River Associates; Lakshmanan and Sridhar, 2002))

	Scrap	Virgin	Ratio
Steel	0.10-0.12	0.20-0.25	2:1
Aluminum	0.2-0.3	2-3	10:1
Copper	0.2-0.3	2-4	12:1

Table 1.5. Global Value of Non-ferrous Metal Industry Recycle Production (Sudbury, 1997)

Metal	Recycle Tonnes (millions)	Recycle % Primary Metal	Recycle value US \$ (billions)
Aluminum	6.6	33	19.8
Copper	5.1	51	5.3
Zinc	0.4	6	0.4
Lead	2.6	96	1.6
Nickel	0.3	35	2.4

A third economic incentive for recycling has developed by the growing recognition, many of the byproducts and those which so far have been considered to be industrial wastes can be processed and converted into products of use in industries and households. This contributes to conservation of resources as well as additional revenue to the industry. A good example is the use of metallurgical slag, which has been processed and converted to a number of valuable products in construction industry. This area will be discussed in Chapter 9.

1.5. Environmental Incentives for Recycling

Environmental protection has been a serious concern, which has been steadily growing in the last 50 years with the increasing intensity of industrial activity in most countries. Until recently, mainly North America, Europe (including Russia) and Japan were considered as major powerhouses of industrial activity resulting in increasing amounts of industrial waste. The picture, however, is rapidly changing as in the last 10-20 years China and more recently India are also becoming major partners in worldwide industrial growth. These countries, with their huge population (1.3 billion of China and 1 billion of India) are becoming bigger consumers of resources, and as an inevitable consequence, contributors to environmental pollution.

The environmental impact of mineral and metallurgical industry is strongly felt in two areas. The first is the volume of industrial waste, effluents, tailings and sludge. Total quantity of non-economic solid products from a 60 million ton ore body with a 20 year mining life has been estimated, as shown in Table 1.6.

The general practice has been to dispose it off in tailing ponds or land fills. The practice is subject to serious and valid criticism. The principal objections are putting vast tracts of land out of reach for constructive activities, and serious health hazards associated with the toxic metals in tailing dumps and land fills. In addition, the tailings carry significant amount of water, which is a valuable resource itself. The processing of such metallurgical wastes and recovery of valuable components and in some cases converting them into useful compounds will not only help to reduce pressure on ponds and land fills but also it will, at least in part, offset the cost of environmental protection. This area will be discussed in Chapter 9.

The second serious environmental concern is the emission of carbon dioxide, a major green house gas, which has been implicated in gradual climate change round the world. The concentration of this essential compound, as vital to life as oxygen, has been rising in the global atmosphere from about 280 parts per million in 1750 to around 360 parts per million. The world has made no effort to find ways of taking advantage of this bounty

and instead have focused on the possible negative effect of this additional carbon dioxide to inhibit the escape of infra-red radiation to space and thereby cause a rise in global atmospheric and hence ocean and land temperatures. Recycling of resources will reduce the energy required to supply raw materials and thereby contributes to a reduction in the rate of increase in atmospheric carbon dioxide in the atmosphere.

Table 1.6. Total Quantity of Non-Economic Products Generated in the Mining of a 60 Million Ton Ore Body (Sudbury, 1989)

Total Production	Quantity, million tons
Waste rock	20
Tailings	48
Slag	12
Sludge	0.6
Gypsum	16.8
	Total 97.4
Used or dispersed	
Mine back-fill	26.0
Gypsum	16.8
	Total 42.8
Accumulation	
	Balance 54.6

The third, equally serious environmental issue connected with metallurgical industry is the emission of toxic gases. Sulfur dioxide, principal culprit in the formation of acid rain is an unavoidable product in the extraction of base metals from sulfide ores. Another frequently occurring waste gas is dioxin produced in the thermal decomposition of organic matter associated with raw material being processed. Technological innovations like catalytic conversion of sulfur dioxide helps to mitigate the harmful effects of toxic gas generation. Recycling of resources from scrap helps to reduce the consumption of virgin sulfide ores and reduce the magnitude of sulfur dioxide emission.

It should, however, be recognized, some of the waste treatment processes for resource recovery also generate toxic gases depending upon the composition of the waste to be processed. Dioxin and its derivatives are often produced when the waste material contains organic matter in large proportion. One example is in the treatment of exhaust batteries by thermal processes. As battery case is made of plastics containing halogens. While a large fraction is physically separated before treating the metal component, its occurrence cannot be totally avoided. The toxic gases have to be contained and decomposed in environmentally harmless ways or their generation has to be minimized, if possible totally eliminated by appropriate operating conditions. Details of such technologies will be discussed in Chapters 7-10.

1.6. The Challenge of Global Population Growth and Aspirations

Environmental protection has been a serious concern, which has been steadily growing in the last 50 years with the increasing intensity of industrial activity in most countries. Until recently, mainly North America, Europe (including Russia) and Japan were considered as major powerhouses of industrial activity resulting in increasing amounts of industrial waste. The picture, however, is rapidly changing as in the last 10-20 years China and more recently India are also becoming major partners in worldwide industrial growth. These countries, with their huge population (1.3 billion of China and 1 billion of India) are becoming bigger consumers of resources, and as an inevitable consequence, contributors to environmental pollution.

Table 1.7 shows indicative numbers on energy and water consumption together with the size, population and carbon dioxide emission for two western economies and two developing economies.

Table 1.7. Selected Indicative Comparisons (from Lakshmanan and Sridhar, 2002)

Country	Population in million (2001)	Land area in 1000 sq. km	Water Consumption		Energy Consumption 1995 GDP per unit of energy use (1987 \$ per kg oil equivalent	CO ₂ emission per capita ton, metric 1995	Motor vehicle per 1000 people
			Fresh water resource 1996, m ³ /per capita	Annual fresh water % total resource			
India	1,003	2,973	1,957	20.5	1.7	1.0	7
China	1,300	9,326	2,304	16.4	0.7	2.7	8
UK	60	242	1,208	16.6	3.5	9.3	399
USA	270	9,159	9,270	19.0	2.6	20.8	767

1.7. Energy Considerations

Table 1.8 records a comparison of energy consumption and air emissions from recycled and virgin aluminum and shows the savings, which are gained for almost every item, the exception being hydrogen chloride (which is used in most processes of aluminum wastes; see Chapters 7 and 10). Of all the metals, aluminum recycling is most widely practiced as it is used extensively in consumer items like beverage cans. Energy savings for metals in general are also very significant. One major energy saving results from the fact that the feed material to recover metals from scrap does not carry the cost of mining and grinding of the virgin ore, which are energy incentive operations.

Energy considerations are also viewed from environmental perspective. In most mineral processing and metallurgical operations, energy requirements are met through conventional thermal energy sources, coal, and natural gas. An unavoidable consequence of their use is the generation and emission of carbon dioxide. This is not a toxic gas as carbon monoxide and sulfur and nitrogen oxides shown in table 1.8, but it is a major contributor to the greenhouse effect. Alternative, renewable energy sources like wind power, solar and hydro-electricity, which do not produce greenhouse gases are useful, but their availability varies with regions.

Table 1.8. Energy Consumption and Emissions from Recycled and Virgin Aluminum Production (McDougall *et al.*, 2001)

Source	Recycled aluminum/ton produced	Virgin aluminum/ ton produced	Savings/ton recycled aluminum produced	Savings/ ton aluminum used
Energy consumption (GJ)	15.6	171.2	155.6	147.8
Air emissions				
Particulates	1222	37,388	36,166	34,358
CO	474	17,713	17,239	16,377
NO _x	2527	27,711	25,184	23,925
N ₂ O	252	1676	1421	1350
Sox	7.90	75,793	68,703	65,268
HCl	760	50	- 710	- 675
HF	0	254	254	241
Total HC	4753	39,870	35,117	33,361
Ammonia	3	20	17	16
Water emissions				
Biological oxygen demand	1	799	798	758
Chemical oxygen demand	3	19,020	19,017	18,066
Suspended solids	1	6	5	4.8
Total organic compounds	28	173	145	138
Solid waste	237.6	87,605	638.9	607.0

Note: Biological oxygen demand (BOD) refers to the oxygen consumed by biologically oxidizable matter in the system.

Chemical oxygen demand (COD) is the total oxygen consumed for the oxidation of all reducing matter in the system.

1.8. Life Cycle Analysis of Materials Recycling

Life cycle analysis is the tool by which a product's impact on the environment through its lifetime is evaluated. In the context of recycling, it helps to determine if waste reduction, recycle, resource recovery or disposal is the best practicable environmental option. It has been extensively applied in solid waste management (McDougall *et al.*, 2001). The analysis quantifies the energy and raw materials used and solid, liquid and gaseous waste produced at each stage of the process, as schematically shown in Figure 1.2. It can be specially useful in comparing the environmental impact of a product made by recycling and the same made from virgin materials.

Life cycle analysis (LCA) of a product, for example, a metal requires detailed measurements in the manufacture of the product from the mining and processing of the ore, including the energy input for mining, transportation, grinding, separation of the minerals, and extraction and refining of the metal, possible re-use or recycling, and final

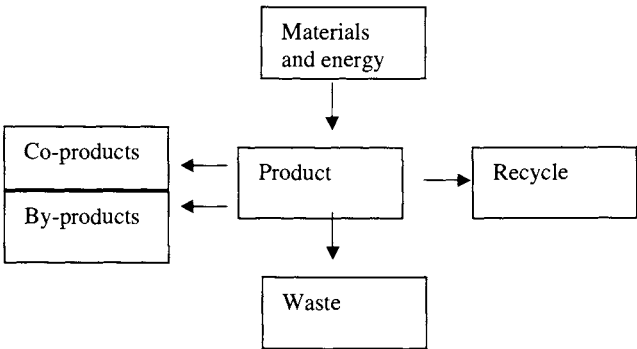


Figure 1.2. Life-cycle analysis, schematic (Warner Bulletin 46, 1995)

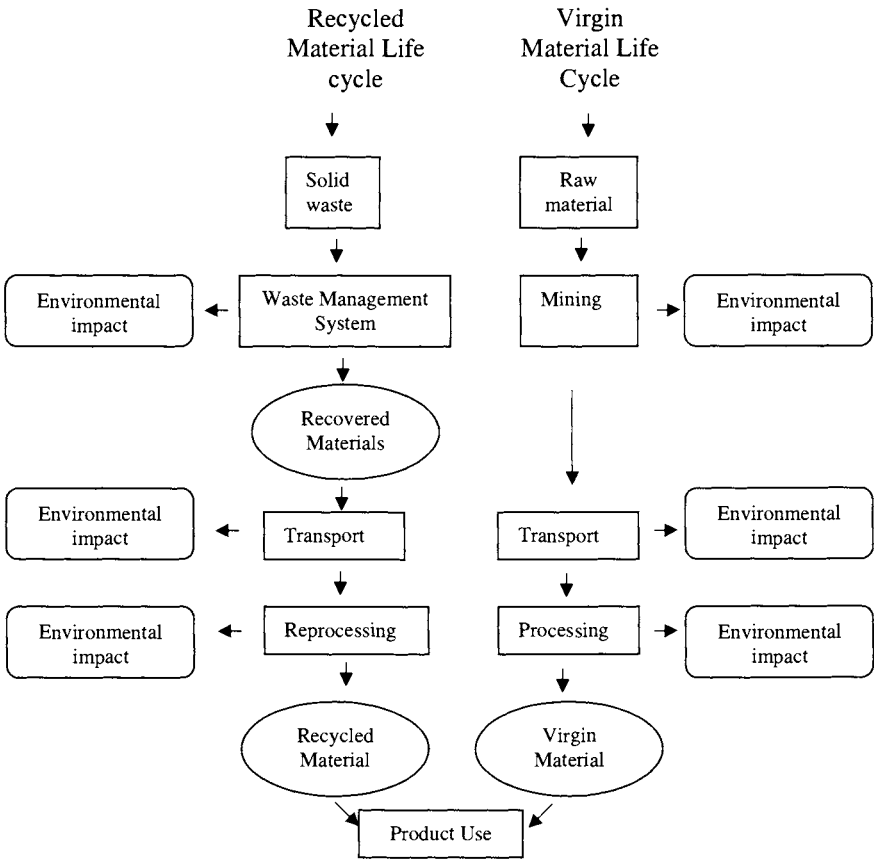


Figure 1.3. Life-cycle assessment for recycled and virgin materials (modified from White *et al.*, 1995)

disposal. Boundaries of the life cycle analysis and the methodologies vary from one system to another. For example, some analyses include the environmental impacts related to emissions to air, water and on to land when the final waste is disposed of as compared with incineration. Others may, in addition, include the life cycle analysis of the machinery used in the processes.

In the first stage of LCA the data relevant to the processes in the manufacture of a product are collected. These data are interpreted in the second part. For example, the production of copper cable involves extraction of copper metal from its sulfide mineral, which in turn, has to be separated from the natural chalcopryrite ore. The extracted metal has then to be refined and cast into the form of cable. Each of the stages involves input of energy. There are additional cost of transportation and the raw material itself, and the environmental costs resulting from emission of sulfur dioxide, which has to be contained, either by reduction to elemental sulfur or conversion to sulfuric acid. There could be some credit by the sale of sulfur or sulfuric acid, but they are not likely to offset the environmental cost. Environmental impact is often difficult to assess as it involves emission of pollutant gases, which could affect the ozone layer., contribute to acid rain or global warming. Often, such environmental impacts are aggregated together.

Similar data are gathered for the process for the manufacture of copper cables from the metal recovered from secondary sources like metal scrap or metallurgical dust. Life cycle for recycled products includes the evaluation of environmental impacts in terms of energy used and emissions at each stage of recycling. These include the separation of the recyclable materials from the metallurgical waste, transportation to the proceeding plant and the various processes to convert the recovered material into the desired products. LCA comparing recycling with manufacture of the product from virgin material often shows the benefits of recycling, as shown before in Table 1.4. The comparison is schematically represented in Figure 1.3.

While life cycle concept is useful in evaluating environmental impact of a product, it has some serious limitations. Sudbury (1997) has listed some of them, which should be considered;

- it requires assumptions
- neglects inventory
- ignores time factors
- processing considerations are not fully taken into account
- changing economic viability is difficult to assess.

The results of life cycle analysis, therefore, have to be interpreted with caution.

Extensive work on LCA has been conducted in the Netherlands, in particular for life cycle impact of passenger car. (Castro and Remmerswaal, 2001; Castro *et al.*, 2003). For a more detailed discussion on the limits of recycling determined by physics, chemistry, economics and process technology, the reader is referred to a recent book by Reuter and coworkers (2005).

1.9. Industrial Ecology

An important aspect of resource recovery and recycling is creation of synergies between various branches of metallurgical processes, sometimes including other operations like chemical process industry and agriculture. It begins with the understanding that waste generated in one process may be converted to be a feed stock for another process. Alternatively, the waste generated in one process may be useful to

treat the waste generated in another. Such synergy between two industrial waste sources is called industrial ecology. A few examples will be described in the book.

1.10. Waste Minimization or Recycling?

Waste minimization, or ideally, elimination of waste is a much sought after objective. Technological advances in recent years, coupled with scientific understanding of the processes occurring, have led to new developments towards achieving this goal. Several examples of in-plant recycling and total utilization of all reaction products leading to elimination of waste will be described in the book. It has to be recognized, however, that recycling continues to be and will remain so for many years to come a major occupation in metallurgical industry for two main reasons. Firstly, metals are a finite source. In industrialized countries, virgin sources of metals, natural ores, are steadily getting depleted. Recycling of metals from scrap, discarded metal products and engineered materials is an obvious necessity to ensure availability of the metals in desired quantities. Secondly, in many metallurgical processes, nature of the reactions is such that products of no direct value for the primary metal industry are inevitably generated. Often considered to be 'waste' many of them find their way into landfills or tailing ponds. Furthermore, such waste products have accumulated in huge quantities and call for serious action for resource recovery and environmental reclamation. Resource recovery from such 'waste' or converting them to useful by-products is a growing necessity as discussed in Section 1.5. They will be increasingly in demand to achieve the goal of **sustainable development**, constant industrial growth for healthy living standards, which requires clean environment and uninterrupted availability of resources. The major part of the book will be devoted for description and discussion of technologies, which have developed to achieve the twin objective of resource recovery and environmental reclamation with reference to various kinds of mining and metallurgical waste.

Selected Readings

- McDougall, F. R., White, P. R., Franke, M., Hindle, P., 2001. *Integrated Solid Wastes Management: A Lifecycle Inventory*, 2nd edition, Oxford University Press, Maiden, MA.
- Reuter, M. A., Heiskanen, K., Boin, U., van Schaik, A., Verhoef, E., Yang, Y. and Georgalli, G., 2005. *The Metrics of Material and Metal Recovery*, Elsevier, Amsterdam.
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Chapter 2

WASTE CHARACTERIZATION

2.1. Introduction

Before exploring methods for waste processing and resource recovery, it is necessary to characterize the waste, both in terms of chemical and mineralogical composition. Chemical composition is determined by digesting the material in appropriate acids, usually hydrochloric acid and when required nitric acid, and analyzing the solution by atomic absorption spectroscopy. Other methods of solution analysis are also sometimes used depending upon the chemical nature of the material and ease of analysis. They include potentiometric titration, conductometric titrations and colorimetric methods employing spectrophotometer. Details are described in standard instrumental analytical chemistry text books; for example, Willard, Merritt, Dean and Settle (1988).

Chemical analysis provides information on the elements in the material and their percentages, but does not identify the minerals or compounds occurring in it. Therefore, in addition to establishing chemical composition of the material, it is often necessary to know the mineralogical nature of the material. This requires characterizing the specific minerals occurring in the material and how they occur together, to what extent individual compounds are liberated from each other. (Liberation refers to the state where the chemically distinct species are physically separated within a solid, for example, a waste rock. Where the two species are locked together, they are said to be not liberated.) This enables the researcher to select the kind of techniques likely to be most efficient for the separation of economically useful metals or compounds. For example, where the individual species are satisfactorily liberated, separation by one of the physical methods (to be described in Chapter 3) may be applicable as they are probably more cost effective in these cases. However, if the liberation is not satisfactory, the chemical treatment will be required. They are hydrometallurgical methods to be described in Chapters 4 and 5. Examples of the knowledge of waste characterization helping in choosing appropriate strategy for separation of the values from metallurgical rejects will be discussed in this chapter.

Many techniques for determining mineralogical composition have been developed in the last 35 years by the use of instruments, which are based on the interaction of electromagnetic radiation on the atoms of the material to be analyzed. They include X-ray diffraction (XRD), scanning electron microscope, (SEM), microprobe (MP), image analyzer (IA), proton-induced X-ray analyzer (PIXE), energy-dispersive X-ray analysis (EDX), secondary ion mass spectrometer (SIMS), laser ionization mass spectrometer (LIMS), infra-red analysis (IRA), cathode luminescence and others. Basic principles of some of the techniques commonly used in characterizing waste materials will be

described in this chapter. Further details of instruments can be found in text books on the subject; for example, Petruk (2000).

2.2. Basic Principle of Spectroscopic Techniques

In the majority of techniques, a surface is analyzed by measuring the emitted radiation after bombardment by one of electromagnetic "particle" or "wave". The particles called photons (also called "quanta") include electrons, ions, X-rays and visible light. A beam of electrons can be accelerated to a velocity close to that of light and may be tightly focused by electromagnetic lenses. An ion has a higher mass than an electron; the mass of hydrogen ion, the lightest ion is 10^{-24} g. As a result it is more difficult to produce a tightly focused beam of ions. Waves interact with atoms or molecules in materials to cause emission of secondary quanta. Figure 2.1 summarizes various excitation sources and modes of emission used in the techniques of surface analysis. For example, when a beam of electrons strikes a sample, a number of secondary particles are generated, such as low energy electrons, high energy back scattered electrons, Auger electrons, characteristic X-rays and ions. Different techniques have been used to measure these secondary quanta.

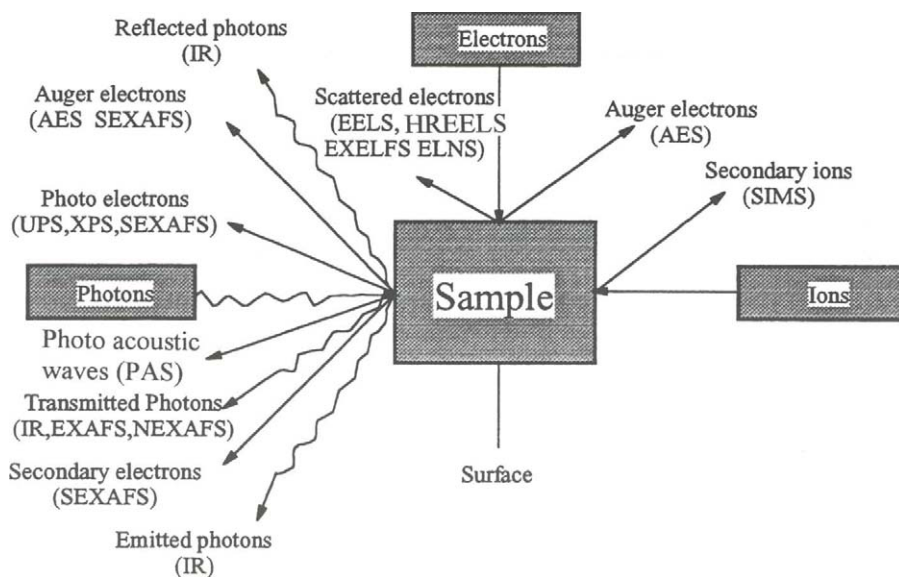


Figure 2.1. Schematic representation of spectroscopic techniques. (Courtesy, S. H. R. Brienne and Q. Zhang, McGill University Professional Development Seminar, 1996).

Abbreviations: IR, infra red; AES, Auger Electron Spectroscopy; PAS, Photo Acoustic Spectroscopy; SIMS, Secondary Ion Mass Spectrometry; XPS, X-Ray Photoelectron Spectroscopy; EELS, Electron Energy Loss Spectroscopy; HREELS, High Resolution Electron Energy Loss Spectroscopy; EXELFS, Extended Electron Energy Loss Fine Structure; ELNS, Electron Energy Loss Near-edge Spectroscopy; EXAFS, Extended X-ray Absorption Fine Structure; NEXAFS, Near Edge X-ray Absorption Fine Structure; SEXAFS, Surface EXAFS; UPS, Ultraviolet Photoelectron Spectroscopy.

In order to perform meaningful surface analysis it is necessary to know the physical properties of the excitation beam together with the physics of interaction with the sample and the character of the emitted particles. Among the approaches in use, the ones using electrons as the excitation source achieve the highest spatial resolution, the ones using photons achieve the highest energy resolution, and the ones using ions achieve the highest sensitivity.

2.3. Infrared Spectroscopy

Infrared (IR) radiation spans the spectrum from approximately 1300 to 10 cm^{-1} (the unit cm^{-1} is called wave number, reciprocal of wave length.) or wave length range 0.78 to $1000\text{ }\mu\text{m}$ ($1\text{ }\mu\text{m}$, also called micron $= 10^{-4}\text{ cm}$.) Infrared absorption by organic molecules follows the same principle as described for UV/visible absorption. Infrared spectroscopy is not often used for quantitative analysis, but it is a powerful tool for characterizing organic compounds. The infrared absorption arises as at temperatures above absolute zero, all atoms in molecules are in continuous vibration with respect to each other. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed on the molecule, it absorbs radiation. (Frequency $= c/\lambda$, where c is the velocity of light and λ is the wave length.) The major types of molecular vibrations are stretching and bending. IR radiation is absorbed and the associated energy is converted into three types of motion. Each vibration corresponds to an IR frequency (denoted by wave number in the IR spectrum). In an IR spectrum percent absorption is plotted as a function of wave number, which is reciprocal of wave length. IR spectroscopy can be performed in transmission, reflection and emission modes, as shown Figure 2.1.

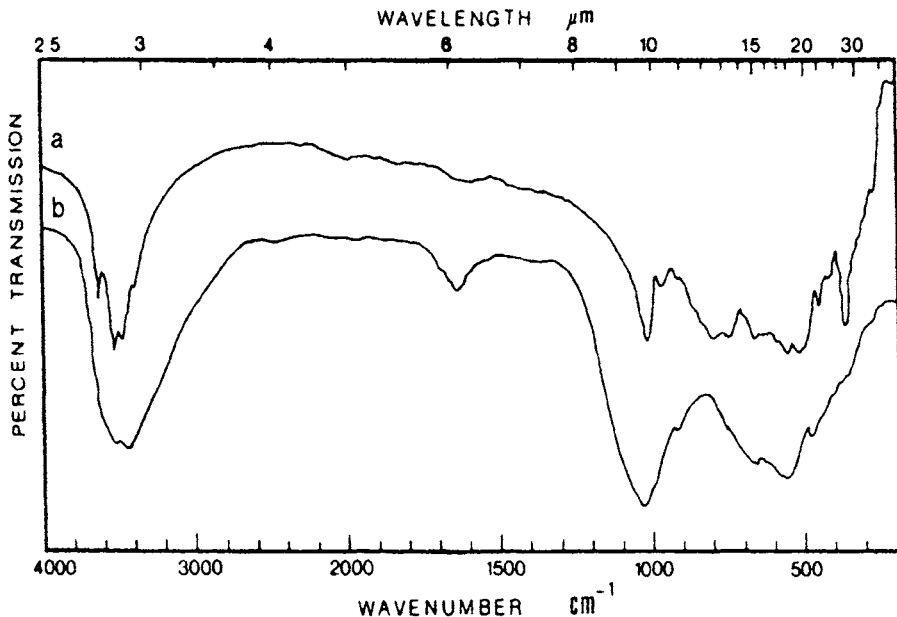


Figure 2.2. Example of an IR spectrum. (a) Gibbsite ($\text{Al}(\text{OH})_3$), (b) Gibbsite-like mineral ($\text{Al}(\text{OH},\text{F})_3$). (From Jambor *et al.*, 1990).

Infrared spectroscopy is used to identify minerals containing tightly bound molecular groups such as CO_2 , SO_4 , OH , etc.; for example, lead sulfate mineral, anglesite PbSO_4 and hydroxy carbonate mineral like malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$. The irradiation by infrared absorption causes changes, which are specific for each mineral, in the vibrational energy of the constituent molecules in the material (Jones, 1987). The changes are recorded as absorption bands at different wavelengths for each molecule group.

Infrared spectroscopy is useful for identification, but it is not frequently at present as more sensitive techniques have been developed.

2.4. Scanning Electron Microscopy

The scanning electron microscope (SEM) uses electrons to form an image. It has a large depth of field and produces images of high resolution, which means that closely spaced features can be examined at high magnification. Preparation of the samples in polished sections is relatively simple since most SEMs only require the sample to be conductive. These advantages make the SEM one of the most frequently used techniques in characterizing waste material.

The conventional SEM uses a beam of electrons focused by electromagnets onto a spot on the test specimen. The electron beam originates from a field emission gun.. A voltage is applied to the filament, causing it to heat up and shed electrons; it functions as cathode. The anode attracts and rapidly accelerates these electrons. Some accelerate past the anode and on down the column, to the sample. The field emission cathode is usually a single crystal tungsten fashioned into a sharp point and spot-welded to a tungsten hairpin. Radius of its tip is 100 nm or less, which enables the electric field to be focused to a high degree. A current density up to 105 A/cm^2 may be obtained from a field emitter.

Three main signals are emitted by interaction of electron beam with the sample. They are:

- (1) **Secondary electrons:** These ejected electrons are low energy, weakly bound electrons. Due to their low energy, they cannot travel far before they are recaptured. They can only be detected if they have escaped from or near the surface of the sample. The secondary electron signal carries topographic information about the sample.
- (2) **Backscattered electrons.** If a primary electron (an electron source from the source beam) strikes the nucleus of a sample atom, an elastic collisions may occur. The rebounding electron is called backscattered electron. These electrons are more energetic than secondary electrons and can escape from deeper within the sample. The elements with higher atomic number backscatter more electrons than those with lower atomic numbers. The backscattered signal thus provide compositional information.
- (3) **Characteristic X-rays.** When an electron beam ejects an inner shell atomic electron from its orbital, outer shell electrons jump in to fill the vacancy. The energy associated with this jump is emitted as an X-ray, whose energy is characteristic of the atom from which it came. This type of signal provides elemental information about the sample.

The **scanning electron microscope (SEM)** produces an electron beam under high vacuum. This beam is either scanned over the entire sample, or is focused on a grain in the sample. The sample should be coated by a thin layer of carbon or gold to prevent charging on the sample. The irradiated material in the sample produces **back scattered**

electrons (BSE), secondary electrons (SE), X-rays and other signals. The BSE detector displays the BSE signal on a CRT screen as a grey level image, which shows the distribution of the minerals in the polished or thin section. Most silicate minerals appear dark grey in BSE images as they have low average atomic numbers. In contrast, minerals of heavy metals (like Cu, Ni, Zn) appear in shades of light grey to white as they have higher atomic numbers. The differences in the shades of grey between the minerals can be either enhanced or reduced by changing the contrast, brightness, voltage and current on the SEM.

X-ray signals are detected with **energy dispersive X-ray analyzer (EDS)**. The EDS detector sends the X-ray signal to the EDS analyzer, which sorts the signal into the different elements present in the particle, and into X-ray counts for each element. The X-ray counts are recorded and displayed as peaks on a CRT screen. The EDS analyzer is programmed to perform either semi-quantitative or quantitative analysis if the X-ray signal is obtained from a smooth flat surface. The signals from irregular surfaces, however, are adequate for even qualitative analysis of the element contents because of interference from the rough sample surfaces. Such interference may be reduced by changing the working distance.

The standard EDS detector employs can detect elements which are heavier than sodium (atomic number 11). Light element EDS detectors which can detect elements heavier than boron (atomic number 5) including carbon (atomic number 6) and oxygen (atomic number 8) are also employed where necessary.

An optimized BSE image is sufficiently sensitive to display very small changes in average atomic number of a mineral, which is taken advantage of to estimate the distribution of trace elements in a waste rock. The SE detector displays signal on a CRT screen as a grey level SE image. The SE signal is based on a combination of the average atomic number and the topography of the sample, it is not as useful as the BSE image for showing mineral distributions, but displays details of surface irregularities much better. It can be produced at a much lower current and voltage than is required for the BSE image.

2.4.1. Image Analysis

Identification of minerals in a sample is facilitated by image analysis. It is often used for the in modern mineralogical analysis. A brief description is as follows: Backscattered electron (BSE) images produced with a scanning electron microscope are transferred to an image analyzer via TV camera and a frame grabber. A digital image is made of many pixels. (*Pixel refers to a unit square in a graph; for most practical purpose, 25 pixels per mm*). To digitally represent an image, the pixels of the BDE image are assigned a value. The image analyzer subdivides the black and white images into 256 grey levels, with black designated 0 grey level, and white as 255. If a mineral displays a unique grey level in the black and white image, or a distinct color in the color image, its image is segmented from the image of the field of view. In the BSE image (which is most often used), the grey levels of the features of the image are proportional to the average atomic number of the mineral. Minerals with relatively small differences in average atomic number (0.5 to 1.0) can display grey levels sufficiently distinct to be segmented from each other. The grey level technique is often used for mineral identification. An example of image analysis in characterizing minerals in metallurgical dust will be described in Section 2.10. Further details of image analysis and instrumentation are found in the book by Petruk (2000) and in the paper by Lastra and coworkers (1998).

2.4.2. Low-Vacuum SEM

A low-vacuum SEM, developed in Australia (Robinson and Nickel, 1979) has extended the application of SEM to the analysis. The low vacuum of the sample chamber causes ionization of the air by the primary electron beam, conducting electricity sufficiently to allow the electrons absorbed by the sample to leak through the air to a ground contact. No coating is needed even at high accelerating voltages (Robinson 1998; Moncrieff *et al.*, 1978). This makes it possible to analyze wet samples from a slurry or sludge.

2.4.3. Variable Pressure SEM

The variable pressure scanning electron microscope (VP-SEM) is the generic name given to an SEM that operates with a gaseous environment in the sample chamber. Electron scattering processes occur in the gas, creating an ionized gas species, which neutralizes charge accumulation at the sample surface. The pressure and type of gas can be altered in order to analyze a wide range of uncoated non-conductors and hydrated materials. There is a suite of variables, which must be monitored in order to optimize the use of this instrument. The following section presents the basic theory behind this technology as well as techniques for optimizing its usage.

2.4.4. General Differences between Conventional SEM and VPSEM

A conventional SEM (CSEM) requires a high vacuum in the sample chamber and column in order to obtain a highly focused electron beam. The presence of gas in the column would scatter the electron beam to the point where a focused probe would be impossible to obtain. Adsorption of molecules onto the filament would create burn outs, making imaging impossible (Goldstein *et al.*, 1992)

Charge implantation typically occurs in specimens under high vacuum because the total electron yield falls below unity at beam energies above a few keV (Goldstein *et al.*, 1992). Grounded conductive materials allow for charge dissipation, however, an isolated conductor or non-conductor will not. Charge quickly accumulates in non-conductors resulting in image drift, distortion, and electrostatic reflection of the primary beam (Cazaux, J., 1999).

Equation 2.1 describes the relationship between electron yield and charge neutralization (Mohan *et al.*, 1998).

$$I_{sc} = I_b [1 - (\eta + \delta)] \quad (2.1)$$

where, I_{sc} and I_b are the specimen current and primary beam current. The secondary electron (SE) and back-scattered electron (BSE) emission coefficient is denoted with η and δ respectively and is an indication of the amount of electrons emitted from the sample surface (Goldstein *et al.*, 1992). When SE and BSE emission is low, more electrons are implanted than ejected resulting in a negative specimen current. At unity, the specimen current is zero resulting in a charge balance. Electron emission is controlled by beam energy, therefore charge neutralization occurs at a specific beam energy as denoted by the E2 and E1 values in Figure 2.3. Below E1 and above E2, negative sample charging is observed. Typical values for E1 are under 1 keV and around 3 keV for E2.

Charging can be eliminated by operating at the E_1 and E_2 accelerating voltage. Low voltage charge neutralization has some drawbacks however. E_1 and E_2 values are material dependant creating heterogeneous charge accumulation across the sample surface. E_1 values are also often too low to operate and therefore, for homogeneous samples the user is limited to one electron beam energy, which can hinder the ability to perform adequate microanalysis.

The traditional method for imaging non-conductive specimens is with a thin conductive coating of carbon or gold-palladium several nanometers in thickness, which allows the charge to flow to ground (Goldstein *et al.*, 1992). A conductive coating is not ideal however due to image and signal artifacts created during image acquisition and X-ray microanalysis. Small microstructures on the sample surface can be masked as well as a reduction in the signal-to-noise ratio (S/N). Low energy signals and X-rays can also be absorbed in this thin coating which limits the reliability of the results in microanalysis (Farley and Shah, 1991).

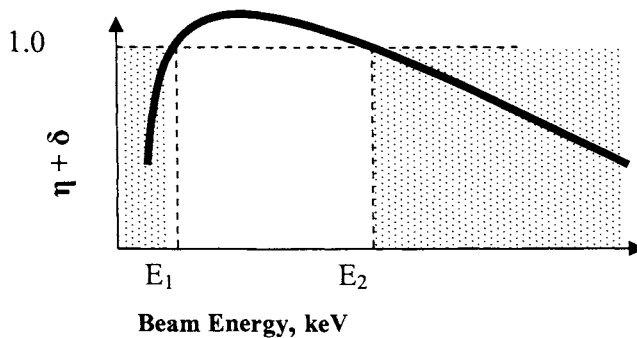


Figure 2.3. SE and BSE emission as a function of beam energy. At E_1 and E_2 , emission is at unity indicating charge balance. Shaded region indicates negative charging.

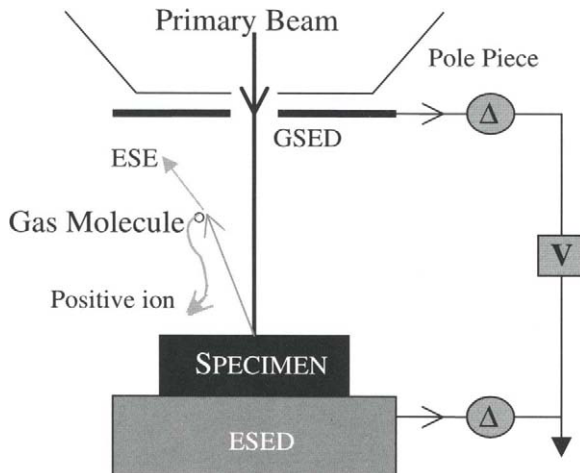


Figure 2.4. An emitted SE accelerates towards the positively biased electrode till it reaches the critical ionization energy, where it starts to ionize the gas molecules. An “environmental” secondary electron (ESE) is ejected and a positive ion is formed. The ESE accelerates and ionizes another molecule creating a cascade/amplification effect. GSED, gaseous secondary electron detector

The VP-SEM avoids these problems through a process of ionized gaseous charge neutralization. The VP-SEM acts as a parallel plate gas capacitor in order to amplify and collect electrons emitted from the sample surface (Mohan *et al.*, 1998). A positively biased electrode at the pole piece along with the negative charge on the sample surface creates an electric field in the sample chamber. This field accelerates low-energy electrons towards the pole piece as in Figure 2.4. Ionization events between the accelerating electrons and gas molecules produce an 'environmental' SE (ESE) and a positive ion. ESE and SE continue to produce more ionization events, resulting in a cascade amplification effect, as shown in Figure 2.5.

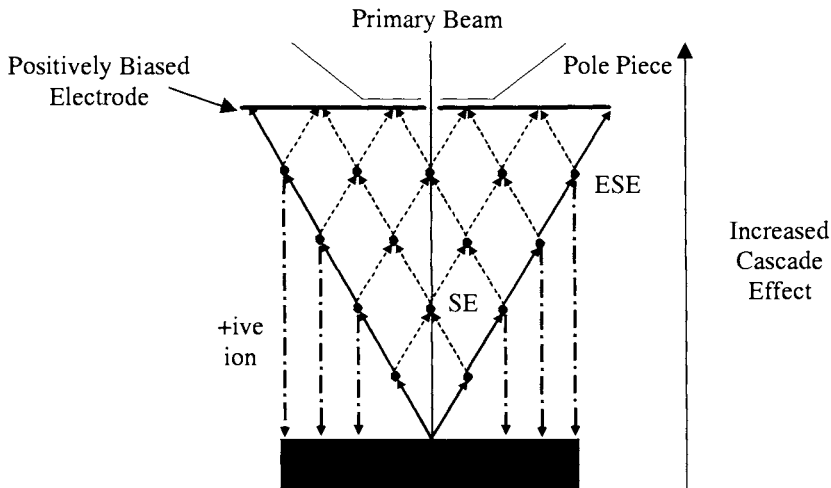


Figure 2.5. The accelerated SE collides with a gas molecule which ejects an ESE and leaves a positive ion behind. The SE and ESE accelerate in the field where more collisions occur. The result is an amplification effect, where majority of ionization events occur near the pole piece. The positive ions drift towards the sample surface.

The chamber is pressurized using a vacuum gradient between the chamber and the column. A differential pumping system allows for this gradient as well as the presence of pressure limiting apertures. Differences between brands relates to the quality of the vacuum gradient as well as the maximum attainable pressure. A complete vacuum in the column is the desired situation but it is rarely achieved. There will always be some gas that enters into the column, which reduces the life span of the filaments as well as the resolution of the imaging probe. Benefits of this system include electron signal amplification, leading to higher contrast images and charge neutralization at the sample surface through positive ion recombination with electrons. The disadvantage such as beam spread will be discussed in a later section.

2.4.5 ESE Detector

Until recently the VP-SEM has been limited to the use of a BSE detector for imaging. Danilatos (1990) has described a way to use the charge carriers produced during amplification as the imaging signal. Imaging is possible through collection of the induced currents from SE's and ESE's at the pole piece or from the positive ions at the sample stage.

The induced currents are generated from the electric field ($\vec{E}$) and the drift velocity of the charge carrier (q) in the sample chamber.

$$I = \vec{E} \cdot v_a \left(\frac{q}{V_{bias}} \right) \quad (2.2)$$

where, I is the induced current, v_a is the drift velocity of the particle and V_{bias} is the voltage applied to the electrode at the pole piece (Mohan *et al.*, 1998; Toth and Phillips, 2000). The biased plate, the sample and the gas behave like a virtual capacitor (Mohan *et al.*, 1998). The sample and the biased electrode are the negative and positive plates, while the ions and electrons are considered space charges. The space charge moves due to the influence of the electric field, which uses energy. This energy is derived from the potential between the plate and the sample (electric field strength) and results in current flow in the circuit.

The GSED (gaseous secondary electron detector) is a proprietary device, which measures the induced current from the electrons, whereas the ESED is the generic name given to the detector measuring the current induced from positive ion drift. The GSED measures the induced current at the pole piece and the ESED measures the current induced at the specimen stage. The SE/ESE's collide with the GSED and create a current flow *to* ground. The positive ions recombine with electrons at the ESED, which creates current flow *from* ground (Figure 2.6). Therefore, for the ESED, the current is based on the ion flux striking the sample surface (Mohan *et al.*, 1998; Danilatos, 1990).

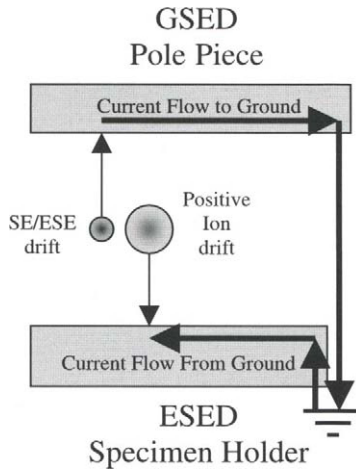


Figure 2.6. Positive ions drift towards sample and induce current from ground, SE/ESE induce a current in the GSED towards ground.

The electric field, gas pressure and gas type influences the degree of ionization events per unit length which effects the ion flux and the resultant ESED current (Fletcher *et al.*, 1997). The ion flux is also a function of the incident and emitted electron currents due to their role in the gas ionization process (Farley and Shah, 1991). An increase in SE production will ionize more gas molecules, which will in turn increase the ion flux (Mohan *et al.*, 1998). The specimen current is based on the emissive properties of the

sample as well as the specific operating parameters used, such as pressure, working distance and plate bias.

2.4.6. Signal-Gas Interactions

The presence of gas in the chamber complicates the interactions between the primary beam, the sample, and the emitted signals. In a CSEM, the primary electrons penetrate the sample and undergo elastic and inelastic collisions. Through this process, SE, BSE, X-rays, auger electrons and photons are emitted (Goldstein *et al.*, 1992). Secondary electrons can be further grouped into SE1, SE2, and SE3. SE1 are created from the scattering of primary electrons. SE2 are generated from the scattering of BSE. SE3 are generated from BSE colliding with the sample chamber; (Figure 2.7). Of these three types of secondary electrons, only the SE1 provide a useful signal at high accelerating voltages. The other signals only decrease the signal to noise ratio (Goldstein *et al.*, 1992).

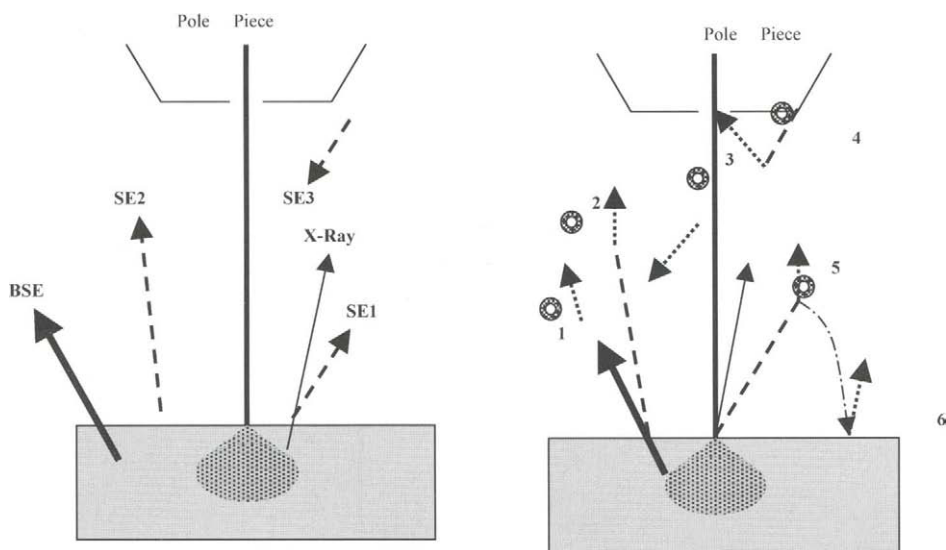


Figure 2.7. **A.** Particle interactions in the CSEM. **B.** Particle interactions in the VP-SEM. Same behavior as in the CSEM accept the signals interact with the gas. 1. BSE-gas 2. SE2-gas 3. PE-gas 4. SE3-gas 5. SE1-gas 6. Positive ion-sample emits SE.

Beam-gas interactions involve the scatter of the primary beam electrons due to elastic and inelastic collisions with the gas. The scattered primary electrons interact with the sample and generate SE, BSE etc. outside of the area of interest. Gas-sample interactions involve the collision of positive ions on the sample surface (Mathieu, 1999). Positive ions recombine with electrons on the sample surface and neutralize the charge build-up (Toth *et al.*, 2002). Upon impact however, secondary electrons can be emitted which contribute to the cascade. This behavior decreases the signal-to-noise ratio as well (Fletcher *et al.*, 1999; Mathieu, 1999). There is a strong source of background noise in

crystal lattice defects, dislocations, grain boundaries, impurities and vacancies (Griffin, 2000). Therefore, it can be hypothesized that the charge contrast the structural features just mentioned. Modeling charge build-up however, is very complicated due to the dynamic nature of the electric fields, as well as the complex variation in charge trapping. Charging is sample dependant therefore a mechanism to describe charge contrast would be sample dependant as well.

Incomplete charge neutralization allows preferential charging to occur in areas where there is increased charge trapping. This is typically observed in areas with increased defect densities and lattice heterogeneities. Areas of compositional and structural variation will show differences in charging, which results in contrast variations called charge induced contrast. It has been shown that this charge contrast is related to the effect of charge neutralization because the contrast is not seen with the SE or BSE detectors (Baroni, 2001).

2.5. Electron Microprobe (MP)

Developed in the late 1950's, the electron microprobe has played a major role in mineralogical characterization of a variety of materials. First applied for the mineralogical characterization of ores, it is now widely used in the study of metallurgical dusts and residues.

Electron microprobe (MP) is also a microbeam instrument, but X-ray counts from the sample surface are detected by wavelength spectrometers (WDS) instead of, or in addition to, the EDS. The WDS are set at specific positions to detect the X-ray counts for specific elements. Unlike the EDS, which detects and counts the X-ray signals for all elements at the same time, the WDS counts X-ray signals for only one element at a time. As the WDS can count many more X-rays for the specific element in the same length of time, it is more accurate than EDS and has a lower detection limit.

The electron microprobe is used to analyze grains, as small as 5-10 μm , for minor elements with the WDS, and for major elements with the EDS. The analysis is usually performed by writing a macro which would:

- control the spectrometers to move to the peak positions of the elements to be analyzed,
- set the count time for each peak (commonly 10 seconds or a maximum number of counts for major minerals, and up to 100 seconds for minor or trace minerals).
- insert beam blanking at appropriate times,
- collect data from the standard under the established analytical conditions,
- move sample to first point to be analyzed,
- collect data for unknown under established analytical conditions,
- move the sample to the next point to be analyzed.

An analytical technique, which can detect trace elements in the 5 to 10 ppm range has been recently developed for modern electron microprobes (Robinson, *et al.*, 1998). The technique uses a high accelerating voltage, a high probe current, long counting times, and background points near the peak without interference. This has been used to detect invisible gold in pyrite arsenopyrite rocks (Kojonen and Johansson, 1999).

The modern microprobe also has mapping facilities, which are used to show different concentrations of elements are shown in different colors. This is useful to show the distribution of minerals, which have different quantities of the same element. The

technique, however, takes along time to produce the maps, the increased mapping time produces higher quality maps.

2.6. Proton Induced X-ray Emission (PIXE)

This is a microbeam analytical instrument used for multi-element quantitative analysis of trace and major elements in selected minerals in polished or thin sections. In most cases elements with atomic number ≥ 26 (Fe to U) can be detected in the range of a few ppm (Cabri and Campbell, 1998). The protons generated by PIXE penetrate much deeper than the electrons generated by MP do, and X-rays are produced from well below the surface of the compound. A large surface area (ideally, 80 μm diameter) is required for analysis, but grains as small as 50 μm can be analyzed. The analysis by PIXE is similar to that by MP. The main difference is that signal to noise ratio is better in PIXE than in the MP, which enables lower detection limits to be obtained. The X-rays produced by the high energy (MeV range) require less corrections for quantitative analysis than the X-rays produced by the electrons in the microprobe (KeV range) (Cabri and Campbell, 1998). The accuracy of the PIXE and MP are comparable, but trace element analysis with a MP require considerable attention to choice of background position and correction for overlapping peaks. PIXE generally has the advantage of a large number of X-ray lines and trace element detection levels are smaller by a factor of two (Cousens *et al.*, 1997). So far, PIXE is an expensive instrument; only a few laboratories in the world have one.

2.7. X-Ray Diffraction

Every crystalline compound has a unique X-ray diffraction (XRD) pattern that is dependent on the crystal structure, and to a smaller degree on the composition of the material. The XRD patterns are obtained by X-ray diffraction, and are used to identify the compounds and to determine their quantities. In X-ray diffractometry, the material is ground to at least -325 mesh (-44 μm), and mounted as either a thin filament a sticky surface on a glass slide, or as a compact powder in a cavity in a sample holder. The ground material on the glass slide is used when only a small amount of sample is available and only mineral identities are required. The compacted powder in a sample holder is used when the sample is analyzed for mineral quantities as well as for mineral identities. The mounted sample is placed in the path of the x-ray beam for X-rays to be diffracted by the compounds in the test material. The diffracted X-ray signal is collected by a detector, which is a scintillation counter. The detector sweeps in an arc across the position of the lines diffracted by the minerals in the sample and measures the intensities of the diffracted X-rays at different peak positions. The data can be read manually from a strip chart or recorded by a computer. In computerized XRD units the compounds are identified automatically using a software package that employs search-match techniques.

Several techniques have been used to determine the quantities of specific compounds by XRD. The most widely used one at present is called relative intensity ratios (I/I_c) method. It is based on relative intensities between the XRD patterns of the minerals analyzed and the XRD pattern of corundum (an aluminosilicate mineral). The technique requires a library of relative intensity ratios between the minerals and corundum, but established ratios are transferable between XRD units. All peak intensities are transformed to a common denominator (for example, the peak intensity of corundum). All compounds in the material need to be identified and the results are normalized to 100%. In early years only the strongest lines could be compared, then three strongest

lines were used, and in 1994 a technique was developed in Canada to use the entire XRD pattern (Szymanski and Petruk, 1994). This provides a better comparison and minimized preferred orientation, which is further reduced by using a stainless steel randomizer punch (Peters, 1970).

2.8. On-line Identification for Recyclable Materials

On-line identification of materials, as they are crushed and separated in different size ranges is of great use to achieve higher recovery of recyclable material as it enables the selection of separation process and optimization of process parameters. Mechanical and manual processes of identification (using one of the techniques described in this chapter) are being replaced by automatic identification.. The pioneering work by researchers at Delft University in the Netherlands, has led to significant advances in this direction (de Jong *et al.*, 2001;) Four identification methods have been recognized. They are based on color and spectral identification, shape analysis (morphology), conductivity measurement, and spectral X-ray transmission.

2.8.1. Identification by Spectral Characteristics and Particle Shape

All materials reflect light of a specific spectral composition. A spectrograph provides an image of defined bandwidth and wavelength. The red, green, and blue composition of a color camera is a simple example of a spectral set of images. By studying spectral reflection bands from the visible spectrum copper and brass can be clearly distinguished (de Jong *et al.*, 2001), and without pre-treatment magnesium could be identified with a recovery over 80%. Identification of other metals is more difficult. Chemical pre-treatment enhances identification between aluminum cast and wrought alloys (Le Guern *et al.*, 1999; Gesing *et al.*, 2000).

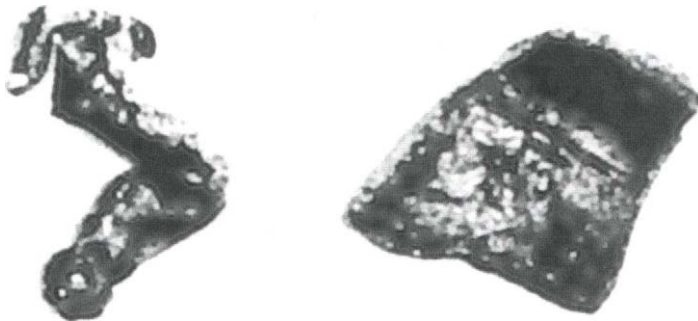


Figure 2.9. Shape differences between wrought (left) and cast (right) aluminum alloys (de Jong *et al.*, 2001)

In addition to spectral information alone, specific differences in texture and morphology assist in identification, if the data processing is sufficiently advanced for 2-dimensional image processing and multi-feature classification; see Figure 2.9. Several useful filtering and feature extraction algorithms are known. AN example is called Fourier descriptor of the particle boundary, which distinguishes different particle shapes. Together with other features such as color reflection and texture parameters, the Fourier

descriptors represent points in a feature space. The different alloys are distinguished as clusters (Bonifazi, 2000).

Some principal drawbacks of optical identification systems are: only information derived from the particle surface can be used for identification. In the example of non-ferrous scrap particles, errors could occur due to surface oxidation, dirt, coatings, or intense reflections. No information about the particle interior can be obtained. In addition, the particle volume itself cannot be determined. These deficiencies could be overcome by combination with other sensors based on electromagnetic and X-ray detection.

2.8.2. Electromagnetic Identification

This is based on inducing current in conducting particles by an alternating current. This effect can be used for classification of metals based on their conductivities. Every metal has a specific electrical conductivity; see Figure 2.10. When an AC flows in a coil in close proximity to a conducting particle, the magnetic field of the coil induces circulating currents, called eddy currents in that particle. Their magnitude and phase will affect the loading on the coil and thus its impedance. Besides conductivity, many other factors affect eddy current response: permeability, signal frequency, particle size and shape, and the distance between particle and sensor.

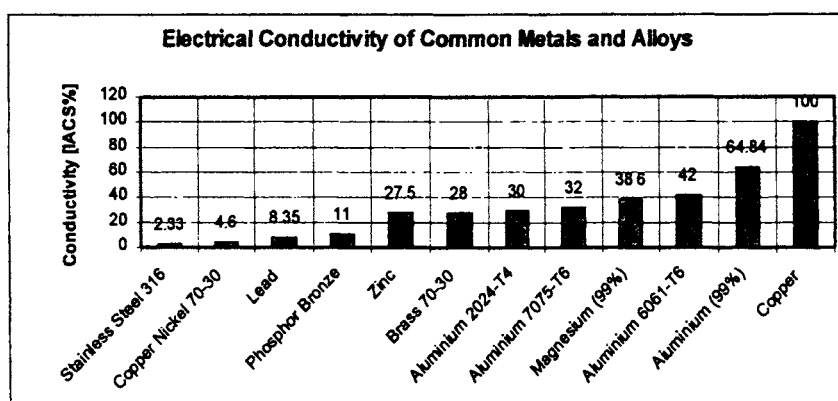


Figure 2.10. Conductivity of some common metals and alloys (relative to copper) (de Jong *et al.*, 2001)

An eddy-current sensor for metal identification has been developed (Kattentidt, 2000). It consists of a transmitter coil and an array of (gradient) receiver coils. Amplitude and phase-shift of the signal are recorded and digitized. The set-up of this sensor and an amplitude image of an 8x8x0.4 mm aluminum particle that is detected with the sensor are illustrated in Figure 2.11. As it appears, the electromagnetic image is several times larger than the particle dimensions.

An electromagnetic sensor successfully distinguishes high conductive (e.g., copper, aluminum) and low conducting (e.g., stainless steel, lead) materials. The electromagnetic sensor can be used for identification of metals when information on particle area and thickness is available from another sensor type. An X-ray transmission sensor seems

particularly useful, as particle shape, area, and thickness can be determined simultaneously, as will be described in the following section.

2.8.3. Identification with X-ray Transmission

X-ray transmission is specially useful for high-speed identification of materials. A transmission X-ray beam has a higher intensity than an induced fluorescent beam, which makes it possible to record an image within a few milliseconds. Transmission imaging enables fast and sharp reading with X-ray tubes. Conveying speeds of over 1 m/s at a resolution of approximately 2-mm are possible. Another advantage of transmission is that the particle volume is detected and not just a surface layer, as is the case with X-ray fluorescence analysis. Disadvantage is that there is no direct detection of specific phases. However, using modern dual X-ray equipment, a fast determination of the approximate average number of the material can be done. That way, many materials in a mixture can be known in advance.

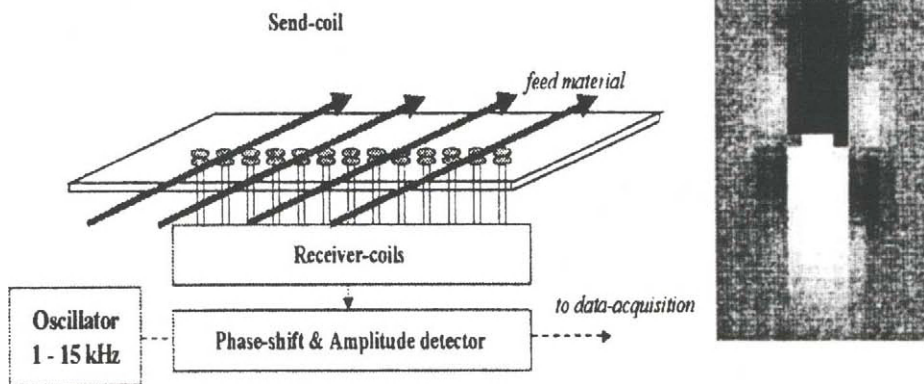


Figure 2.11. Set-up of an electromagnetic sensor for bulk solids (left), and electromagnetic image on an 8x6x0.4 mm aluminum metal particle passing an EC sensor. (de Jong *et al.*, 2001)

The transmission damping of a sample of thickness d at an X-ray source intensity I_0 is given by the equation (called Lambert's law):

$$I_{\text{det}} = I_0 e^{-\mu(\lambda)d}$$

Where I_{det} is the recorded intensity, and $\mu(\lambda)$ the linear damping coefficient that is a function of the wavelength λ . Monochromatic X-ray transmission can be useful for structural identification of particles, or for finding inclusions or contaminants in a relatively homogeneous particle flow.

I_{det} varies exponentially with d . In recyclables thickness variations in the material can vary several factors. Monochromatic X-ray identification of non-ferrous scrap metals and alloys, and other recyclable materials will be problematic and in many cases impossible. By simultaneous observation at two or more different wavelengths the effect of particle thickness can be ruled out; $\mu(\lambda)$ is a known function depending on wavelength, density, and average elemental composition of the material. The relationship between I_{det} at a higher energy level and I_{det} at a lower energy level is a function of $\mu(\lambda)_{\text{high}} / \mu(\lambda)_{\text{low}}$ and

d. $\mu(\lambda)_{\text{high}}/\mu(\lambda)_{\text{low}}$ and d can be solved by Lambert's law for the higher and for the lower energy levels. In this way, it is possible to approximate the average atomic number of the observed sample and to determine d. Methods have been developed in other X-ray imaging applications, specially for safety inspection systems.

Dual energy X-ray imaging systems have been applied for the identification of recyclable materials. The linking of dual energy X-ray imaging to a particle identification system enables automatic identification and sorting of scrap metals, plastics, building rubble and waste glass packaging. As an example, Figure 2.12 shows an image of some non-ferrous metal particles is compared with their X-ray transmission image.

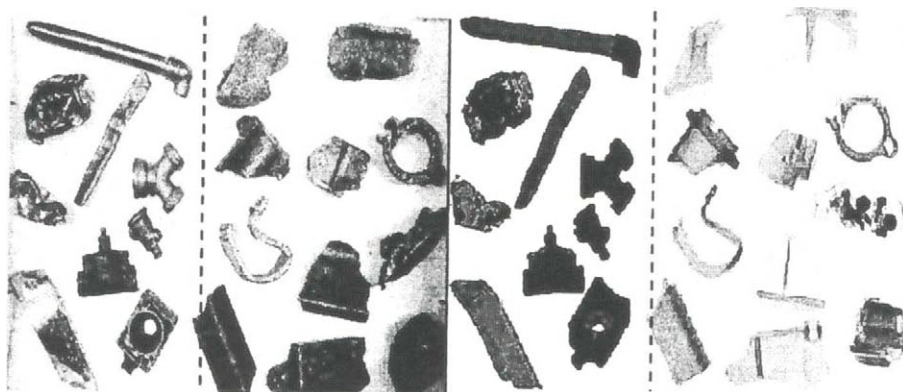


Figure 2.12. Non-ferrous metals (left) and their X-ray transmission image (right) taken with a dual energy X-ray scanner. Heavy non-ferrous metals have a darker shade (left side of the transmission). (de Jong *et al.*, 2001)

2.9. Using Waste Characterization in Waste Processing and Resource Recovery

When a waste material contains several components, the information from characterization helps to determine what specific objectives one can set in the separation process and which techniques the separation is best done. An example is the identification of the species present in a fly ash from thermal power plants where coal is used to generate electricity (Kramer *et al.*, 1994). Examination by SEM shows that the material is primarily an aluminosilicate. Iron, titanium, potassium and calcium are minor components in bulk composition. The fly ash consists primarily of amorphous particles. Many amorphous particles consist of aluminum and silicon in varying amounts and often contain carbon. Carbon particles are common and the carbon purity varies from a small amount of fly ash contamination to particles appearing to contain more ash than carbon. Some carbon particles qualitatively show a higher sulfur content. An iron oxide phase occurs as spheres and angular particles. Large, squarish grains of pyrite are observed. The presence of sulfide minerals in the sample suggests that the original sulfides in the coal are not altered by the combustion.

The identification of the species led to a process of separation to recover four products for possible applications – iron-rich magnetic particles, cenospheres, clean fly ash and carbon. The fly ash is mixed with water to make a slurry and pumped into a wet magnetic separator (see Chapter 4 for details of magnetic separation). The magnetic material is collected in a field of 5 kilogauss, filtered and dried. After removing the magnetic fraction, the remaining material is fed into a settling tank to capture the

cenospheres and provide a constant feed to the flotation circuit, which follows magnetic separation. The cenosphere fraction floats at the top of the tank and is skimmed off. The underflow material is pumped into a conditioning tank, where flotation reagents (collector, frother and dispersant) are added and mixed with the slurry. From the conditioner, the slurry is pumped to the rougher flotation circuit. The tailings (non-float) product is clean fly ash. It is pumped to a thickener and dried. After the rougher flotation, the carbon product recovered in the float fraction is cleaned further in a series of flotation cells, serving as cleaning stages.

The process typically yields clean fly ash with 0.6 % LOI (loss on ignition). Carbon grades are high (approximately 75 % LOI) at the expense of low recovery (approximately 30 %). Conversely, high recoveries can be achieved at the expense of the higher grade.

Each of the products is also examined under SEM to assess their identity and the occurrence of impurities. This knowledge is important in determining their potential uses.

2.9.1. Characterization of Basic Oxygen Furnace (BOF) Dust

Another example is found in the characterization of basic oxygen furnace (BOF) dust, generated in steel plant (Kelebek *et al.*, 2004). X-Ray diffraction analysis of the dust showed the presence of hematite, iron oxide and zinc ferrite (ZnFe_2O_4) to be the principal chemical species in the material; see Figure 2.13. Additional work with scanning electron microscope and energy dispersive x-ray showed relative distribution of iron and zinc components of selected particles. The electron micrograph (Figure 2.14) shows a very high level of zinc and concentration of zinc-bearing species around spherical iron cores. It also shows tendency for particles to agglomerate. Indications are that the constituents of the BOF dust cannot be separated by gravity methods. Even flotation method did not give satisfactory results. Processing of such material can be done only by a hydrometallurgical route.

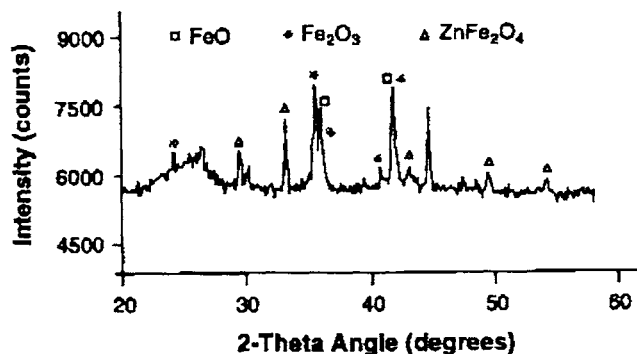


Figure 2.13. XRD analysis of BOF dust sample (Kelebek *et al.*, 2004)

Mineralogical composition of an electric arc furnace (EAF) dust to identify the mineral species by different analytical techniques has been described by Menad and coworkers (2002). The chemical and mineralogical analyses showed that the EAF dust contained 21.9% zinc; 63% of it was in the form of zincite (ZnO) that is easy to leach. The remaining zinc was found to occur as a zinc ferrite, franklinite (ZnFe_2O_4), which is more difficult to dissolve by leaching. Up to 63 % of the zinc is thus readily recoverable

by simple leaching in sulfuric acid. The fraction present as franklinite would require more energy consuming, pyrometallurgical treatment.

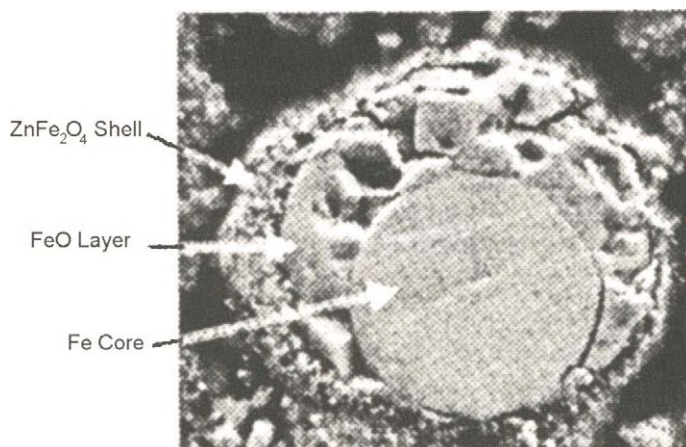


Figure 2.14. Cross-sectional composition of a spherical particle from BOF dust (Kelebek *et al.*, 2004)

2.9.2. Metallization of Electric Arc Furnace (EAF) Dust

Electric arc furnace (EAF) dust is a hazardous waste from the steelmaking industry. A process has been described by Aota and coworkers (2003) comprising metallization and fuming process to recover metals from the dust that could be operated economically at a small capacity and on-site of the EAF production. The EAF dust was made into pellets by a process of agglomeration known as cold bond process (details will be described in Chapter 9, Section 9.6). A cold bonded method was developed to make coal-bearing EAF dust pellets. The product pellets were characterized by electron microscopy and image analysis to evaluate metal separation from the EAF dust.

Discrimination of the phases in the pellets is done using the grey values of BSE images. BSE images of 512*512 pixels were used, thus each image contained a total of 264,144 pixels. The image analyzer was used to get the grey value of each pixel. The grey values from each individual pixel of multiple BSE images were obtained. Various magnifications (40, 100X and 200X) were used and enough multiple BSE images were acquired to cover the area of a pellet. The grey level values of several millions of pixels were plotted to obtain a frequency histogram. The frequency histogram in Figure 2.15 shows in a simple way the abundance of the phases. It shows the BSE grey level histograms for images at 200X magnification. The observations derived from the BSE images at 200X magnification are similar to those derived from the grey level histograms of BSE images at the other lower magnifications.

The EAF dust contains many different oxide phases, description of these phases has been the topic of numerous investigations (e.g. Jenkins *et al.*, 1982), and will not be covered here. In very simple terms the EAF dust consists of a complex mixture of Fe, Zn, Mn, and Pb oxides. The attached figure clearly shows that the metallization starts at 800°C, where the amount of oxides starts to decrease and pig iron starts to be formed. At

1200°C the amount of pig iron is maximized and a metallic iron of high purity appears, the phase at grey level 150. At 1250°C there is indication of re-oxidation as the amount of pig iron decreases and the high purity metallic iron disappears. Thus the appropriate metallization temperature is 1200°C.

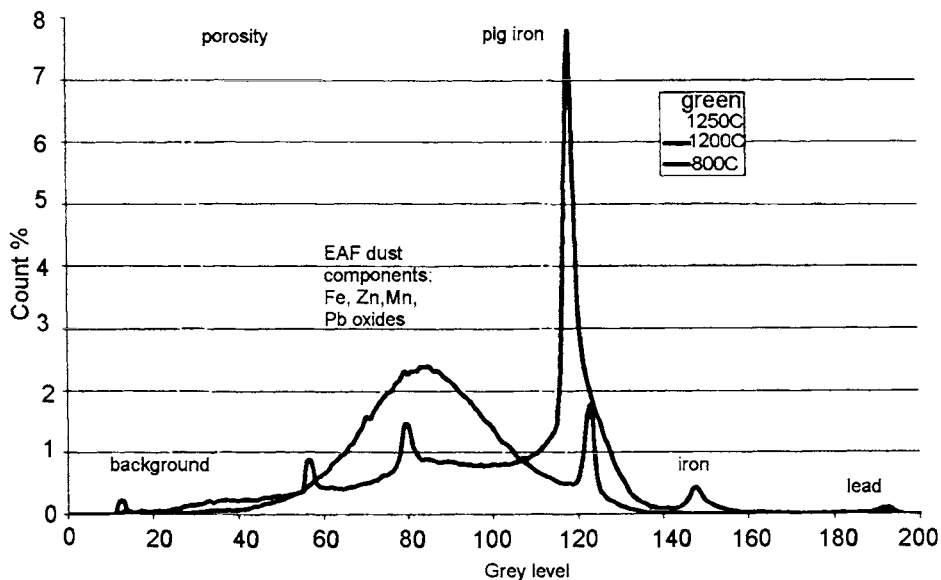


Figure 2.15. Grey level histogram of multiple BSE images at 200X magnification from EAF pellets (Aota *et al.*, 2003)

EAF dust has been successfully pelletized. The coal in the pellets, the reducing gases and the high temperature are enough to reduce the iron oxides and produce pig iron. The problem is the other metals in the EAF dust. Zinc is fumed away; however, a small but significant amount of metallic lead remains in the metallized pellet. Metallic lead is the phase at grey level ~195 in Figure 2.10. Metallic lead, even in a small amount is very detrimental in steel. Thus the lead in the metallized pellet needs to be virtually eliminated before recycling to steelmaking.

2.9.3. Sludge Characterization

There has been a moderate amount of work in characterizing the waste sludges. The most comprehensive sludge characterization study was conducted in Canada under the Mine Environment Neutral Drainage (MEND) program, which was a multistake-holder program to study the sludge produced by the neutralization of acid mine drainage (AMD) by lime (CaO) in terms of its problem and solutions (MEND, 1997). This study sampled and characterized AMD sludge from a wide range of mines across Canada.

Note: Acid mine drainage (AMD), also called acid rock drainage (ARD) is the name given to the effluent produced by the atmospheric oxidation of the tailings and waste rocks containing pyrite. The oxidation of the pyrite sulfur produces sulfuric acid, which dissolves many residuals base metals in the waste rock. In the sludge treatment, the acid

is neutralized by lime and the metal hydroxides are precipitated. Further details are described in Chapter 10.

Sludge is difficult to characterize due to its high variability in the natural environment. The composition of sludge is directly influenced by the chemistry of the acidic effluent, which in turn is a function of the tailings impoundment. Different mines will have different mine waste compositions which ultimately results in specific sludge compositions.

Generally speaking sludge has high iron content. Iron sulfides are a common component of waste rock no matter what type of base metal mine we are dealing with. All sludges contain an amorphous phase, which serves as the sink for many of the metal species. Gypsum is the main reaction product between calcium and sulfate. Detrital silicates are often found in the sludge. The sludge stability appears to depend on the stability of the amorphous mass rather than the other components.

Particle size is often bimodal in sludge, this bimodality is believed to be related to different structures. The smaller size fraction related to the amorphous hydroxide mass. The larger size fraction is believed to represent the unreacted lime and detrital silicates.

Sludge is alkaline, ranging between a pH of 8 and 11. As mentioned above the alkalinity depends on the process used and the specifications designated by the mine chemistry and environmental factors in the case of aged sludge.

Base metals are present in high concentrations, representing a potential for metal recovery. Trace level chemicals often include arsenic, boron, cadmium, chromium, mercury, and lead. Sulfate content is a direct relation to the amount of sulfur present in the waste rock.

The major mineralogical phase appears to be hydrated, amorphous, and metal rich. Typical metals found in this phase are the base metals, which tend to be leached quite readily. Carbonates and silicates are more crystalline and they tend to stabilize the amorphous phase.

2.10. Environmental Testing

In all waste processing and recycling operations the feed material is a 'waste' product generated in the primary production. The end products are recycled metal or a by-product produced by chemical treatment of the feed material, and a discharge produce. As a good portion of the feed material has been recycled, the volume of the discharge product is usually much smaller than that of the original 'waste' material (the feed). A criterion of the success of the recycling operation is the extent of reduction of the volume of the material to be finally discharged to environment. Ideally, this should be zero, but, at this time, there are only a few operations, which achieve this target. In many case, a small quantity remains to be discharged. In these cases, the success of the operation will be measured not only by the volume of the discharge product but also its environmental characteristic measured by toxicity and leachability of elements, which could impact on the environment. This is evaluated by standard environmental tests chosen to determine possible environmental impact of the discharge product. The environmental conditions in which the product is discharged, like pH of the water in which the discharge product would interact are taken into account to assess the environmental impact.

Environmental protection agencies of different regions in various countries, Canada, the U.S. and European have set procedures for testing the waste leach. They vary in specific details, but the basic principle and objectives are generally the same. They were

developed for a broad class of solid wastes disposed off in the environment, and have been adopted to test the environmental impact of discharge product in recycling industry. Basic description of two principal tests applicable to recycling systems will be given in the present Section. More details and a comparison of various tests used for different kinds of waste products can be found in "Compendium of Waste Leaching Tests" published by Environment Canada (Report EPS 3/HA/t, May 1990).

The first one commonly used to determine the leachability of the discharge sludges is **leachability extraction procedure (LEP)**. This is based on contacting the sludge (or any solid to be discharged) with a liquid of pre-determined composition. This is usually water of pH 5.2, set by acetic acid. The objective is to measure the concentration of metal ions released into the natural water, whose pH is usually around 5.2 (caused by natural acidity) with which the sludge interacts after it is discharged. The solid to liquid ratio is kept at 1:4. the solid is agitated with the water for 24 hours. If, during this time pH goes down, more acetic acid is added to maintain it at 5.2. After 24 hours interaction, the solid is separated from the water and the concentrations of toxic metals, which may have been leached into the water are measured by atomic absorption spectroscopy (AA). If the concentration exceeds regulatory limits (5 mg/L toxic metals including As, Cd, Cr, Cu, Mg, Ni, Pb, Zn), alkalinity of the sludge has to be increased by mixing lime until satisfactory result is obtained.

The second commonly used test is called **toxicity characteristic leaching procedure (TCLP)**. It is based on the same assumptions as LEP, but it includes some modifications. Volatiles are prevented from escaping to the atmosphere by using a modified leaching vessel, which eliminates head space. Two leachants are employed. For highly alkaline wastes, a solution of acetic acid is used to pH 2.88. For other wastes, a buffered leachant (pH 4.93) is used, which eliminates the need for continual pH adjustment. TCLP is specially suited for discharge materials, which may carry organics. They are analyzed by appropriate technique like ultra-violet spectrophotometry or liquid chromatography-mass spectrometry (LC-MS).

Details of the analytical techniques (AA and LC-MS) are found in text books of instrumental chemical analysis (e.g., Willard *et al.*, 1988).

In a modification of the LEP test, the pH of the leach liquid varied from 5.7 to 7.6. This is found to be suitable to measure the leachability of slags as the higher pH takes into account the neutralizing capacity of the slag (Koren *et al.*, 1997). However, as slags are increasingly processed to make useful industrial and construction materials (as will be described in Chapter 9), this is not widely used in recycling industry.

Selected Readings

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Chapter 3

PHYSICAL AND PHYSICO-CHEMICAL PROCESSES

Physical processes, which usually do not require chemical agents are often sought after for materials separation. They are based on exploiting the differences in specific physical properties like specific gravity, magnetic properties, and electrical conductivity. Physico-chemical processes are based on the surface chemical characteristics of the components to be separated. Such processes, including froth flotation, ion flotation, precipitate flotation require the application of surface active agents, but the quantities required for a process are usually small, often in mg/L range. The success of the physical and physico-chemical methods is determined by variations in such properties between individual components to be separated and recovered. This will be discussed in this chapter, with examples of separation processes.

3.1. Material Preparation for Physical Separation

Separation of chemical species by physical separation has to be often preceded by material preparation to ensure desired separation by the technique used. In the physical techniques of processing the chemical composition of the components is unchanged; no chemical treatment occurs. The separation is based entirely on using the differences in physical properties between the chemical components. They include, as will be explained in the Chapter, specific gravity, magnetic properties, thermal and electrical conductivity and properties related to surface chemistry of the compounds. (Surface chemical treatment does not alter the bulk chemical composition of the compound thus treated).

3.1.1. Comminution

A principal requirement for the success of any physical separation process is that the individual components to be separated should be satisfactorily liberated from each other; that is, the two should not be bound together in a chunk. For example, in a waste rock, several minerals are clumped together and before proceeding to separate the desired components, the rock has to be crushed and ground to the extent, the individual components are freed or liberated from each other. This is done by crushing in appropriate crushers and grinding in ball mills. Rod mills are used for fine grinding, but that is not usually required in waste processing.

Both crushing and grinding lead to size reduction of the material. Comminution is the general term for size reduction in mineral industry.

Most waste materials originating from metallurgical and mineral processing plants, like slag, dust and tailings, would have already gone through the process leading to

liberation in course of the primary treatment to separate minerals or extract metals. Waste rocks in mining areas, which are found to contain valuable recoverable components in small proportion requires crushing and grinding for satisfactory liberation. Metal scraps have often to be crushed and ground before separating the metallic components. In some wastes, for example, the ones originating from discarded automobiles, the metal components have to be separated from plastic components as well.

Crushers and ball mill of various designs have been described in textbooks of mineral processing (see for example, Wills, 2000). Basically the same equipment is used in waste processing. In addition, a novel process, which is not used in mineral processing, which has been developed in recent years and is applied in some scrap recycling process will be described in the following section.

3.1.2. Cryogenic Comminution

Sometimes it can be advantageous to operate the comminution process at a low temperature as many materials then become more brittle, which facilitates crushing. This is called cryogenic comminution. It is used in some metal recycling plants for treating the scrap.

The low temperature is usually achieved by liquid nitrogen (LIN). Carbon dioxide has also been used in some places (Allen and Biddulph, 1979). The design of a cryogenic comminution plant must allow for dissipation of the heat generated. Smaller particle size leads to greater heat generation. Possibility of explosion caused by heat generation must be guarded against.

Cryogenic comminution plants have four basic sections: LIN storage chamber, cooling zone(s) (conveyor, screw or tank), impact type size reduction mill and crushed component separator. In an industrial process (called Inch Scrap process) operated in Belgium, complete motor cars are first compressed into cubes, chilled to 266 K by spray of LIN, then further to 133 K by immersion in LIN before feeding to a 375 kW hammer mill operating at this temperature. Washing machines and refrigerators are also similarly processed. Dust and fabric from the product are removed by a fan. Screening, density and magnetic separation techniques are used to separate plastics, rubber, glass and non-ferrous metal. Cast iron and alloy steels are separated from mild steel.

The advantage of cryogenic comminution is that it reduces power consumption relative to that consumed in equivalent ambient temperature process. It also avoids or minimizes heat build-up in materials that might otherwise degrade or fuse. However, it requires expensive equipment and constant use of liquid nitrogen compared with conventional comminution techniques. The technique is used only where economics of the process and products justifies the cost. For example, in scrap metal processing, cryogenic comminution is used for treating relatively high value metal scraps, which are electric motors, transformers and car generators, which contain typically 20% copper and 80% steel (Daborn and Derry, 1988), even appreciable quantities of precious metals.

A potentially useful application of cryogenic fragmentation in the shredding of automobiles has been described by Schmitt (1990). Typically, old automobiles are shredded using a hammer mill-type shredder. In the process of tearing the automobile apart, the shearing action of the mill tends to smash different metals together, thus diminishing the possibility of separating and recovering metals. The use of cryogenics in scrap processing has the potential to produce a cleaner and denser scrap than the conventional process and possibly reduce the volume of the fluff produced. The scrap

automobiles are baled and the bales conveyed through an insulated tunnel where they are cooled at -7°C by cold nitrogen vapors from liquid nitrogen. Exiting through the tunnel, the bales are partially immersed in the liquid nitrogen bath and the temperature lowered to -120°C . The frozen blades are then processed through a hammer mill where they are fragmented into coin size pieces. Nitrogen consumption is reported to be about 0.3 L per kg steel produced. Separation of the glass, dirt, rubber, plastic and metal scrap is done by appropriate physical techniques like air classification, magnetic or density separation. (Chindgren *et al.*, 1971; Bilbrey *et al.*, 1979).

3.2. Gravity Separation Processes

Gravity separation is an old technique, widely used in mineral processing for the separation of minerals from ores. As the name implies, gravity separation is based on differences in specific gravities of two or more components in a recycle system. The separation is carried out in water, but air is used in places where water is scarce, or when some significant special benefits are found from its use. Water is, however, preferred, as the separation is influenced by a density difference term ($\rho_s - \rho_f$) and a particle size term, and as the significance of the difference in particle densities is most pronounced in water. In gravity concentrating devices, particles are held slightly apart to facilitate their movement relative to each other and thus to separate the components. In ideal case, separation occurs in layers of dense and light components.

A number of gravity separation devices are used in mineral processing. Some of them have been adopted in metallurgical waste processing and recycling where the density differences are significant and the solids are relatively coarse. The ones, which are frequently used will be described with a discussion of the principles on which they operate. For more detailed descriptions text books in mineral processing should be consulted [Wills (2000); Kelly and Spottiswood (1982)].

3.2.1. Shaking Table.

This is a relatively old device, but has evolved in different forms. A typical table is illustrated in Figure 3.1. Feed enters through a distribution box along part of the upper edge and spreads out over the table by the shaking action and the wash water. Product is discharged along the opposite edge and end. The table is essentially rectangular, but has an adjustable slope of about 0° - 6° from the feed edge down to the discharge edge, with a much lower rise from the feed end to the discharge end. The surface is made of rubber or fiber glass, a smooth material and has an arrangement of riffles on it, which decrease in height along their length toward the discharge end. Differential shaking action is applied to the table along its horizontal axis. This action opens the bed causing the dense particles to sink, and by its symmetry facilitates particle transport along the table. The particles move diagonally across the deck from the feed end. As the effect depends on the size and density of the particles, the smaller, denser particles ride towards the concentrate launder at the far end, while the larger lighter particles are washed into the tailings launder running along the path of the table.

The earliest model using the differential shaking action which was widely used in ore dressing operations is called Wilfley table. Several new developments have been described since the early model. One of the most significant is a three-deck table, also called Deister table; Figure 3.2. The table can be suspended from the roof, which eliminates the need for heavy foundation to sustain the table motion, or table can be

stacked (up to 6 in height) to save floor space. The operating variables of shaking table are listed in Table 3.1.

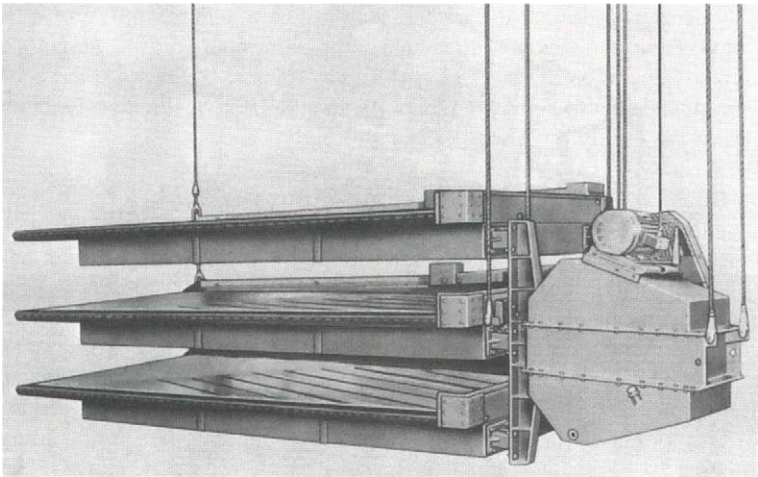


Figure 3.1. Schematic of a shaking table, showing the distribution of the products (Kelly and Spottiswood, 1982).

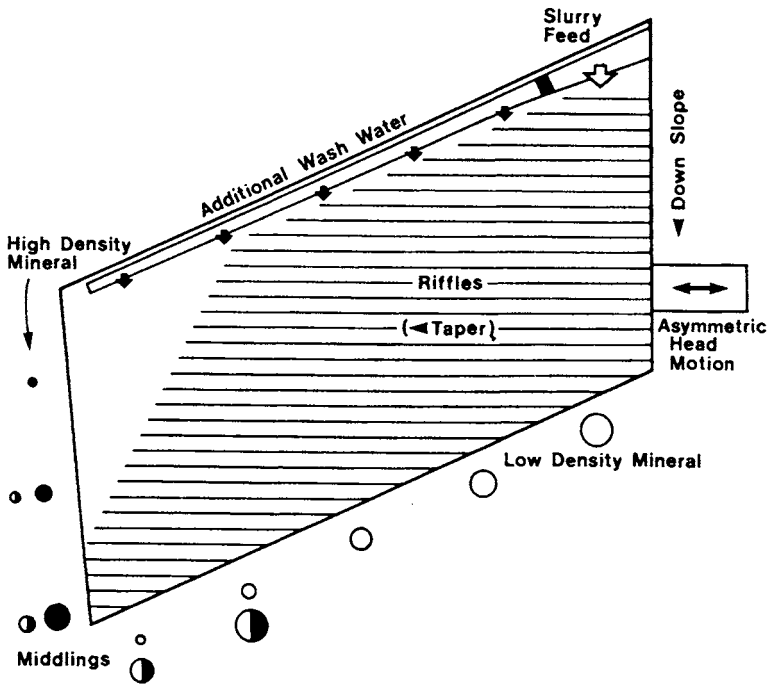


Figure 3.2. A 3-deck shaking table (Deister Table)

3.2.2. Bartles-Mozley Concentrator

Originally developed in Cornwall, England, to recover fine cassiterite, which was irrecoverable by other means (Burt and Otley, 1974), this device consists of a suspended assembly of 40 fiberglass decks arranged in two sandwiches of 20 (Figure 3.3). Each deck is 1.2 m wide by 1.5 m long, separated by a 13 mm space that defines the pulp channel. In a typical operation, feed is distributed to all decks for up to 35 min, when the flow is briefly interrupted and the table tilted to wash off the concentrate. The cycle is the repeated. This concentrator can recover over 60 % of 10 μm particles.

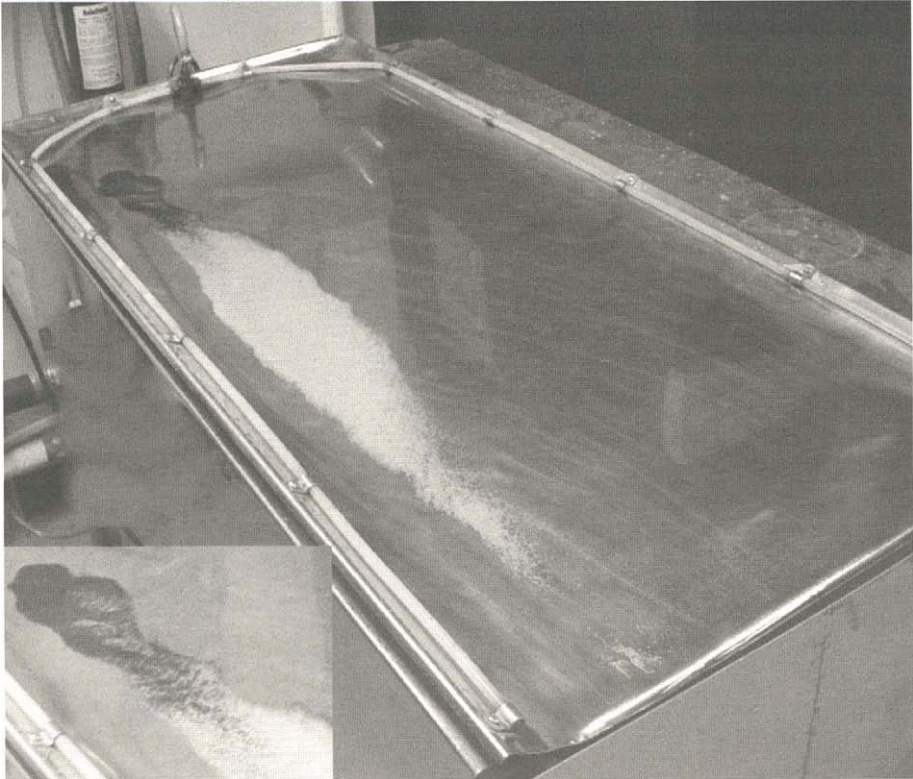


Figure 3.3. Bartles-Mozley gravity concentrator (courtesy, Ray Langlois, McGill University)

3.2.3. Pneumatic Table

Also known as air tables, these devices function by a throwing motion to move the feed along a flat riffled deck, and blow air continuously up through a porous bed. The stratification results in the separation of particles based on size and density differences. The larger size and higher density particles concentrate on the top, the size and density decreasing from the top of the concentrate towards tailings. The coarse particles in the middlings band have the lowest density. The mechanism of separation is very complicated and has not been well understood; however, some basic separation principles can be understood from Figure 3.4.

The feed is introduced at one end of the table deck, where the air flowing upward through the porous deck and the particle mixture causes an immediate stratification of the material on the deck. As a result, the heavier particles settle down to the deck surface, while the lighter ones are lifted up and float on an air cushion in such a way that the feed materials are stratified in vertical layers with a decreasing specific gravity from the bottom (deck surface) to the top. Simultaneously, the deck oscillation promoting the stratification pushes the heavier particles up the longitudinal slope towards the higher end of the deck. As a results of the side tilt, the lighter particles move down towards the lower end of the deck. Intermediate fractions, depending on the particle size, shape and density, distribute between the two ends and are discharged into separate collection bins.

Table 3.1. Variables of Shaking Table

Design variables:	Running Speed:
Table shape	Motor speed
Table surface material	Pulley size
Shape of riffles	
Pattern of riffles	Operating Controls:
Acceleration and deceleration	Table tilt
Feed presentation	Pulp density of feed
	Wash water
Stroke:	Position of product splitters
Toggle	
Or Vibrator settings)	

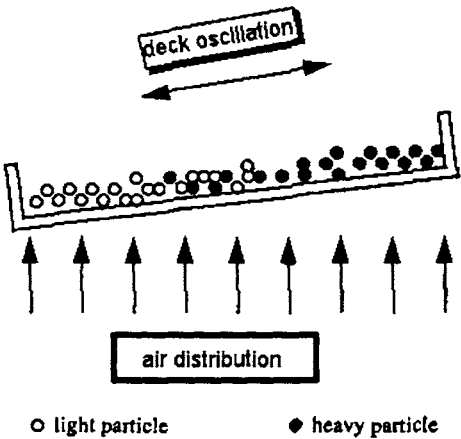


Figure 3.4. Cross section of the air table deck and particle bed. Particle flow is perpendicular to the page (Zhang *et al.*, 1998)

A crucial step in material separation on an air table is stratification. Materials to be separated are introduced by a feeding hopper into the stratification zone; see Figure 3.5. Stratification of materials on the air table is schematically illustrated in Figure 3.6.

Mixed materials with different densities and sizes are fed onto the porous deck and distribute randomly (A). With an appropriate air velocity, the materials can stratify in such a way that light particles are at the top and heavy particles at the bottom (B). An excessive air velocity can, however, break down the stratification by blowing heavy particles into the upper zone, thus causing them to mix randomly with light particles (C). Optimizing the air velocity is therefore of great importance for effective stratification. After the stratification of the materials into vertical layers over the table deck, separation of different layers occurs through a differential motion system of the deck. Separation takes place in both B and C zones of the table, as shown in Figure 3.5.

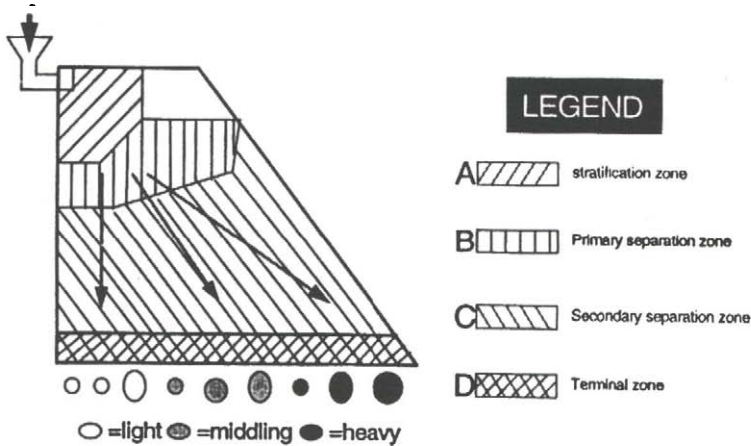


Figure 3.5. Schematic presentation showing the stratification and separation zones on the table deck. (Zhang *et al.*, 1998)

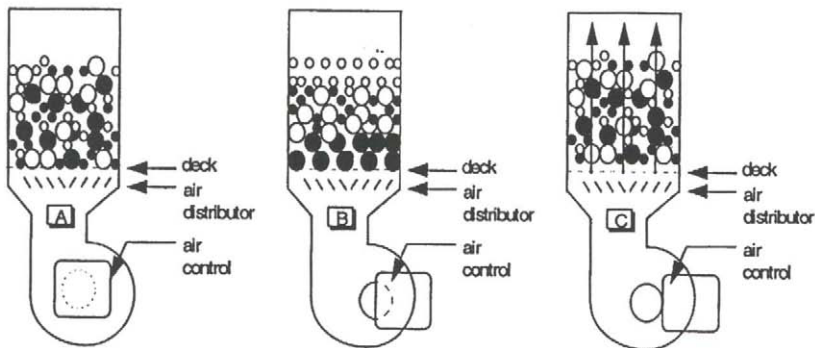


Figure 3.6. Stratification of particles on the table deck (Zhang *et al.*, 1998)

By mathematical analysis Zhang and coworkers (1998) have shown that particles in the bed stratify according to their specific gravities so that light particles tend to move upwards, while the heavier ones sink downwards. If particles to be processed differ in both size and density, the stratification becomes complicated. It can be expected that both heavy and small particles will move upwards in the bed. In a practical example, fine

copper wires (heavy particles) stratify with plastics (small particles) when recovering copper from electronic scrap (Zhang *et al.*, 1998).

As materials move across the deck, the side tilt makes them flow across an inclined deck surface. As the air particles are suspended on air cushion and fail to touch the deck surface, they slide downwards to the lowest side of the deck due to the gravitational force. However, the heavy particles staying in contact with the table are subjected to an asymmetric acceleration, thus moving uphill towards the higher end of the deck.

Optimum operation of an air table is shown in Figure 3.7. The elevation of the deck shown the Figure decreases from the left to the right (X direction), and increases from the bottom of the Figure to the top (Y direction). The lower right hand corner is the lowest position of the table deck where light particles are concentrated, while the higher right-hand corner is the highest position where heavy particles are upgraded.

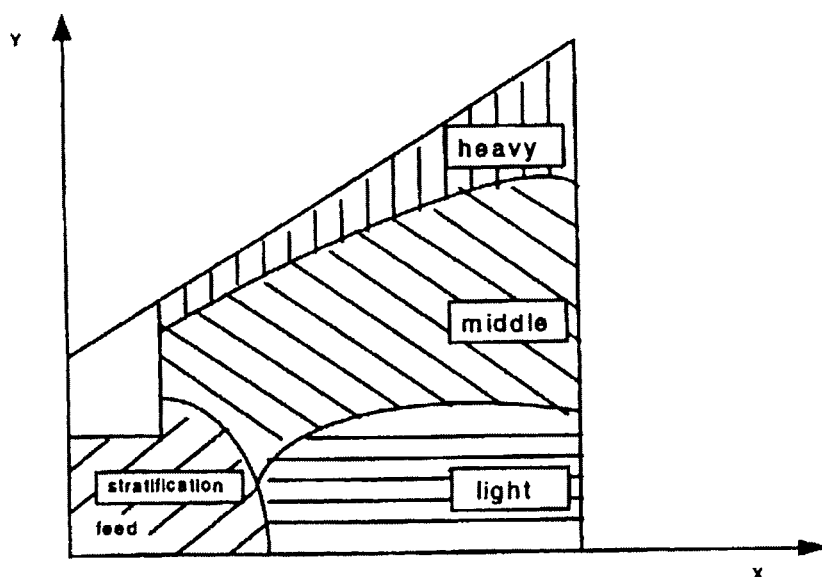


Figure 3.7. Optimum separation of an air table (Zhang *et al.*, 1998)

Air tables are employed where the heavy fraction is minor in the two-part separation into light and heavy fractions, and with a density difference between the two of at least 1.5:1 (Wills, 2001). A laboratory study to separate copper and plastic from electronic scrap has been described by Zhang and coworkers (1998). The materials to be separated must have similar size. Recovery of aluminum from shredded and screened waste, the separation of copper from plastic insulated wire scrap and recycling of metals from electronic scrap are some of the applications of air tables.

3.2.4 Jigs

Jigging is another technique, which has been used for almost 200 years in ore dressing to separate minerals with significant differences in specific gravity. The light and heavy particles are separated by using their abilities to penetrate an oscillating fluid bed supported on a screen. A pulsating current of water by a plunger dilates the material

so that the heavier, smaller particles penetrate the interstices of the bed and the larger high specific gravity particles fall under a condition of hindered settling. The process is schematically described in Figure 3.8.

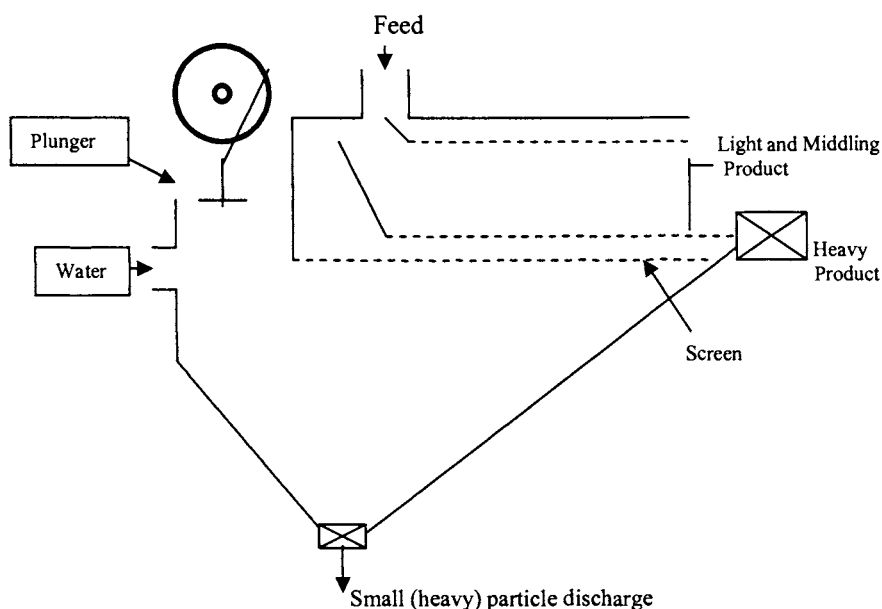


Figure 3.8. Plunger-type jig; a schematic representation

3.2.4.1. Multi-cell Jigging

A novel jigging concept developed by Yang has led to the development of jigs with multi-cell design. It is schematically shown in Figure 3.9.

The machine consists of a single column fitted with specially designed packing plates. The packing acts as a partition dividing the unit into a great number of jigging cells and also functions as a riffing system similar to thin film separators (as described under Shaking Tables; Section 3.2.1). The velocity profile of the pulsed water leads to stratification of solid particles along the vertical direction according to the specific gravity of the particle. The length and frequency of the stroke can be varied to suit the application. During suction (downward water movement), particle beds build on the packing in layers and then cascade down the vessel to the next packing stage as a combined semi-compacted mass. During the pulsion cycle (upward water flow), the downward movement of the particle bed is halted and the upper portions are re-suspended, with a portion hydraulically lifted up the column and the other fraction trapped in a zone under the inclined packing above. Particle trapped in the water current return to the original packed bed by hindered settling classification and the lighter particles tend to settle near the top of the bed. The fine heavy particles also trickle down into the weakly agitated bed during this phase. The net effect of the operation is improved transportation of high density particles down the column to the concentrate stream (metals or heavy minerals) by virtue of the mass movement of the bed on the suction stroke as the bed helps protect these fines from high upward current. The vertically

induced stage of the high capacity multi-cell machine reduces both floor space requirements and construction costs.

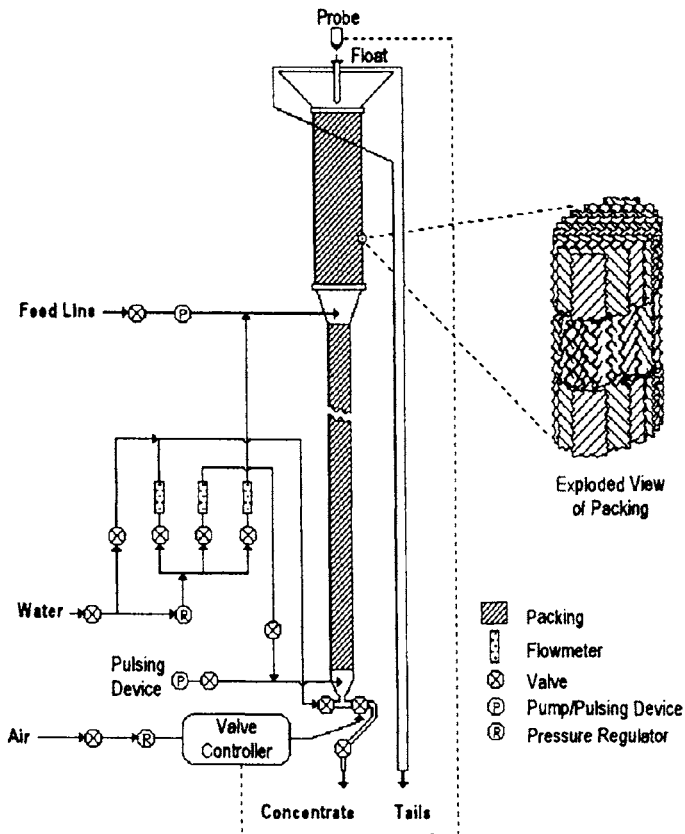


Figure 3.9. Yang jig schematic design (Yang *et al.*, 2002)

The Yang jig has been installed in a South African ferrochrome plant for metal recovery from slag. It treats the finest cut of the slag feed of a 2 mm top size.

3.2.5 Classifiers

In classification mixtures of solids are separated into two or more products making use of differences in velocities with which the particles fall through a fluid medium, usually air or water. In a typical classifier fluid is rising at a uniform rate in a column. Particles whose terminal velocities are greater than the upward velocity of the fluid sink and are recovered in the underflow and those, whose velocities are less rise and are carried in the overflow. The process is called elutriation.

Air classifiers are used on a wide variety of feeds and are simple and efficient. Several designs have been described. In vertical air classifier, shown in Figure 3.10 feed is either added near to the top of the air elutriating column, or shredded material placed on a conveyor belt is subjected to an upward blast of air which entrains lighter components like paper and plastics while the heavier components, like metal and glass,

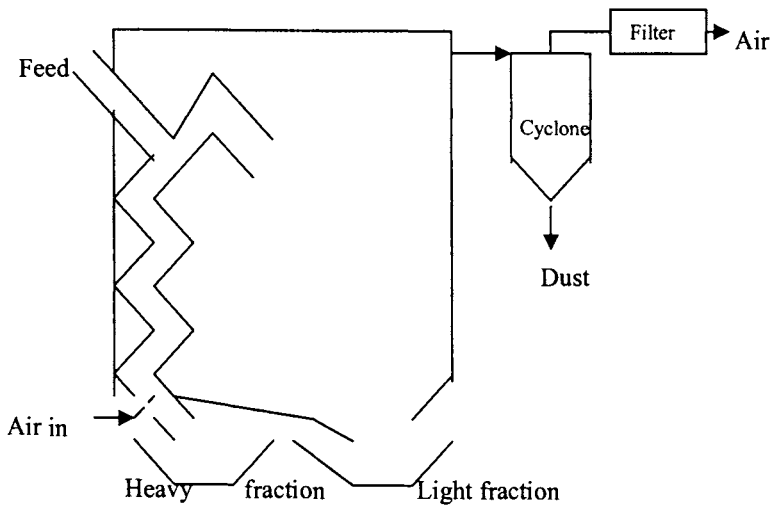


Figure 3.10. Pneumatic vertical air classifier

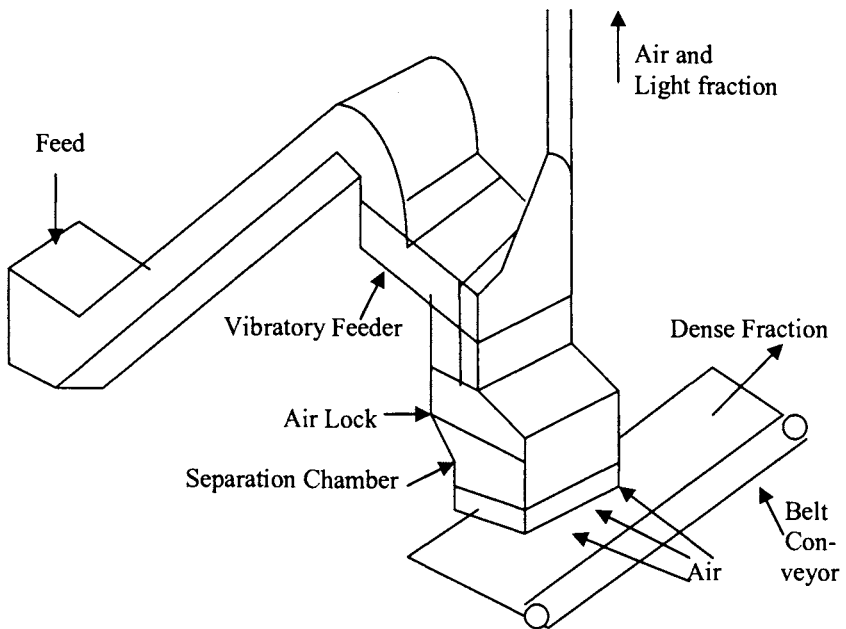


Figure 3.11. Zigzag air classifier

fall down. The lighter fraction is pulled upwards by a blower and heavier fraction is discharged onto a conveyor belt

A second design is zigzag air classifier (Figure 3.11). This is specially useful to treat the material containing flocs of particles and give clean separation as it combines

turbulence and shear forces. The largest particles should be no greater than three quarter of the diameter of the zigzag chamber (Bridgwater and Mumford, 1979; Vesilind and Rimer, 1981)

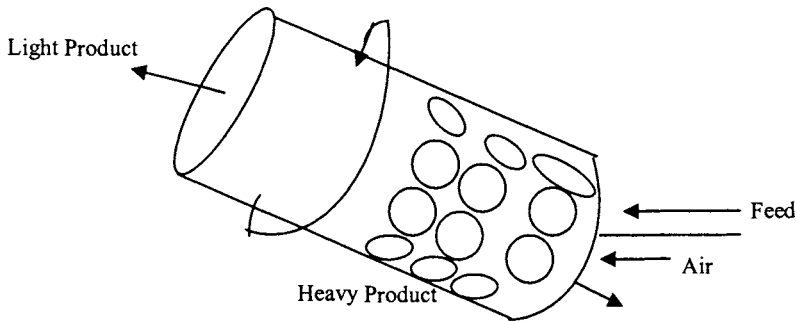


Figure 3.12. Rotary air classifier

In another design, rotary air classifier (Figure 3.12), the feed is treated in a rotating drum. As the drum rotates, the lighter fraction is suspended in the air stream and carried up into a collection hopper. Small, heavy particles fall through the holes while large heavy particles exit at the lower end of the drum.

Other designs, less frequently used are described in the books by Porteus (1977), Vesilind and Rimer (1981) and Veasey, Wilson and Squires (1993).

3.2.5.1. Wet Classification

In wet classification water is used in place of air as elutriating fluid. Light particles are carried in a rising current of water while dense particles sink. In one design described by Veasey *et al.* (1993), the wet classifier consists of a steel tank structure with an internal conveyor and two compartments. In one there is a strong upflow of water which separates metals from the waste (usually lighter component in the feed). The metal fraction sinks and is collected on a conveyor under water and taken into the second compartment, then out by another conveyor. The light component is washed over the sides onto a screen through which the water is drained.

3.2.6. Spiral Concentrators

This is another variation of gravity separation, using density differences and centrifugal force; Figure 3.13. Originally known as Humphreys spiral (after the inventor) a wide range of devices are now available. A spiral concentrator consists of a helical conduit of semi-circular cross-section. Feed pulp of between 15 and 45 percent solids in the size range 3 mm to 75 μm is introduced at the top of the spiral. As it flows downwards, the particles stratify due to the combined action of centrifugal force, the differential settling rates of the particles, and the effect of interstitial trickling through the flowing particle bed. The higher specific gravity particles are removed through the port located at the lowest point in the cross-section. Wash water added at the inner edge of the stream, flows outwardly across the concentrate band. Adjustable splitters control the width of the concentrate band removed at the ports. The grade of concentrate drawn from descending ports decreases progressively, with tailings discharged from the lower end of the spiral conduit.

3.2.7. Heavy Media Separation

In this technique, also referred to as dense medium separation, the separation occurs in a medium of density higher than that of water and between the densities of the two components to be separated. This medium can be dissolved salts in water, or more commonly, a suspension of finely divided high density particles in water. Magnetite (iron oxide, Fe_3O_4) or ferrosilicon (FeSi) or a mixture of the two are commonly used. They are physically stable and chemically inert, can be easily removed from the products and recycled. In earlier times, bromoform, an organic halogen compound (halo hydrocarbon) of high density used to be a choice medium, but its use has largely been eliminated due to its high toxicity.

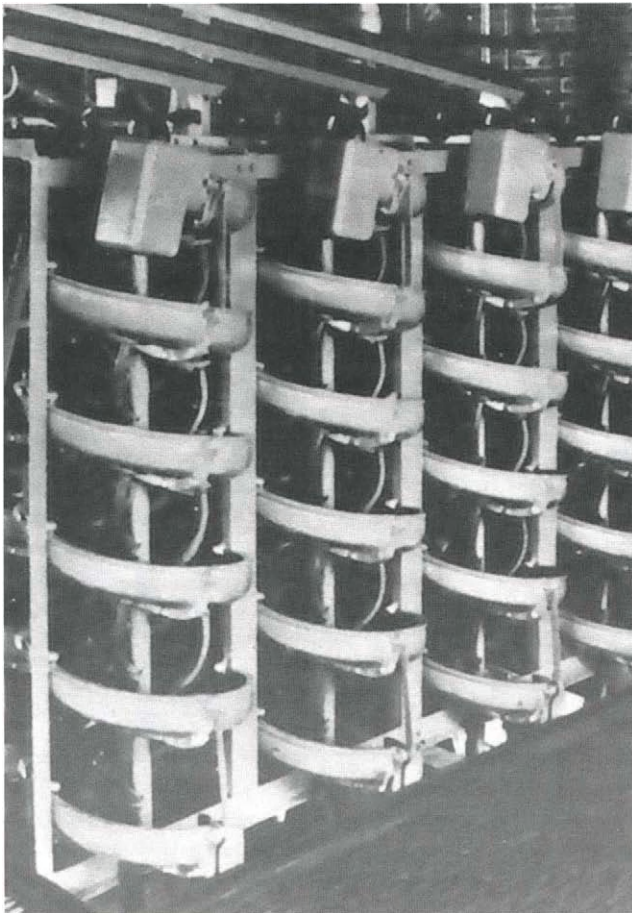


Figure 3.13. Humphrey spiral concentrator (Kelly and Spottiswood, 1982)

In heavy media separators, the feed and medium are introduced at the surface of a large pool of the medium. The float material overflows or is scraped from the surface of

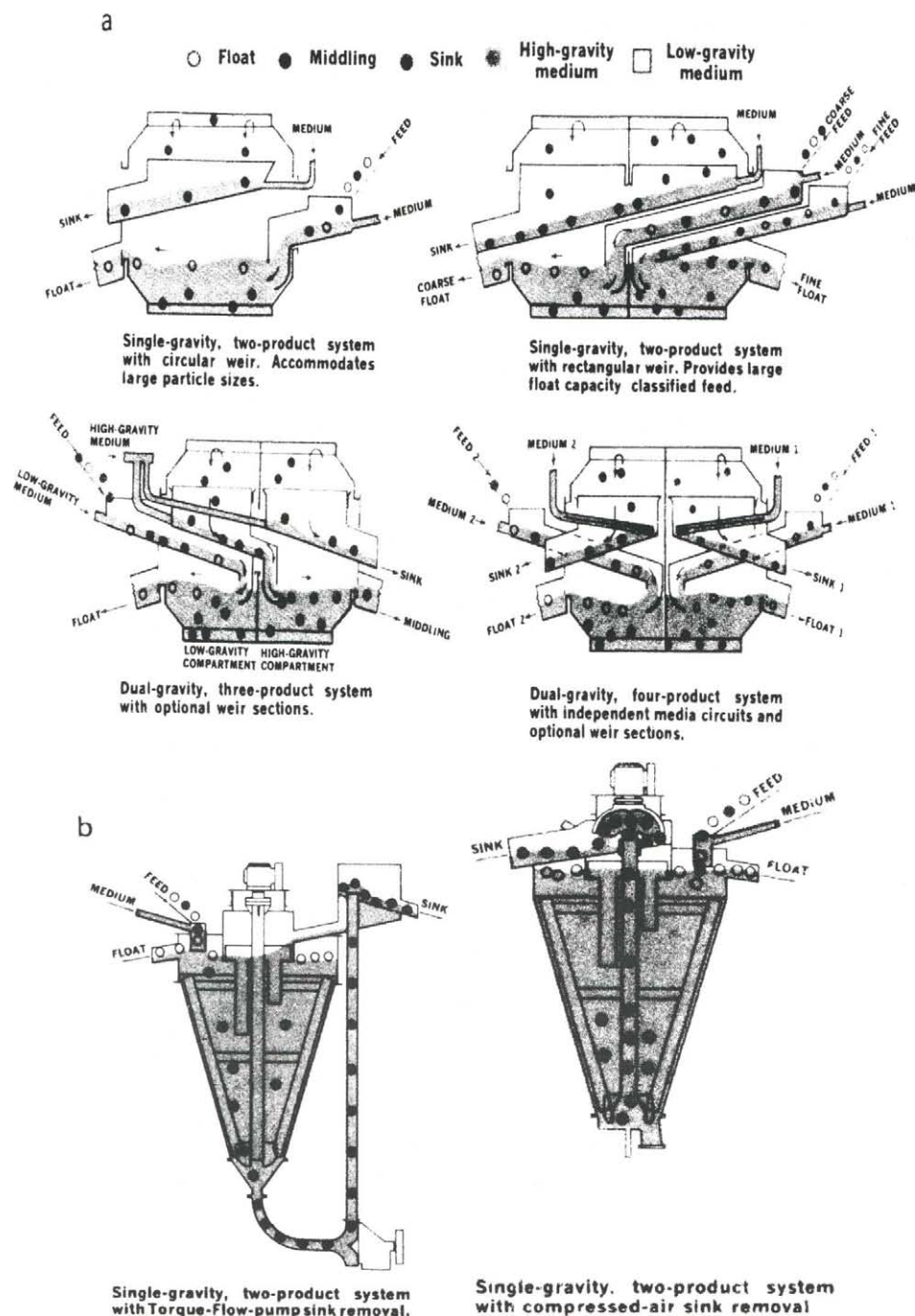


Figure 3.14. Dense medium separators. (a) Drum type. (b) Cone type. (Courtesy, Wemco Division, Envirotech Corp.) (from the book of Kelly and Spottiswood, 1982)

the pool, while the sink component is recovered from the bottom of the vessel. Two main designs of separator are drum separator (Figure 3.14a) and cone separator (Figure 3.14b). The drum type is more widely used. In this design, the sink product is lifted clear of the bath by the rotation of the drum. In the cone separator, the sink product is removed from the bottom of the cone either directly or by an airlift in the center of the cone.

When the feed contains material of fine particle size, a greater acceleration has to be applied to produce sufficient force to achieve separation. This is done in centrifugal separators.

3.3. Magnetic Separation

Separation of magnetic substances, in particular, iron, has been used for over 200 years in the concentration of iron ores. In the last 100 years, the technique has been applied for a wide range of ores and mineral wastes using a wide variety of devices. The removal of small quantities of iron and iron-bearing components and the separation of ferrous and nonferrous components are important applications.

The property of a material, which determines its response to a magnetic field is the magnetic susceptibility. Materials are classified in two groups based on magnetic susceptibility. Paramagnetic materials are those attracted by a magnetic field, and diamagnetic materials, which are repelled by a magnetic field. The materials which are very strongly paramagnetic e.g., iron and magnetite, Fe_3O_4 are placed in a separate group called ferromagnetic. Examples of paramagnetic materials are hematite, ilmenite and pyrrhotite. Non-metallic compounds like silica, silicates and aluminosilicates are diamagnetic.

3.3.1. Low Intensity and High Intensity Magnetic Separators

Two categories of equipment are low intensity and high intensity magnetic separators. Low intensity separator is used primarily for ferromagnetic materials and for paramagnetic materials of high magnetic susceptibility. High intensity separators are used for paramagnetic materials of lower magnetic susceptibility. Both low and high intensity separations may be carried out either wet or dry. Some very large wet high intensity magnetic separators have been applied in the separation of paramagnetic components.

Low intensity separators employ either electromagnets or permanent magnets. Electromagnets provide relatively high magnetic strengths. Separators are also made in the form of drums, magnetic drums. They have five poles symmetrical about the centerline of the magnetic yoke, with the poles alternating, which helps to improve the agitation at the drum surface, thus reducing entrapment of nonmagnetic components. Some of the drum type low intensity magnetic separators are shown in Figure 3.15.

Wet high intensity magnetic separators (sometimes referred to by acronym WHIMS) are made in carousel type (Figure 3.16) and cannister type (Figure 3.17). The ferromagnetic matrix on which paramagnetic particles are collected may be in the form of steel balls, steel wool, or sheets of expanded material. Further details of wet high intensity magnetic separators are found in the papers by Lawver and Hopstock (1974), Jones (1960) and Iannicelli (1976).

A schematic representation of dry magnetic separator is shown in Figure 3.18. It consists of three magnetically induced rolls. The magnetic material is attracted on the role and discharged at the point where the roll moves away from the magnetic pole. And is passed round the second role. The process is repeated at the third role. The nonmagnetic

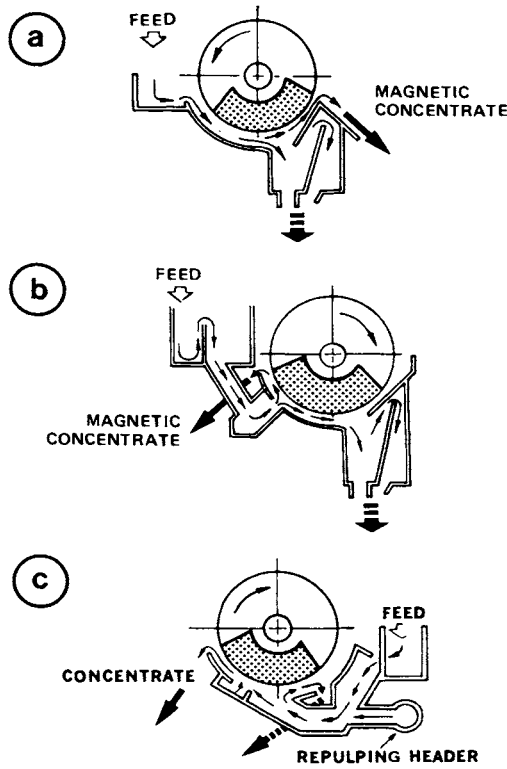


Figure 3.15. Wet drum low intensity magnetic separator designs. (a) Concurrent; (b) Counterrotation; (c) Countercurrent. (from the book of Kelly and Spottiswood, 1982; reprinted with permission of Eriez Magnetics, copyright 2006)

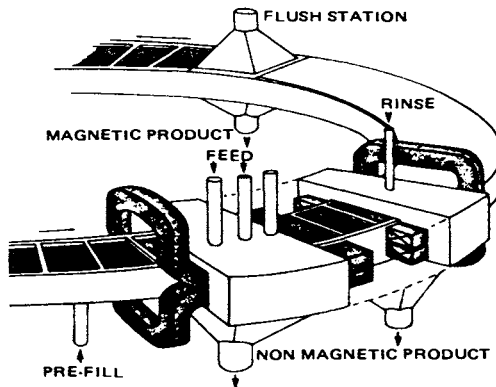


Figure 3.16. Carousel-type wet high intensity magnetic separator operating components. (Courtesy KHD Humboldt Wedag AG) (from the book of Kelly and Spottiswood)

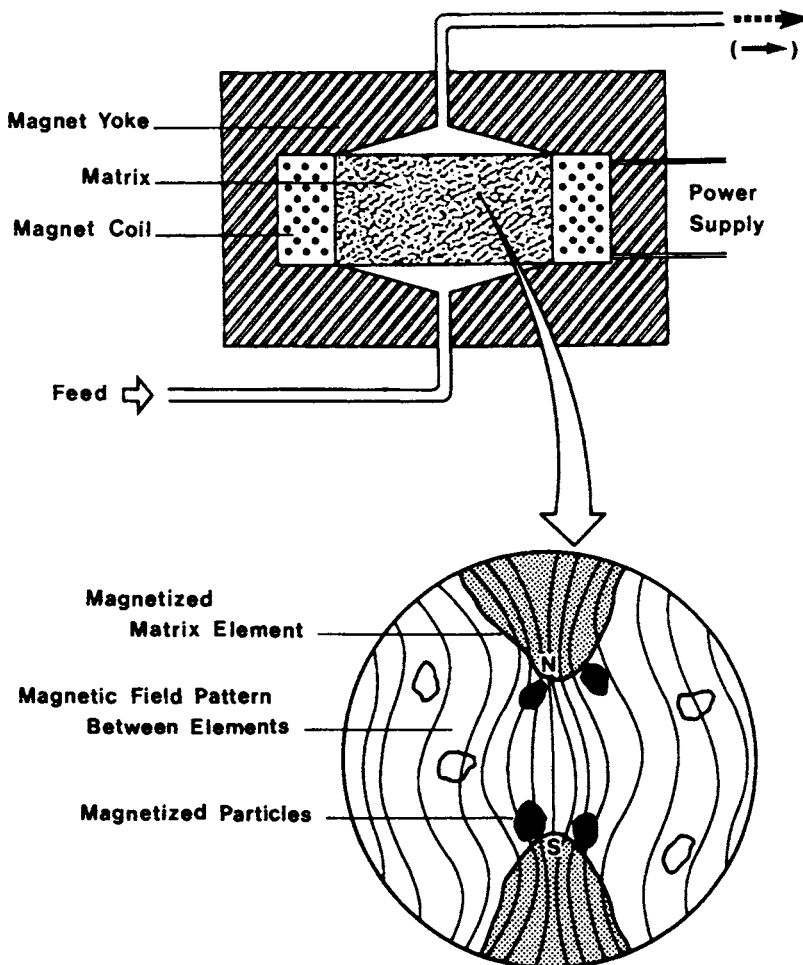


Figure 3.17. Schematic diagram of a cannister-type high intensity magnetic separator (Kelly and Spottiswood, 1982).

component, which is not attracted towards the magnetic role is separately discharged as shown in Figure 3.18.

3.3.2. High Gradient Wet Magnetic Separators

The general relationship for magnetic force F_m in a magnetic separator is given by

$$F_m = \mu_0 V_p M_p \text{grad } H \quad (3.1)$$

where μ_0 denotes the permeability constant of the vacuum, V_p the particle volume, M_p particle magnetization, and $\text{grad } H$ the gradient of the magnetic field strength at the position of the particle. As the shape of the particle to be separated is usually given, the

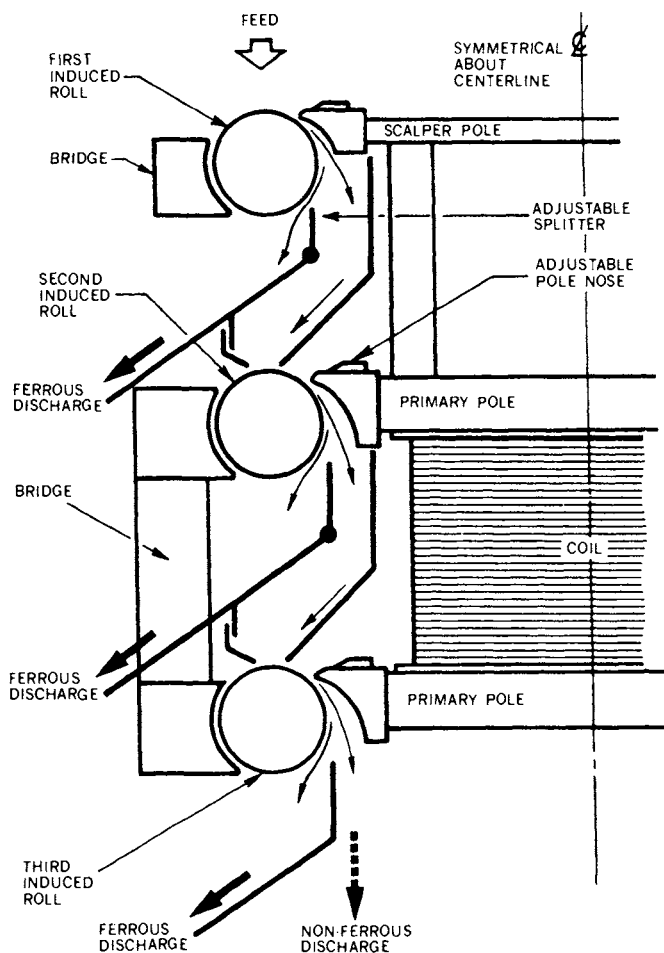


Figure 3.18. Schematics of a 3-stage induced roll dry magnetic separator. (from the book of Kelly and Spottiswood, 1982; reprinted with permission of Eriez Magnetics, copyright 2006).)

magnetic force achievable in a separator is influenced by the field strength and in particular by its gradient ($\text{grad } H$ in Equation 3.1). Simple drum-type separators reach only moderate values for these parameters. In the type called high-gradient magnetic separators (HGMS) based on electromagnets field strengths of 1-2 Tesla and gradients of up to about 10^5 T/m are attained. The limits of magnetic particle separation are thus determined by HGMS. Detailed theory is discussed in textbook on the subject (Svoboda, 1987).

A schematic drawing of a high gradient magnetic separator is shown in Figure 3.19. The main part of the separator looks like a permanent magnetic system with an iron yoke. The matrix is surrounded by a sheet metal housing forming chambers for flow distribution. The supply and discharge connectors are placed at the end of the flow distribution chambers. The filter matrix can be replaced by a service opening in the

housing. During operation, the suspension is pumped through the filter until a certain pressure drop or effluent turbidity is exceeded. The fluid supply is then stopped and the magnet system is switched off, the matrix is cleaned by a short intensive rinsing, preferable in the direction of the flow. The magnet is switched on again and new cycle is started.

The HGMS has been applied for recycling ferrous microparticles from aqueous rolling mill effluents (Franzreb and Habich, 2002). Its maintenance and running costs are low and it has great potential in steel recycling.

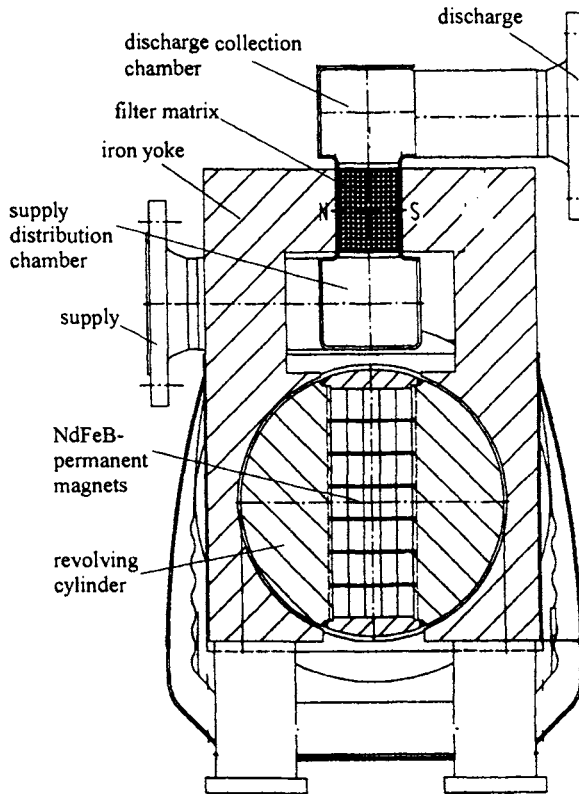


Figure 3.19. Schematic view of a switchable permanent magnet system (Franzreb and Habich, 2002)

3.3.3. Magnetic Fluid Separators

These separators combine the gravitational force with magnetic force from high magnetic fields to which a fluid is subjected. Magnetic fluid is usually a suspension of ferrosilicon and magnetite in water. When subjected to a magnetic field, the levitation force of the magnetic fluid can create densities up to 10 g/cm^3 . With magnetic fluid particles with a broad range of densities can be removed. As shown in Figure 3.20 density range of materials to be separated is greatly enhanced when magnetic fluid system is used as compared to that with dense medium separation with magnetite or ferrosilicon without magnetic field (Vesilind and Rimer, 1981). Figure 3.21 shows

schematic diagram of a magnetic fluid separator. Other designs are described in the book by Veasey *et al.* (1993).

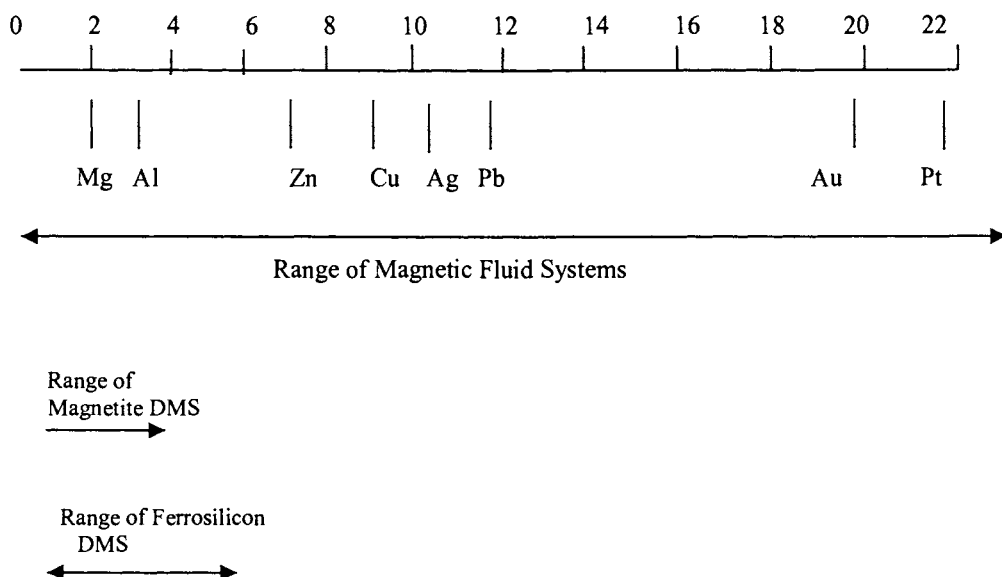


Figure 3.20. Separation ranges of dense medium separation and magnetic fluid systems (Veasey *et al.* 1993).

3.4. Electrostatic Separation

This technique is based on differences in electrical conductivities of the materials. The separators are commonly called high tension separators. Figure 3.22 illustrates the principle. The feed is carried by a grounded rotor into the field of a charged ionizing electrode. A charge is imparted to the feed particles by ion bombardment. The conductor particles lose their charge to the ground rotor and are thrown from the rotor surface by centrifugal force. They then pass along a nonionizing electrode and are further repelled from the rotor. The nonconducting particles are held to the rotor surface as they do not dissipate their charge rapidly. Their charge is slowly lost and eventually they drop from the rotor. The middling particles (those with conductivity in between those of conducting and nonconducting components) lose their charge faster and drop first. The residual nonconducting particles are removed from the rotor by a brush. Since the charge on the surface of a coarse particle is lower in relation to its mass than that on a fine particle, the separation is also influenced by the particle size. Thus a coarse particle is more readily thrown from the rotor surface and the fine particles tend to be trapped by nonconducting particles and report preferentially with the nonconductor fraction. In practice, therefore, it is often necessary to use multiple stages of cleaning.

Electrostatic separation is frequently applied as a step in metal recycling operations, for metal recovery from electronic scrap and in the recovery of precious metals from used catalysts. Some examples will be described in Chapters 7 and 9.

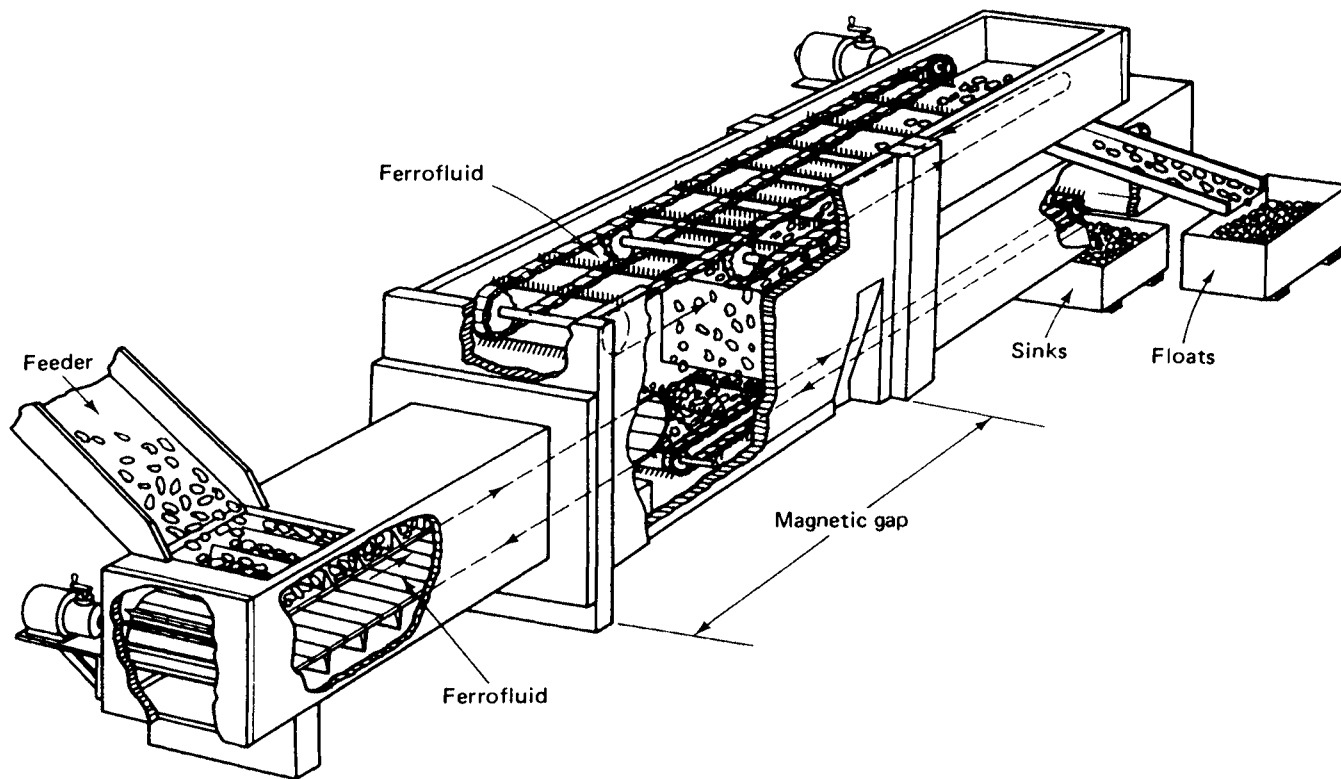


Figure 3.21. Typical magnetic fluid separator (AVCO Systems)

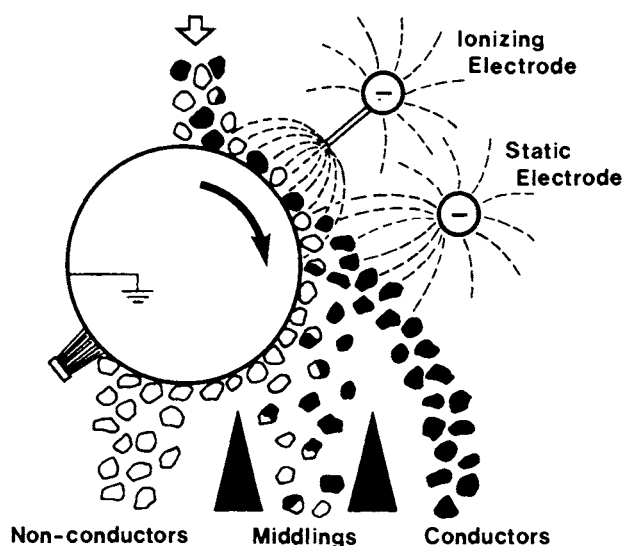


Figure 3.22. A high tension separator (Kelly and Spottiswood, 1982)

3.4.1. Eddy Current Separators

Eddy currents are a manifestation of electromagnetic induction occurring when a magnetic field is applied to a conductor. If the magnetic induction B in a material changes with time, a voltage is generated in the material, according to the equation

$$- \frac{dB}{dt} = \frac{V}{A}$$

where b = magnetic flux density, V = voltage and A = cross section of enclosed area normal to the lines of magnetic flux, m^2 . This is known as Faraday's law of magnetic induction.

In an electrical conductor, the induced voltage produces a current called eddy current which is produced. If the magnetic flux density is increasing, the current direction will be such as to create a magnetic field that opposes the applied magnetic field. If the flux density is decreasing the current direction will be such as to create a magnetic field that reinforces the applied field. The direction of the current loop is determined by a principle called Lenz's law. If B is decreasing, the direction of the current will be such as to create a magnetic field that opposes the applied magnetic field; if B is increasing, the direction of the current will be such as to create a magnetic field that reinforces the applied field. The force that orients a current loop or magnet in a stationary field and that moves a current loop or a magnet in a moving magnetic field is called the Lorentz force. The net Lorentz force is zero when the field is uniform over a conducting material, for example an aluminum can. If the field is stronger on one side than on the other the can would be propelled in the direction in which the magnetic flux density is increasing. When the magnetic field is moved the eddy currents produced in a conductor will cause a net force in the direction of field motion. Eddy currents in metals can be generated by one of the four methods (Vesilind and Rimer, 1981): (i) by physically moving a sample through a

magnetic field; (ii) by moving the magnetic field through the sample by moving the magnet; (iii) by moving the magnetic field through the sample by an electrical phasing technique; and (iv) by temporarily changing the magnetic field intensity in a sample.

Eddy current separation technique is used for separating metals from nonmetal component; for example, aluminum from glass, which cannot be done by gravity methods as the difference in the densities of aluminum and glass is very small. Other applications will be described in Chapter 7 on Metal Recycling. A schematic representation of eddy current separation is shown in Figure 3.23. An alternating magnetic field is produced by a high speed cylindrical assembly of permanent magnets rotating inside an outer drum over which the material is passed. The materials leave the drum in various product splits - non-ferrous metal component, which is thrown clear of the drum; non-metallics which are drawn away from the drum by gravity; and ferrous metals, which are attracted to the drum and brushed off.

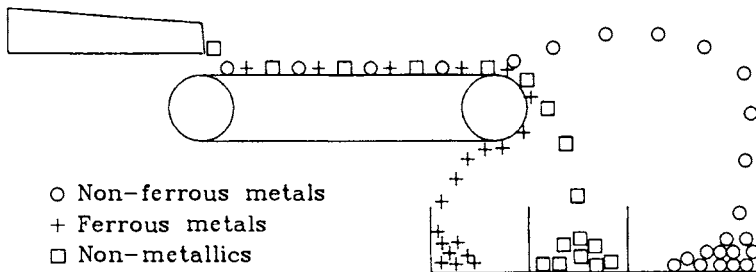


Figure 3.23. Schematic diagram of an eddy current separator (Wilson *et al.*, 1994)

Since eddy current separation depends on the levitation of the conducting component by the magnetic field (by magnetic repulsion), the ratio of conductivity to density indicates a measure of selectivity of separation. The values shown in Table 3.2 indicate, for example, aluminum has a ratio of conductivity to density almost twice as great as for copper (Sommer and Kenny, 1975), which suggests a high degree of separation of aluminum is possible by eddy current technique. On the same principle, eddy current separation could be possible between good conductors like Al, Cu, Ag and other materials. However, due to economic reasons, at this time, eddy current separation technique is used mainly for the separation of aluminum cans made of this metal are widely used.

An effective separation method using permanent magnets, developed by Schloemann (1982) is called sliding ramp technique, schematically shown Figure 3.24. In its simplest configuration the separator consists of an inclined table, which is partially covered by an array of permanent magnets that are arranged in the stripe pattern shown on the left side of the illustration. Barium or strontium ceramic magnets, which are usually inexpensive are used. They are covered with a nonmagnetic layer (like stainless steel) to create a smooth upper surface. The mixed feed material is introduced on one side of this inclined table. The non-metallic particles slide straight down, as they are not affected by the magnetic fields. Metallic particles, however, experience a lateral force due to the electric eddy currents induced in them as they move through the magnetic fields. Thus the metallic and the non-metallic particles can be collected in separate containers at the

bottom of the ramp. The lateral deflection of a metal particle on the sliding ramp depends upon many physical parameters. The more important ones are: the length and inclination of the ramp, the strength and spatial period of the magnetic field at the ramp surface, the conductivity (σ) and mass density (ρ) of the material comprising the metal particles, and the shape and size of the metal particle. When deflection is small compared to the ramp length, the lateral deflection is proportional to σ/ρ when other parameters are kept constant.

Table 3.2. Electrical Conductivity/Mass Density ratio for Various Nonferrous Metals (from Sommer and Kenny, 1975)

Metal	Electrical conductivity, σ (10^8 mho/m)	Mass density, ρ (10^3 kg/m ³)	σ/ρ (10^3 mho-m/kg)
Aluminum	0.35	3.7	13.0
Copper	0.59	8.9	6.7
Silver	0.63	10.5	6.0
Zinc	0.17	7.1	3.4
Brass	0.14	8.5	1.7
Tin	0.09	7.3	1.2
Lead	0.05	11.3	0.4

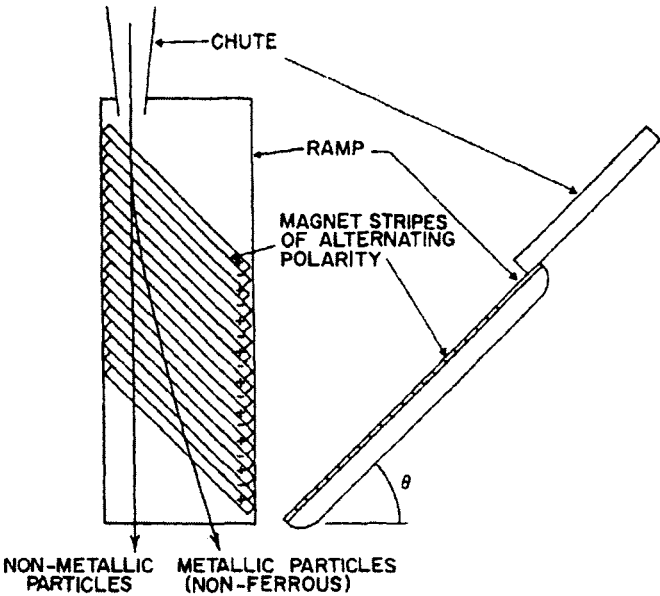


Figure 3.24. Schematic diagram of sliding ramp separator in frontal view (left), side view (right). The shredded material reaches the separator ramp through a chute. Non-metallic particles continue

to slide straight down and metals are deflected in the way shown in the diagram (Schloemann, 1982)

A new version of eddy current separators is an **eddy current rotor (ECR)**. It is a fast spinning cylinder with alternative rows of north and south poles of permanent rare earth supermagnets. The rotor generates an intense alternative magnetic field near its surface. The rotor is housed in the head pulley of a belt conveyor carrying a mixture of shredded metal and nonmetallic particles as shown in Figure 3.25. The alternating magnetic field induces eddy currents in the metallic particles. The direction of the eddy currents is such as to produce an induced magnetic field that repels the particle from the field of the rotor. Metallic particles are thrown ahead while the nonconducting non-metallic particles follow the trajectory dictated by the conveyor belt. The metal and nonmetal streams are separated by a splitter placed at a properly chosen location. In practice, the particle trajectory depends on its size, shape, density and orientation in addition to electrical conductivity. This spreads out both metal and nonmetal streams to the point where they overlap in space and clean separation is no longer possible. If contamination of the metal by nonmetal particles is tolerable, all metal could be recovered. If, however, some metal loss is acceptable, high-grade metal concentrate could be obtained. This is shown in Figure 3.26 in which metal recovery in the concentrate is plotted as a function of the grade of the metal concentrate. In a perfect separation recovery and grade are both 100%. In practice, the performance curve defines for a given separator the best separation that can be achieved for a given feed material composition as one of the separator variables is changed while others are kept constant. The ECR performance can be downgraded leading to lower recovery rates for a given grade of concentrate due to various factors such as overfeeding, feed surges, uneven feeding, material buildup on the splitter, erosion of the splitter, size range (too wide) of the shred, or incomplete particle liberation.

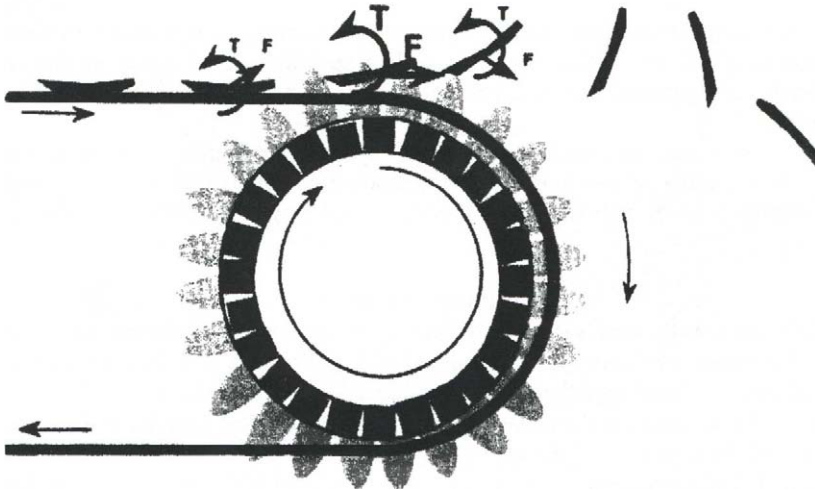


Figure 3.25. Schematic of the interaction of metal particles with the magnetic field of spinning eddy current rotor (T, torque; F, force) (Gesing *et al.*, 1998)

Eddy current rotors have been applied for nonferrous metal recovery from auto-shredder residue. After steel is extracted from shredded automobile scrap, the

nonmagnetic fraction consists of approximately a third of various metals, the remainder being glass, plastic, rubber, rocks and dirt. The metals contained are mainly zinc and aluminum alloys with smaller amounts of magnesium, copper, stainless steel, lead, and the iron, which escaped magnetic separation. The metal components can be separated by heavy medium separation technique described before. This is the current practice in many places; but as heavy medium separation is fairly expensive eddy current method that achieves the same separation has been considered (Schloemann, 1982). Even where eddy current technique does not produce the desired separation grade, it can serve a useful function in automobile scrap processing as a supplement to heavy media separation.

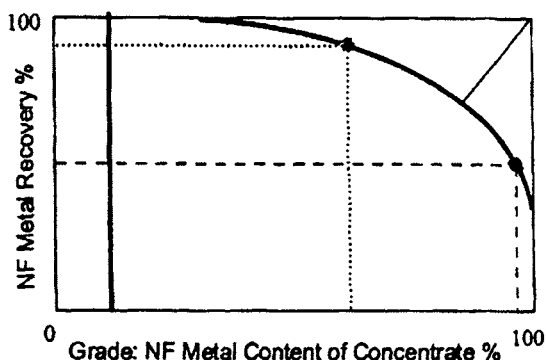


Figure 3.26. ECR performance curve varying the horizontal distance to the splitter edge (Gesing *et al.*, 1998)

The aluminum concentrate generated by a heavy media separator frequently contains contaminations of glass and rocks, materials with a specific gravity close to that of aluminum. Such contaminants can be effectively removed by eddy current separators. (Dalmijn *et al.*, 1979).

Theories of eddy current separation are discussed in the paper by Gesing and coworkers (1998). Details of equipment and applications are reviewed by Schloemann (1982) and Dalmijn (1990). Specific applications in metal recycling will be described in Chapter 7.

3.5 Shredding Systems

Automobile processing and metal recycling from domestic appliances (washing machines, refrigerators, etc.) require the material to be shredded and fragmentized to liberate ferrous metals. These applications require special shredding systems.

Two basic shredding systems, wet/damp and dry have been described by Wilson and coworkers (1994). Dry shredders are generally followed by an air classifier and dust extraction system. The dense fraction is magnetically separated and a ferrous concentrate and non-ferrous preconcentrate are separated. A drawback of dry shredders is they require a sophisticated air cleaning systems to remove all airborne particles. This is partially overcome in wet shredders. In wet state dust is suppressed. The water used, however, requires cleaning, which is considered to be less of a problem (Wilson *et al.*, 1994). Wet shredders are usually directly followed by magnetic separation. The non-

magnetic fraction is separated in a rising current separator, giving a non-ferrous preconcentrate of 30-40% metallics.

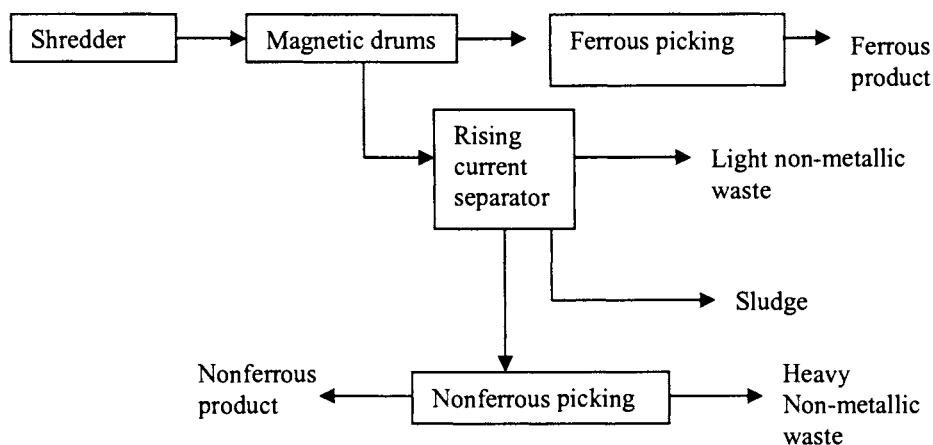


Figure 3.27. Wet shredding system (Wilson *et al.*, 1994)

3.6. Adsorptive Bubble Separation Techniques

These techniques are based on differences in surface activity. Solid in particulate or colloidal form is selectively recovered by a gas (usually air) bubble by a process of attachment. The bubbles rise to the surface of water and the captured particles are recovered. A substance which is not naturally surface active can often be made so by the use of reagents called **collectors** which are adsorbed at the solid surface and makes it surface active.

There are a number of adsorptive bubble separation (sometimes referred to as *adsubble*) techniques. The ones, which are found useful in the processing of metallurgical wastes and resource recovery from them will be described.

3.6.1. Froth Flotation

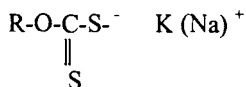
Froth flotation technique was invented in early 20th century and has been widely used for the concentration of a wide range of low grade ores. It is based on interfacial chemistry of solid in solution. From a heterogeneous mixture of solids, one of the components is separated by attachment to air bubbles and being carried in the froth. In order to be attached to the air bubbles the surface of the solid should be hydrophobic. The solids with hydrocarbon type surface, for example, plastics, are naturally hydrophobic and can be floated from those components, for example, metals, which are hydrophilic and do not get attached to air bubbles. Even the solids, which are not naturally hydrophobic can be made so by the action of surface active agents (also called surfactants) which react at the solid surface. Those reagents are collectors mentioned before. Essentially, a collector molecule consists of a **heteropolar structure** with a polar group which interacts with a solid component by a specific mechanism and a non-polar hydrocarbon chain. For example, sodium oleate is used as a collector for iron oxide. In this case, the long hydrocarbon chain of the oleate group is the nonpolar group which makes contact with air bubble and the carboxyl group of the oleate is the polar group

interacting with the silica surface, thus creating a hydrophobic surface film on silica with the hydrocarbon group oriented towards an air bubble.

There are several theories to explain the mechanism of interaction of the collector at a solid surface. The mechanism is determined by the surface chemistry of the specific solid and the chemical structure of the collector. Two principal mechanisms are widely recognized and explain collector action in most of the flotation systems. The following is a brief explanation of these mechanisms. In the first, the interaction takes place by a process of electrostatic adsorption. This happens when the sign of ionic charge of the collector species is opposite to that of solid surface. This is the mechanism of the action of oleate on ferric oxide. In the pH range <8 ferric oxide has positive surface charge and electrostatically adsorbs negative oleate ions. The mechanism is known as electrostatic adsorption. It is observed in most oxide minerals. When the surface charge is negative, as in the case of silica at pH >2, a cationic surfactant like long chain amine acetate or chloride is used as collector to float silica.

The charge on the mineral surface arises by the ions traveling across the mineral solution interface, caused by the preference of one of the lattice ions for sites at the solid surface as compared to the aqueous phase. This gives rise to an electrical potential across the interface. It is called zeta potential. When the surface is preferentially attracting cations, the zeta potential is positive and when anions are preferentially adsorbed at the surface, it is negative. The ionic species, which pass between the two phases are known as potential determining ions. In most nonsulfide minerals hydrogen and hydroxyl ions are potential determining. When the zeta potential at a mineral surface is negative, it is possible to bring the surface charge to neutral, then raise it to become positive by increasing the hydrogen ion concentration of the aqueous phase. The pH at which the zeta potential is zero is referred to as *point of zero charge* (PZC) or zero point of charge (ZPC). At pH higher than PZC the mineral surface is negative and therefore, would attract a cationic collecting agent.

The second mechanism is essentially of chemical nature. In this case, the collector ion or molecule interacts at the surface by a chemical process. The collector species forms a chemical compound at the surface by reaction between the polar group of the collector and the ionic species present at the solid surface. This is specially observed with sulfide minerals. The surface of the sulfide minerals contains sulfoxyl ionic species (like sulfite, thiosulfate) produced by the superficial oxidation of the mineral by atmospheric oxygen and moisture. These anionic species are exchanged for the anionic polar group of the collector. One of the most common collectors for sulfide minerals is a group of surfactants called xanthates which have the chemical formula,



Xanthate reacts with the sulfoxyl ionic species by an exchange mechanism, where the sulfoxyl species are released into solution and a metal xanthate is formed at the surface. It should be noted that the xanthate at the surface, while it may resemble a metal xanthate formed by the precipitation in solution, is often not exactly identical with it as has been observed by comparing the infrared spectra of the bulk metal xanthate and the surface xanthate produced by adsorption. The essential consequence of surface reaction is that a hydrophobic surface film is produced which makes the sulfide mineral floatable.

In addition to collectors froth flotation requires frothers to produce a stable froth when air is bubbled through the slurry or pulp. Frothers are also surfactants with heteropolar structure, but, unlike collectors, their polar group does not interact with solid surface (there are some exceptions), instead, it forms bridge with water mainly by the molecular attraction between the polar group of the frother and water which is a polar molecule by itself. The nonpolar group, a hydrocarbon chain (either linear or more commonly cyclic) is oriented towards air bubble. The net result is lowering of the surface tension of water and production of froth.

The above is a simple explanation of the mechanisms governing flotation. Further details of the collector mechanisms and various other aspects of froth flotation will be found in the book by Rao and Leja (2004). A more concise discussion is found in the book by Kelly and Spottiswood (1982) and in the chapter by Fuerstenau and Healy in the book edited by Lemlich (1972).

3.6.1.1. Factors Affecting Froth Flotation

Froth flotation is influenced by several operating factors. The most important of these is pH. Interaction with collector and formation of hydrophobic film at a mineral occurs within certain pH range. In the case of sulfide minerals, at pH above a certain value, called critical pH, the collector uptake does not occur and the mineral ceases to float. This critical pH varies for different minerals and is taken advantage of for selective separation of minerals from slurry containing more than one mineral.

Another influence of pH is in influencing the state of ionization of the collector. Amines are cationic in acidic pH range. In alkaline pH, the long chain amines occur in neutral molecular state and not suitable as cationic reagents. In between the two ranges, within a narrow pH range they occur as ionomolecular complexes comprising ionic and neutral molecule species and they are highly surface active in this form. This also applies to weak acid collectors like sodium oleate, which is anionic in the alkaline pH range, but occurs in neutral molecular state at pH below 4. For further discussion see Rao and Leja (2004).

3.6.1.2. Equipment

Many designs of flotation machines are currently in use. They all have the primary function of making the particles that have been rendered hydrophobic contact and adhere to air bubbles, then allowing those particles to rise to the surface in the froth, which is removed. To fulfill this function, a flotation machine must maintain all particles in suspension. For this, upward pulp velocities must exceed the settling velocity of all particles present. All particles entering the machine must have the opportunity to be floated. Fine air bubbles must be dispersed throughout the pulp by aeration at the desired rate. The extent of aeration required depends upon the particular system and mass fraction to be floated. Vigorous agitation promotes particle-bubble collision, which facilitates the rise of hydrophobic particles in the froth. A commonly used design of a flotation machine currently in use is represented in Figure 3.28. It has an impeller that rotates within baffles. Air is introduced through the impeller to provide good dispersion and sufficient mixing to cause the bubble-particle collisions for effective bubble-mineral attachment. The air is drawn through the impeller shaft by the suction created by the impeller design and speed, or introduced under pressure.

Other designs are described in the book by Kelly and Spottiswood (1982).

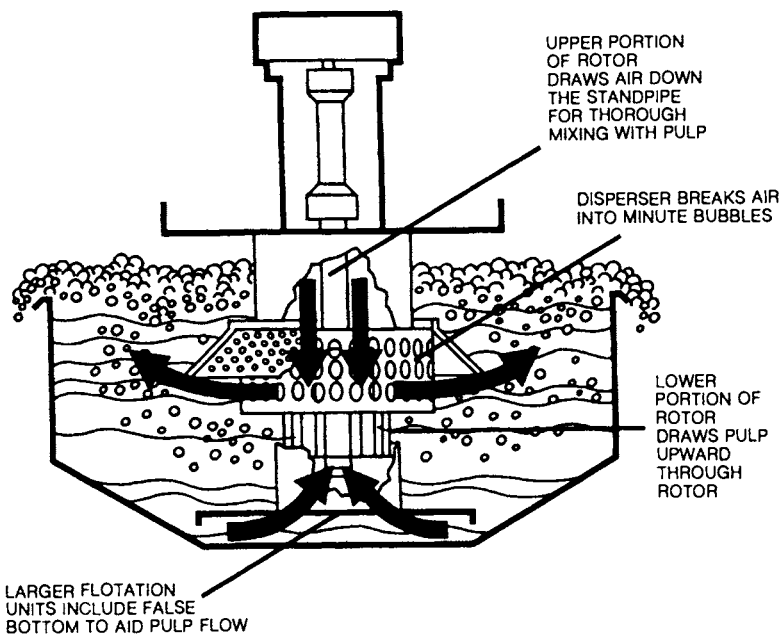


Figure 3.28. Schematic representation of a flotation machine of a design called Wemco-Fagregren flotation cell. Courtesy, Wemco Division of Envirotech Corporation) (from the book of Kelly and Spottiswood, 1982).

3.6.2. Dissolved Air Flotation

This is a variation of froth flotation, in which air or another gas is dissolved into the water under pressure, followed by the precipitation of bubbles on fine particles when the pressure returns to atmospheric pressure. In comparison, the froth flotation described before is dispersed air flotation where air introduced from external source, usually ordinary atmosphere, is dispersed in the slurry. This is specially useful in wastewater treatment to remove fine suspended matter from water.

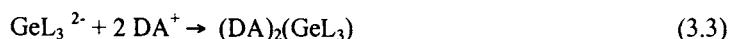
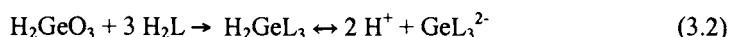
Froth flotation and dissolved air flotation are applied to recover suspended solids from waste streams. They could contain material of economic value. It has also been used to separate pyrite from waste rocks. Details will be described in Chapter 10.

3.6.3. Ion Flotation

This is a relatively new technique, first described by Sebba (1962). It involves the removal of surface-inactive ions like those of metal or anionic species by adding a surfactant and the subsequent passage of gas through the solutions. By this flotation process, a solid, which contains the surfactant as a chemical component, appears on the solution of the surface of the solution. The surfactant also functions as collector and, usually, it consists of an ion of charge opposite to that of the surface-inactive ions to be collected, known as colligend ion. Thus, cations and anions are floated with anionic and cationic collectors, respectively. There are, however, many examples of uncharged collector (nonionic surfactant) which attaches itself to the colligend ion by co-ordination

bond. For example, Cu^{2+} ions can be floated by octadecylamine molecules (Pinfold, 1972).

The mechanism is illustrated by the following example of the collection of germanium present as germanic acid by ion flotation. It is first mixed with a ligand activator which is a surfactant. It converts germanium to the anionic state, which is then combined with a cationic reagent like dodecylamine to produce the sublate.



where H_2L denotes the ligand activator, pyrogallol and DA denotes dodecylamine cation.

The collector-colligend product is called sublate (a term coined by Sebba). Initially it comprises groups of ions held to the surface of the bubble by the surface activity of the collector as a solid, but when it reaches the surface of the solution it floats as a solid. Usually, the concentration of the collector and colligend are low, in the range 10^{-4} - 10^{-5} M and flotation occurs from a true solution. If, however, higher concentrations are to be processed, precipitation of the sublate may occur before gas is passed into the solution. In such cases, the process becomes precipitate flotation, explained in the following Section.

The collector to colligend ratio, denoted by ϕ must at least be a stoichiometric one. In most systems, however, this ratio is found to be higher than that required for stoichiometric combination. The excess of collector is required as the collector and colligend ion meet on a bubble surface and the residence time of the bubble must be sufficient to allow this to proceed to completion. On the other hand, if the colligend is precipitated before flotation (precipitate flotation) the amount of collector needed will be close to the stoichiometric requirement.

Ion flotation is most efficient when the concentration of colligend is in the range 10^{-5} to 10^{-3} M. At higher concentrations the quantity of the sublate formed is often inconveniently large, while at lower concentrations, the amount of collector present is insufficient to form a supporting foam and flotation would be incomplete. As such, ion flotation is specially useful to remove and recover metal ions present in low concentrations from industrial effluents. Some examples will be described in Chapter 7.

3.6.3.1. Selectivity in Ion Flotation

Two main kinds of interaction govern the process of ion flotation according to the ion exchange model. The first interaction is essentially of an electrostatic nature and depends upon the size and charge of ions. (Rubin and Jome, 1969). The second, ion-water interaction is much more complex. The structure of water and its changes caused by dissolved ions play an important role. When there is significant dissimilarity of the behavior of cations and anions in the solution the anions are generally lower hydrated than cations. Small ionic species and those of large ionic size are 'structure breakers' because of their high electric field, which polarizes, immobilizes and counteracts water molecules at the immediate vicinity of an ion (Kavanau, 1964). There is also an ordering of water molecules at long distance range. Lower mobility of water molecules in the hydration sphere over the bulkier water molecules leads to an increase of viscosity at the intermediate vicinity of an ion and thus in positive values of viscosity coefficient. On the other hand, large monovalent anions are found as 'structure breakers'. Dipole-dipole

interaction between water molecules in the hydration sphere of such anions can allow for polarization and immobilization of water molecules only at the first layer. Outside this layer, the structure of the surrounding water is highly disordered. As a result, neighboring water molecules are more mobile than bulk water leading to negative values of the viscosity coefficient for large monovalent anions in aqueous solution.

Walkowiak (1992) has obtained the following sequence of growing affinity of metal cations to anionic surfactants. These are found to parallel the sequence of ionic potential values (inV):

	$\text{Mn(II)} < \text{Zn(II)} < \text{Co(II)} < \text{Fe(III)} < \text{Cr(III)}, \text{Ag(I)} < \text{Cd(II)} < \text{In(III)}$						
Ionic							
Potential	2.08	3.25	3.27	3.80	3.95	0.78	1.83 3.23

The situation is different in the case of anionic flotation. Here, monovalent large ions have the highest affinity to a cationic surfactant. It suggests that ion-water interactions govern the selectivity of the ion flotation process.

3.6.4. Precipitate Flotation

In precipitate flotation an ionic species is concentrated from an aqueous solution by forming a precipitate which is then removed by flotation. It includes three variations.

In *precipitation flotation of the first kind*, precipitate particles are floated by a surface active species, which is not a chemical component of the precipitate substance and occurs only on the surface of the particles. In *precipitate flotation of the second kind*, no surfactant is used to float particles, but two hydrophilic ions precipitate to form a solid with a hydrophobic surface. The third variation is form of ion flotation (Section 3.5.3) in which ions are precipitated by surfactants, and the resulting particles are floated.

In precipitate flotation of the first kind, one or other of the ions which constitute the precipitate is adsorbed from the solution onto the particles. The surface becomes charged and is rendered hydrophobic by a surfactant of charge opposite to that of the surface. Coulombic attraction between surfactant ions and the particle causes the surface to become covered with the surfactant, thus the precipitate is carried by a fine stream of bubbles.

An important feature of precipitate flotation is the low value of collector to colligend ratio ϕ (explained before in Section 3.5.3) as each macroscopic particle contains a large number of colligend ions but only requires a monolayer of collector on the surface for good flotation. Usually values between 0.005 and 0.1 are necessary to form a foam to support the precipitate on the surface of the solution and prevent its redispersion in the bulk. This is a great advantage over ion flotation as it implies much less consumption of the surfactant.

The lower limit of the colligend concentrations for which flotation remains efficient is determined by several factors including the solubility of the precipitate and pH. The colligend concentration must be sufficiently high to ensure virtually complete precipitation. Excess of the precipitant should be avoided as it increases ionic strength which is believed to affect the process adversely in most cases, The reasons for the effect of ionic strength have not been clearly understood. Three possible causes suggested are the following (Pinfold, 1972):

1. The attachment of the collector to the bubble is less secure because increased ionic strength leads to lower surface charge and thus weaker attraction between the bubble and the precipitate.
2. Flotation of the collector is more rapid as repulsion between bubbles is reduced enabling them to leave the solution more easily (Sheiham and Pinfold, 1968).
3. There is an increase in drainage of the foam. The stability of the foam is in part due to repulsion of the positive surfactant ions adsorbed on the inside and outside surfaces of the bubble film. The increased concentration of anions in the film reduces this repulsion and causes to become thinner. That makes the bubbles more susceptible to rupture. As a result, redispersion occurs more freely thus reducing recovery of the precipitate by the bubbles.

3.6.4.1. Effect of pH

The pH of the solution must be within a range of values suitable for complete precipitation of the ion to be removed. The charge on the surfaces of the particles may vary with the pH and determine the nature of the collector to be used. For example, at a pH of 6.5 cupric hydroxide particles are positively charged by the adsorption of Cu^{2+} ions and require an anionic collector, but at higher values the particle surface is covered by OH^- ions and a cationic collector must be used. The pH also affects the state of ionization of the collector. For example, amines and weak acid collectors (like, for example, sodium oleate) will not be ionized in solutions of high or low pH respectively. Ionic strength increases at extreme high or low pH values affecting flotation as discussed before. The stability of the foam supporting the precipitate may also change with pH leading to redispersion. Just as in froth flotation, pH control is an important parameter influencing the efficiency of and selectivity in ion flotation.

Precipitate flotation is used to recover metals and complex anionic species from effluents. Examples will be described in Chapter 10. A fundamental study on the various parameters affecting the flotation of various metal ions has been described by Rao and Doyle (1994).

3.6.4.2. Precipitate Flotation of the Second Kind

There are only a few examples of this variation of precipitate flotation. No surfactant is required, but the precipitate formed when colligend and collector ions react must have a hydrophobic surface. This can occur when the precipitant ion has both polar and nonpolar parts. When present in solution, the influence of the polar part is predominant and the ion is hydrophilic and surface inactive. On precipitation with colligend, however, the charges are neutralized, and the nonpolar group plays the dominant role producing hydrophobic surface on the newly formed precipitate. The elements that have been floated by this technique are, Cu by benzoinoxime, U by benzoyl acetone, Ni by α -furfildioxime, Cu and Zn by 8-hydroxy quinoline, Ni and Pd by nioxime, Ag, Co, Pd, U by α -nitroso- β -naphthol, and Au by phenyl- α -pyridylketoxime ((Mahne and Pinfold, 1966, 1968a, b; 1969). The reagents are probably impracticable for use in industry for economic reasons. Nevertheless, in view of its several advantages including surface inactivity of the collector, independence from ionic strength, a great advantage in the treatment of industrial effluents containing electrolytes in high concentration, and ease of separating the solid from the bubbles makes this an attractive process worth considering in special situations.

3.6.5. Foam Fractionation

Foam fractionation is a separation method using foam as a medium of large specific interfacial area, for partial separation of components of a solution containing surface active solutes (Rubin, 1972). There is no solid phase in this process.

3.7. Separation by Picking

Reference should be made to one of the oldest methods of physical separation, picking. It was quite common in the fields of farming. In mineral industry, it was used in the beneficiation of coal, that is, to sort out better quality coal from lower quality ones by visual recognition. As the materials to be separated became increasingly complex, such physical separation by visually distinguishing the components was totally inadequate and before long became obsolete. In recent years, however, the progress in the computer and sensor engineering has led to the development of automatic picking devices of far greater efficiency than could ever be envisaged in handpicking. Such automatic picking devices have been designed for the separation of metals. Typical tasks carried out are the selective sorting of stainless steel, copper and brass. The principle of the working is illustrated with a modern unit called "CombiSense 1200" (Mutz *et al.*, 2003).

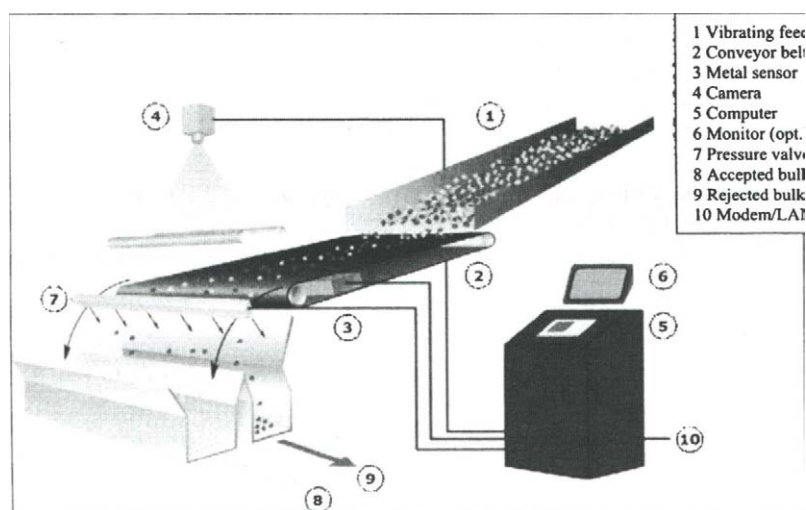


Figure 3.29. Principle of identifying and sorting by automatic picker (Mutz *et al.*, 2003)

A vibrator feed (1), in combination with conveyor belt (2) running at 3 m/s is designed to isolate the particles. The metal sensor (3) located under the conveyor belt delivers the initial characteristics of each single particle to the computer (5). In addition, the color camera (4) also processes particle data. This mass of information is then transferred to a special software (6), which then transmits the impulses, instructing the nozzles (7) to blow out the single particle or allow it to pass. Both the accepted (8) and the rejected (9) products are then transported by single belts to further treatment or storage. The connection (10) is optional; through modem or Local Area Network (LAN) it facilitates the management of the whole process from a remote location.

Automatic picking systems combine special characteristics of multi-sensor systems. They incorporate a high-speed camera with 1 billion colors with a special conductivity

sensor that permits the separation of a variety of metals. With a belt width of 120 cm and depending on the feed material a throughput of 2-150 t/h with a grain size of 3-250 mm can be handled.

Various technologies have been applied in the development of picking devices to recognize the particles to be processed. They include X-ray, laser, infrared conductivity and combination of different electronic systems. Separation devices applying these technologies are in the developmental stage. In the long run, they can potentially lower the cost of separation as they do not require the use of chemicals like the ones used for heavy media separation and froth flotation.

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Chapter 4

HYDROMETALLURGICAL PROCESSES

Recovery of metal values and other potentially useful products from metallurgical wastes often requires chemical treatment. While physical separation (Chapter 3) is still the most desirable route as it requires no chemical input and, therefore could be easier for environmental control, as explained in chapter 3, the application of those methods is limited to material where the components are liberated from each other and show significant differences between them in at least one of the physical properties exploited for the separation. Such conditions do not exist with many metallurgical waste, where the solids are very fine and do not differ significantly in physical properties. Chemical treatment or thermal treatment has to be used for such materials. The chemical treatment route is called hydrometallurgical processing, which will be discussed in this chapter. Thermal treatment route is called pyrometallurgical processing, which will be discussed in Chapter 6.

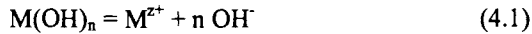
4.1 Selective Precipitation

Precipitation of dissolved metal ions in water by the addition of a suitable precipitant, which form a sparingly soluble compound has been known and applied in many areas for several centuries. Most commonly, the precipitant could be an alkaline compound like sodium or calcium hydroxide to precipitate metallic hydroxides, a soluble sulfide like sodium sulfide. Other precipitants are a soluble sulfate to precipitate those metals (e.g., lead), which form sparingly soluble metal sulfates or a soluble chloride, which precipitates those metals which form sparingly soluble chlorides (e.g., silver and mercury as mercurous). Specific conditions have to be met to achieve selective precipitation of any desired components. It will be discussed in this Section.

Dissolved metal ions in solution can be precipitated as insoluble or sparingly soluble compounds. Most of the common heavy metal ions, Fe, Cu, Zn, Ni, etc. in metallurgical effluents can be precipitated as hydroxides, sulfides, carbonates or phosphate. Precipitation as hydroxide using sodium hydroxide or lime (calcium oxide) and sulfide (using a soluble sulfide like sodium sulfide) is most common in effluent treatment mainly for economic reasons. In addition to the removal of metal ions, one of the main objectives of effluent treatment is to selectively precipitate the individual metal ions by control of pH. This is based on the variation with pH of the solubilities of hydroxides and sulfides. Selective precipitation by pH control is the basis for one of the methods of metal recovery from effluents.

4.1.1. Hydroxide Precipitation

When a metal hydroxide is equilibrated with water it partially dissociates into metal and hydroxyl ions:



The equilibrium constant, known as *solubility product*, is expressed in terms of activities of ions denoted by a :

$$K_s = a_M^{z+} \times a_{OH^-}^n \quad (4.2)$$

Table 4.1 lists some solubility product values. From these values the thermodynamic tendency of a metal hydroxide to precipitate at a given pH can be determined. For example, consider a solution containing Cu(II) ions and it is required to lower the cupric ion concentration down to 10^{-5} M. From Table 4.1 the equilibrium

$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2 OH^-$ at 25 °C is given by

$$K_s = a_{Cu^{2+}} \times a_{OH^-}^2 = 4.79 \times 10^{-20}$$

$$\text{and therefore, } a_{OH^-}^2 = \frac{4.79 \times 10^{-20}}{1 \times 10^{-5}} = 4.79 \times 10^{-15}$$

$$a_{OH^-} = 6.92 \times 10^{-8},$$

which leads to pOH = 7.16 and pH = 6.84.

When the pH is raised to 6.8, cupric ions are precipitated, practically completely.

When similar calculations are made for Mg^{2+} ions, it can be shown that at pH of 6.8, concentration of Mg^{2+} will be 1.48×10^3 M, that is, they remain completely in solution. For precipitating Mg^{2+} the pH has to be lowered to 11.3 as it follows from similar calculations. This is the principle of selective precipitation of metals as hydroxides.

Based on the solubility products data and the thermodynamic calculations explained before, hydroxide precipitation diagrams (Figure 4.1) have been constructed for a number of metal ions. They are used to determine the pH for selective separation of metal ions. It is seen that ferric ions are precipitated at pH 4.2-4.5. At this pH cupric and zinc ions remain in solution. Thus, in precipitation of metals as hydroxides ferric ions, most common in metallurgical effluents are first precipitated, followed by copper (II), and zinc (II). As mentioned before and as seen from Figure 4.1, magnesium remains in solution at pH below 10.

4.1.2. Precipitation as Sulfides

The precipitation of metal ions as sulfides follow the same principle of solubility products, in this case, of metal sulfides. The solubility product is the equilibrium constant of the dissociation of metal sulfide: $M_mS_n \rightleftharpoons mM^{z+} + nS^{2-}$ expressed by

$$K_s = a_{M^{z+}}^m \times a_{S^{2-}}^n \quad (4.3)$$

which is rearranged to $a_{M^{z+}}^m = K_s / a_{S^{2-}}^n$ and on logarithmic form,

$$\log a_{Mz+} = \frac{\log K_s}{m} - \frac{n \log a_{S^{2-}}}{m} \quad (4.4)$$

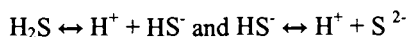
On the basis of this equation, and from the known values of solubility products (Table 4.2) sulfide precipitation diagram is constructed for a number of metal ions; Figure 4.2. They are similar to metal hydroxide precipitation diagram (Figure 4.1) and enable the determination of sulfide ion concentration in solution for the precipitation of specific metal ions.

Table 4.1. Solubility Products of Some Metal Hydroxides at 25° C; from Smith and Martell (1976)

Metal hydroxide	Solubility product K_s	$\log K_s$
AgOH	$a_{Ag^+} \times a_{OH^-} = 1.95 \times 10^{-8}$	-7.71
Al(OH) ₃	$a_{Al^{3+}} \times a_{OH^-}^3 = 3.16 \times 10^{-34}$	-33.50
Be(OH) ₂	$a_{Be^{2+}} \times a_{OH^-}^2 = 5.01 \times 10^{-22}$	-21.30
Ca(OH) ₂	$a_{Ca^{2+}} \times a_{OH^-}^2 = 6.46 \times 10^{-6}$	-5.19
Cd(OH) ₂	$a_{Cd^{2+}} \times a_{OH^-}^2 = 4.47 \times 10^{-15}$	-14.35
Co(OH) ₂	$a_{Co^{2+}} \times a_{OH^-}^2 = 1.26 \times 10^{-15}$	-14.90
Co(OH) ₃	$a_{Co^{3+}} \times a_{OH^-}^3 = 3.16 \times 10^{-45}$	-44.5
Cr(OH) ₃	$a_{Cr^{3+}} \times a_{OH^-}^3 = 1.58 \times 10^{-30}$	-29.8
Cu(OH) ₂	$a_{Cu^{2+}} \times a_{OH^-}^2 = 4.79 \times 10^{-20}$	-19.32
Fe(OH) ₂	$a_{Fe^{2+}} \times a_{OH^-}^2 = 7.94 \times 10^{-16}$	-15.1
Fe(OH) ₃	$a_{Fe^{3+}} \times a_{OH^-}^3 = 1.58 \times 10^{-39}$	-38.8
Mg(OH) ₂	$a_{Mg^{2+}} \times a_{OH^-}^2 = 7.08 \times 10^{-12}$	-11.15
Mn(OH) ₂	$a_{Mn^{2+}} \times a_{OH^-}^2 = 1.58 \times 10^{-13}$	-12.8
Ni(OH) ₂	$a_{Ni^{2+}} \times a_{OH^-}^2 = 6.31 \times 10^{-16}$	-15.2
Ti(OH) ₄	$a_{Ti^{4+}} \times a_{OH^-}^4 = 1.0 \times 10^{-53}$	-53.0
Zn(OH) ₂	$a_{Zn^{2+}} \times a_{OH^-}^2 = 3.47 \times 10^{-17}$	-16.46

It is not convenient in practice to measure the concentration of sulfide ions in solution for making selective separation. This difficulty has been overcome by considering the ionic equilibrium of hydrogen sulfide in water. Hydrogen sulfide is often the source of sulfide ions. Even when it is not directly used for the precipitation, the ionic equilibrium of sulfide with water is governed by that of hydrogen sulfide in water since sulfide ions with hydrogen ions of water produce HS⁻ (hydrosulfide) ions and as the pH is progressively lowered the sulfide will occur as molecular hydrogen sulfide.

Hydrogen sulfide is a gas, which dissolves in water, and is dissociated as a weak dibasic acid in two stages:



The equilibrium constants for these reactions are expressed by the following equations:

$$K_1 = \frac{a_{H^+} \times a_{HS^-}}{a_{H_2S}} = 1.02 \times 10^{-7} \quad (4.5)$$

and
$$K_2 = \frac{a_{H^+} \times a_{S^{2-}}}{a_{HS^-}} = 1.66 \times 10^{-14} \quad (4.6)$$

The values of dissociation constants are those that have been selected by Rao and Hepler (1977) as the 'best' in their analysis of the published data.

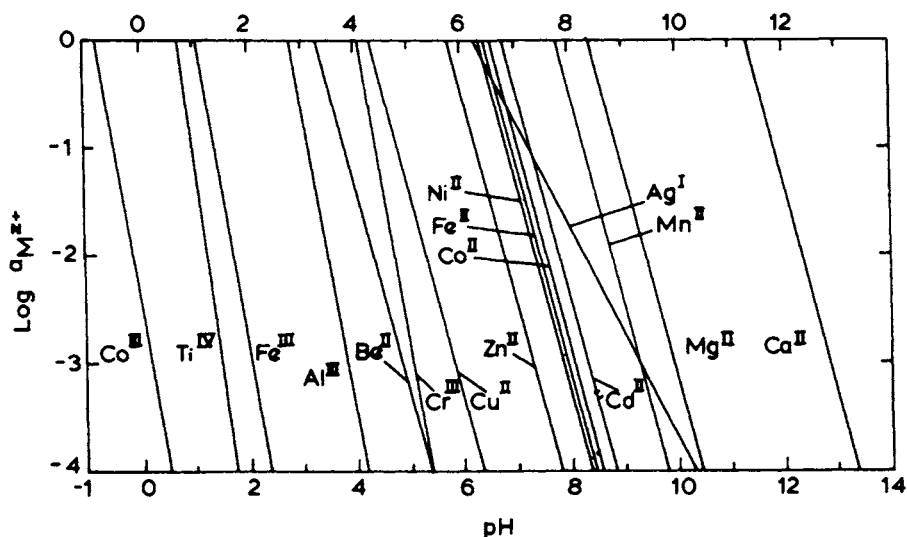


Figure 4.1. Metal hydroxide precipitation diagram based on solubility product data at 25 °C

Table 4.2. Solubility Products of Some Metal Sulfides. from Smith and Martell (1976) at 25 °C; Simons (1964) at 100 °C.

Metal sulfide	Solubility product at 25 °C		at 100 °C	
	K_s	log K_s	K_s	log K_s
Ag_2S	$a_{Ag^+}^2 \times a_{S^{2-}}$	7.94×10^{-51}		
Bi_2S_3	$a_{Bi^{3+}}^2 \times a_{S^{2-}}^3$	1.0×10^{-100}		
CdS	$a_{Cd^{2+}}^2 \times a_{S^{2-}}$	1.58×10^{-26}	6.31×10^{-23}	-22.2
CoS	$a_{Co^{2+}}^2 \times a_{S^{2-}}$	5.01×10^{-22}	6.31×10^{-20}	-19.2
CuS	$a_{Cu^{2+}}^2 \times a_{S^{2-}}$	7.94×10^{-37}	2.00×10^{-30}	-29.7
Cu_2S	$a_{Cu^+}^2 \times a_{S^{2-}}$	2.00×10^{-48}		
FeS	$a_{Fe^{2+}}^2 \times a_{S^{2-}}$	7.94×10^{-19}	2.51×10^{-16}	-15.6
HgS	$a_{Hg^{2+}}^2 \times a_{S^{2-}}$	2.00×10^{-53}		
MnS	$a_{Mn^{2+}}^2 \times a_{S^{2-}}$	3.16×10^{-11}		
NiS	$a_{Ni^{2+}}^2 \times a_{S^{2-}}$	3.98×10^{-20}	2.51×10^{-19}	-18.6
PbS	$a_{Pb^{2+}}^2 \times a_{S^{2-}}$	3.16×10^{-28}	6.31×10^{-26}	-25.2
ZnS	$a_{Zn^{2+}}^2 \times a_{S^{2-}}$	2.00×10^{-25}	1.26×10^{-21}	-20.9

The equilibrium constant of the overall reaction $H_2S \leftrightarrow 2 H^+ + S^{2-}$ is derived as

$$K_1 \times K_2 = \frac{[H^+]^2 \times [S^{2-}]}{[H_2S]} = 1.69 \times 10^{-21} \quad (4.7)$$

(expressing activities in terms of molar concentrations)

At 25° C the saturation concentration of hydrogen sulfide in water is ~ 0.09 M . Substituting this value for $[H_2S]$ leads to

$$[S^{2-}] = \frac{1.52 \times 10^{-22}}{[H^+]^2} \quad (4.8)$$

This is a useful relationship, which enables the sulfide ion concentration to be determined by measuring pH. The data in Table 4.3 is calculated using this equation.

Using the same relationship the sulfide ion concentration is also expressed on pH scale in the precipitation diagram (Figure 4.2). The diagram shows that the K_s values for the sulfides of bismuth, mercury, silver and copper are so small that their precipitation is virtually zero at any pH. The pH scale of the diagram is useful to select optimum pH value for the selective precipitation of metals as sulfides in the same way as the precipitation diagram for metal hydroxides.

Table 4.3. Relationship between pH and Sulfide Ion Concentration for Standard Conditions (25 °C and 1 atmosphere pressure of hydrogen sulfide.)

pH	$[S^{2-}]/\text{mol.dm}^{-3}/(M)$
-2	1.5×10^{-26}
0	1.5×10^{-22}
2	1.5×10^{-18}
4	1.5×10^{-14}
6	1.5×10^{-10}
8	1.5×10^{-6}
10	1.5×10^{-2}

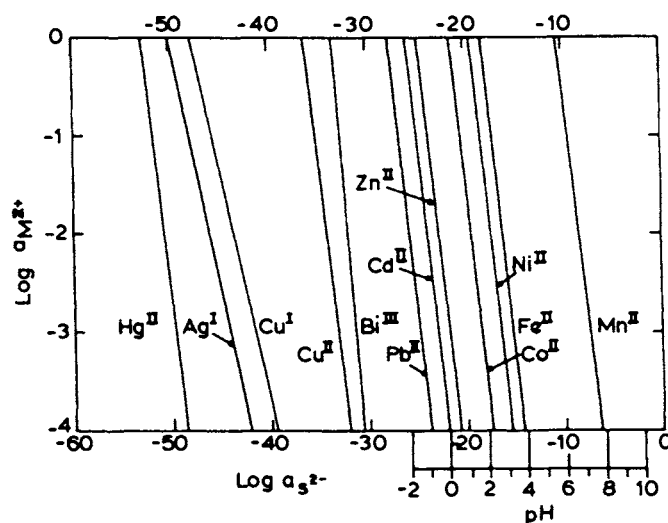


Figure 4.2. Metal sulfide precipitation diagram for 25 °C and 1 atmosphere pressure hydrogen sulfide

4.1.3. Other Precipitation Processes

Precipitation of metals as hydroxide or sulfide is most widely used for the removal and recovery of metals from metallurgical effluents. Other pH-dependent precipitation systems like carbonates, phosphates and arsenates are also available and may be used in special situations. They follow similar principles. Details are described in Jackson (1986).

4.2. Ion Exchange Processes

Recovery of metal ions from solution by ion exchange process has been used for many years in process industry. Ion exchange phenomenon has been known for over 150 years. Natural clays, usually aluminosilicates were used to adsorb metal ions by exchange of sodium or potassium ions of the clay minerals. Their application was, however, limited to the bulk removal of metal ions. The metal ions thus adsorbed could not be recovered.

Development of synthetic resins starting with the phenol-formaldehyde condensation product in the 1940s, marked a significant advance in the application of ion exchange technology as it led to the development of recovery of the adsorbed material by a process of elution, which is essentially, desorption of metal ions from the resin.

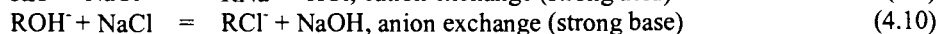
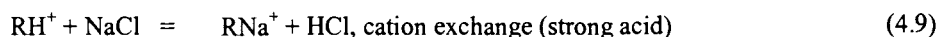
Synthetic ion exchange materials commonly used are put in four categories as shown in Table 4.4.

Strong acid resins are produced by introducing sulfonic acid groups into the 3-dimensional hydrocarbon backbone structure of a polymeric resin. Weak acid resins are based on a carboxylic acid grouping achieved by synthesis of a polymer. Ployacrylic polymers usually serve the purpose. Strong base resins are made by introducing a quaternary ammonium grouping onto the hydrocarbon backbone of the resin. Weak base resins are similarly made by the inclusion of a tertiary ammonium group.

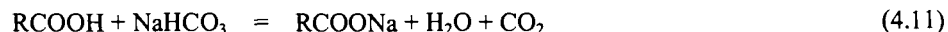
Table 4.4. Types of Ion Exchange Resins

Type Group	pH range	Functional Type	Ion	Capacity, mequivalent/g
Strong acid	0-14	R-SO ₃ H	Anionic	5.0
Weak acid	4-14	R-COOH	Anionic	10.0
Strong base	0-14	R-CH ₂ N ⁺ (CH ₃) ₃	Cationic	4.0
Weak base	0-5	R-CH ₂ N(CH ₃) ₂	Cationic	~ 5.0

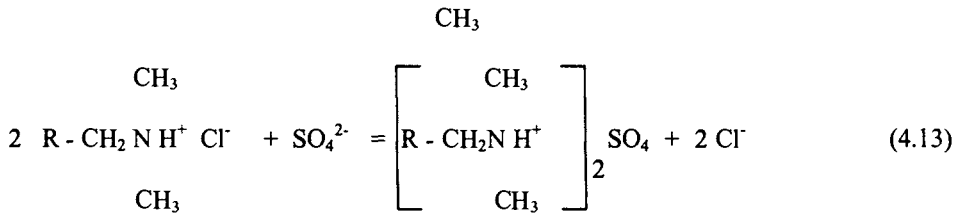
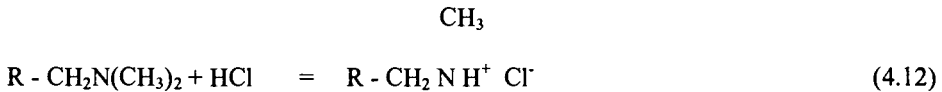
Strong acid and strong base resins can exchange ions over the entire pH range and can split the salt: for example,



Weak acid resins respond on dissociation of the carboxylic acid grouping and usually exchange in alkaline solution, for example,



Weak base resins require protonation of the functional group, in acid media, thus they exchange anions in acid solution:



Weak acidic or basic resins are more advantageous for recovering the adsorbed metals by a process called elution. The metal ions are recovered by passing a strong electrolyte like NaCl through the resin. The metal ions are displaced by sodium ions and the resin is regenerated. If the resin is an acidic resin, that is, the exchangeable ion is hydrogen ion, a strong acid is used as eluant to desorb the metal ions and regenerate the resin.

4.2.1. Selectivity

Ion exchange resins show good selectivity with respect to metal ions. It depends largely on the structure of the resin and specifically on the ionic radius and ionic charge density of the metal ions. An ion of higher charge density tends to displace an ion of smaller charge density. Trivalent ions are preferentially adsorbed, then divalent ions. Within ions of the same charge selectivity is governed by bond strength. This is determined by the electrovalent characteristic of the metal ion. Metal ions which are more electrovalent bind more strongly and are preferentially adsorbed. For example, copper is more electropositive than zinc; as a result, from an effluent containing dissolved copper and zinc, cupric ions are preferentially adsorbed.

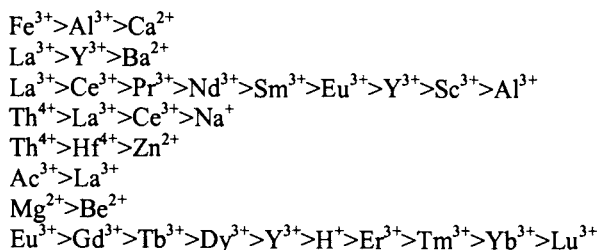
A selectivity coefficient can be defined by applying the laws of mass action to the ion exchange process:

$$z_B \text{ R A}^{z_A+} + z_A \text{ B}^{z_B+} = z_A \text{ R B}^{z_B+} + z_B \text{ A}^{z_A+} \quad (4.14)$$

$$K_A^B = \frac{(y_B)^{z_A} (x_A)^{z_B}}{(x_B)^{z_A} (y_A)^{z_B}} \quad (4.15)$$

K_A^B is not a thermodynamic quantity. It is a rational selectivity coefficient used to quantify the performance of one ion over another. Usually it is expressed on a relative scale with a "standard" cation as the base. The selectivity scale for some metal ions is given in Table 4.5.

Some qualitative affinities of a sulfonated copolymer of styrene and divinyl benzene given by Calmon (1979a) are as follows:



Selectivity is experimentally determined by subjecting a given volume of resin to a number of sequential contacts with a fresh solution of metal ions to obtain a saturation profile. This procedure simulates the gradual saturation of the resin in a real process (e.g., a column). At the beginning, when the resin is not saturated, it tends to pick up ions indiscriminately. As it gets saturated, however, the resin usually releases some of the initially adsorbed ions (ion A in Figure 4.3) and adsorbs more of the ions for which it has maximum affinity (ion C). A typical saturation profile is shown in Figure 4.3.

Table 4.5. Relative Selectivity Coefficients (RSC) of a Sulfonated Polymeric (Styrene and Divinyl benzene) Resin for Some Metal Ions with Lithium as the Base (Calmon, 1979a)

Cation	RSC	Cation	RSC
Li^{+}	1.00	Cs^{+}	3.25
Ca^{2+}	5.16	H^{+}	1.27
Mg^{2+}	3.29	Sr^{2+}	6.51
Na^{+}	1.98	Zn^{2+}	3.47
Ag^{+}	8.51	Co^{2+}	3.74
UO_2^{+}	2.45	Hg^{2+}	9.31
Mn^{2+}	2.75	Cu^{2+}	3.85
Pb^{2+}	9.91	Cd^{2+}	3.88
K^{+}	2.90	Ba^{2+}	11.55
Rb^{+}	3.16		
Ni^{2+}	3.93	Tl^{+}	12.4

Dividing the metal loading by the equilibrium concentration produces the distribution coefficient. The ratio of two distribution coefficients produces the separation factor for those two metals. It should be noted that the separation factor does not include the ionic charges in the resin and thus it differs from the selectivity coefficient explained before. The separation factor is, however, all that matters when considering a practical application of a resin.

An additional set of useful data can be obtained from the saturation profile experiment by plotting the metal loading as a function of its equilibrium aqueous concentrations. This plot is called ion exchange isotherm. It provides the process engineer with the basic information for the designing of the ion exchange process. A typical ion exchange isotherm is shown in Figure 4.4.

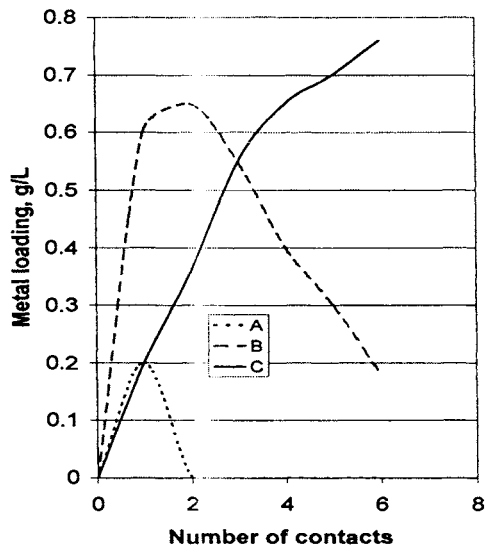


Figure 4.3. Saturation profile for three metal ion

It follows from Figure 4.3 that the selectivity measured after one contact may be quite different from the selectivity at saturation.

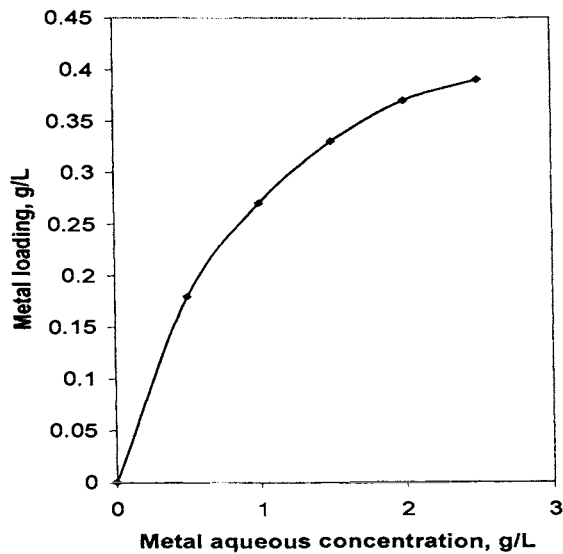


Figure 4.4. Ion exchange isotherm for zinc ions (from L. Hubbard, Ph.D. thesis 1997, McGill University)

Note. In Figures 4.3 and 4.4, 'Metal loading' corresponds to quantity of metal uptake per unit volume of the resin.

4.2.2. Chelating Resins

Synthesis of chelating resins marks a new advancement in the application of exchange resins in hydrometallurgy and effluent treatment as they have markedly greater potential for selective separation of metal ions. They differ from ion exchange resins as they do not exchange metal ions for cations of the compound in the resin, instead they bind them by co-ordinate chemical bond, much like the precipitation of a metal ion as a coordinate complex in solution. In general, chelating agents are coordinating polymers with covalently bound side chains, which contain one or more donor atoms that can form coordinate bonds with the transition metal ions, most of which happen to be toxic. Due to coordination type interactions, all such chelating exchangers provide very high selectivity toward commonly encountered metal ions in effluents, for example, Cu^{2+} , Pb^{2+} , Ni^{2+} , Cd^{2+} and Zn^{2+} over competing alkaline (Na^+ , K^+) and alkaline earth (Ca^{2+} , Mg^{2+}) metal ions. Depending on the number of donor atoms in a ligand attached to the polymer, the repeating functional groups are often referred to as mono-, bi-, or polydentate. More details are described in the reviews by Hudson (1986) and Warshawsky (1986).

As an example, Figure 4.5 shows experimentally determined Cu(II)/Ca and Ni(II)/Ca separation factors at pH 4.0 for three different chelating exchangers, and the high selectivity of the metal ions can be readily noted. As explained before, separation factor is a dimensionless measure of relative selectivity between two competing ions and, in this case, equal to the ratio of distribution coefficient of the metal (II) ion concentration

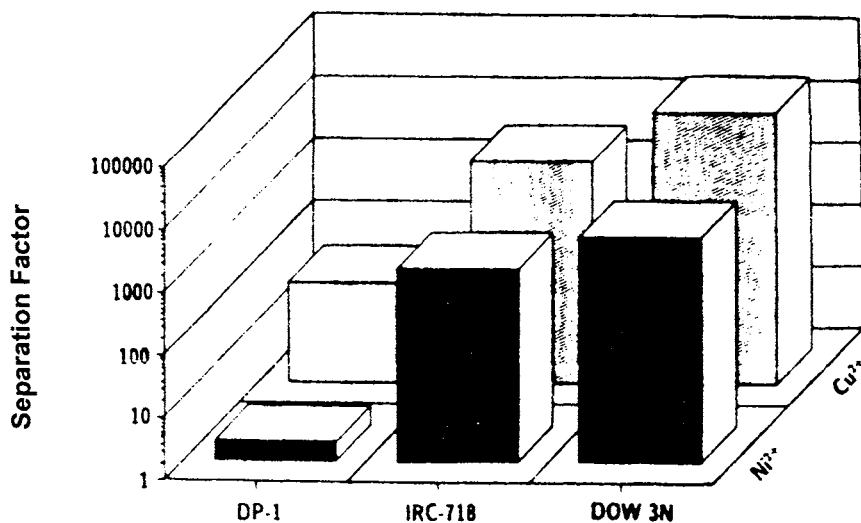


Figure 4.5. Experimentally determined $\text{Cu}^{2+}/\text{Ca}^{2+}$ and $\text{Ni}^{2+}/\text{Ca}^{2+}$ separation factors for three different chelating exchangers (Sengupta *et al.*, 1991).

between the exchanger phase and the aqueous phase to that of Ca(II) ion and is expressed by the equation,

$$\text{Separation factor } a_{\text{M}}/a_{\text{Ca}} = \frac{[\text{RM}][\text{Ca}^{2+}]}{[\text{M}^{2+}][\text{RCa}]} \quad (4.16)$$

where $[RM]$ and $[M^{2+}]$ correspond to exchanger and aqueous phase concentrations of $M(II)$, respectively.

Figure 4.6 shows examples of general schematic for the binding mechanisms in chelate exchange resins.

Differences in metal ion selectivities among different chelating exchangers are related to the metal-ligand stability constants. This is a thermodynamic equilibrium constant corresponding to the dissociation of a complex into the free metal ion and the ligand. Such constants are known for many widely used chelating compounds; see Martell and Smith (1988). However, the constants for newly synthesized ligands are not known. In such cases, selectivities have to be experimentally determined by measuring the separation factors as explained before.

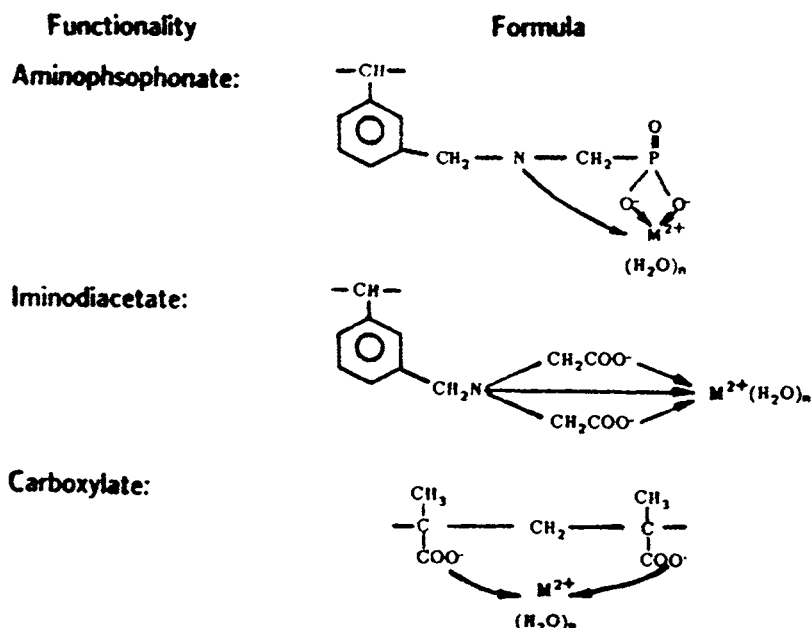


Figure 4.6. Schematic representation of the nature of metal ion binding for three functional groups (Sengupta *et al.*, 1991).

4.2.3. Redox Resins

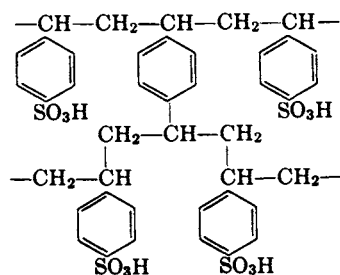
In this class of cationic resins, described by Alexandratos (1987) ion exchange functional group consists of a redox functional group, that is, one with reducing action. It serves a dual function, ion exchange coupled with a reaction leading to the reduction of metal ion to metal if that is reducible under the experimental conditions. The example described by Alexandratos is a polystyrene resin with derivatives of phosphorous acid (H_3PO_3) acid as ion exchange group. The hydrogen ions from the acid are exchanged for metal ions. Additionally, the binding of the metal ion is governed by the redox potential of the metal/metal ion couple, that is, the metal ion which is more readily reduced binds stronger than the one which requires a stronger reducing agent (see Section 4.4 for explanation of redox potentials of metal/metal ions). Those ions, which are not reduced to

metal by reducing agents are adsorbed as metal ions. Zinc is an example. The reduction of zinc ions to zinc metal does not occur by reducing agents in aqueous medium. Silver and mercury, on the other hand, can be reduced to the metallic state by suitable reducing agents in solution. With the redox resins, when silver ions are adsorbed, they are reduced to silver metal, and mercurous ions to mercury. This is shown by the action of the redox resin, on which the uptake of mercury is seven times greater than that of zinc (Alexandratos and Wilson, 1986).

The action of redox resins has been demonstrated by laboratory studies, and they may have some specific applications for the recovery of metals from dilute effluents, but no industrial application has been reported.

4.2.4. Practical Considerations

A principal property of ion exchange resin is its exchange capacity. It is the number of ionogenic groups per gram of resin free of sorbed solutes and solvents. For example, monosulfonated styrene-divinylbenzene copolymers shown by the chemical formula



consists mainly of the units $-\text{CHCH}_2-\text{C}_6\text{H}_4-\text{SO}_3^-\text{H}^+$. Each unit, $\text{C}_8\text{H}_8\text{O}_3\text{S}$, has the formula weight 184.2 and carries one fixed ionic group. The capacity of the resin is $1/184.2 = 5.43 \times 10^{-3}$ equivalent or 5.43 milliequivalent per g. This is the *maximum* or *total capacity of resin*.

The **effective capacity of a resin** is the number of exchangeable counterions per specified quantity of resin. When the resin is completely ionized as with strong acid and strong base resins, the effective capacity and maximum capacity are the same, as the number of exchangeable groups equals the number of ionogenic groups. For weak acid and weak base resins, which are not completely ionized, the effective capacity is lower than the maximum capacity. In these cases the effective capacity depends external factors such as pH and concentration of the solution.

One method of experimentally determining the resin capacity is by titration of the resin with an acid or base. A more precise method is to monitor the metal ion concentration in the effluent, c during sorption step. This is plotted as a ratio of the influent metal concentration c_0 against the volume of influent solution passing through the column or against the quantity of metal ion it contains. The resultant plots are called **breakthrough curves**. A typical set of curves is shown in Figure 4.7. The resin capacity is obtained by extrapolating the curves to $c/c_0 = 0$. It is also called **breakthrough capacity**.

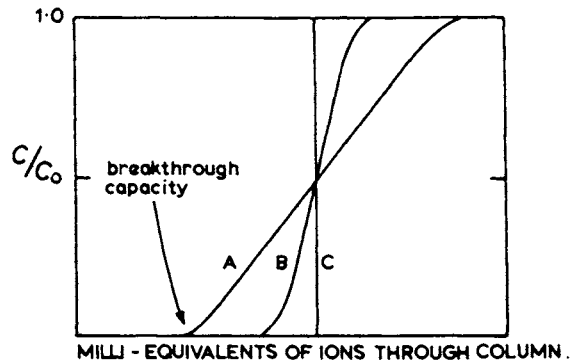


Figure 4.7. Sorption breakthrough curves showing effect of flow rate on breakthrough capacity (c_0 , influent concentration; c , effluent concentration.)

Decreasing flow rate leads to a steeper curve and a higher breakthrough capacity. For an infinitely slow rate (curve C) the breakthrough capacity would be identical with total capacity.

In the elution step where the resin is regenerated, the adsorbed ions are displaced from the resin by passing an excess of electrolyte, which is called eluant. A plot of metal ion concentration against the volume of the eluate (the solution leaving the column) is referred to as elution curve shown in Figure 4.8.

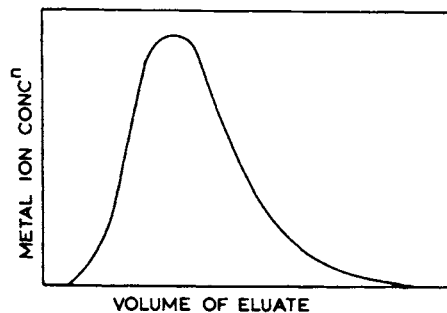


Figure 4.8. Elution curve for a metal ion.

Ion exchange is carried out in columns. In the sorption process the effluent containing metal values is passed through a bed of resin. The metal ions to be recovered enter the resin phase. When the bed gets saturated with the metal ion in the feed, the outgoing solution will carry the unadsorbed metal ions. This is the breakthrough point when the flow of feed should be stopped. In the next, elution stage, a small volume of the eluent solution is passed through the column and the metal ions are removed from the resin. The bed is then washed to remove loosely held ions. A concentrated solution of the desired metal ions is obtained which can be processed further to recover the metal, and the resin regenerated by washing.

Ion exchange may be carried out under equilibrium conditions. A certain volume of a solution is contacted with a certain weight of the resin and shaken long enough till equilibrium is reached. The uptake on the resin is defined by distribution coefficient,

$$D = \frac{\text{Concentration of metal ions in resin phase}}{\text{Concentration of metal ions in aqueous phase}}$$

The higher the value of D, the higher the affinity of the resin for that particular metal ion.

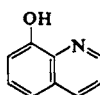
Ion exchangers are usually made in the form of beads or spherical particles of 0.5-2.0 mm diameter. Ion exchange columns are normally cascaded in order to give continuous operation.

4.2.4.1. Separation and Regeneration of Resins

For the ion exchange process to be economical it is necessary for the resins to be regenerated and reused for several cycles. As mentioned under 'Practical Considerations' in many systems, where the resins are used in a column, after the elution step the resin is washed and regenerated. There are, however, examples, especially in the use of chelating resins, where the resin is mixed with an effluent solution and mechanically stirred to promote metal uptake. In such cases, it becomes necessary to separate the resins from the slurry and then recover the adsorbed metal. This has been attempted by conditioning the resin with a surfactant, which makes the surface hydrophobic and separating the resin by flotation technique (described in Chapter 3). In the study described by Duyvesteyn and Doyle (1998) a chelating resin was conditioned with anionic surfactants of long chain alkyl sulfonate family. The conditioned resin was mixed with dilute cupric sulfate solution to recover the metal. After the metal uptake, the resin was floated using isopropyl alcohol as frother. The main advantage of this process is that it makes it possible to work with very fine resins, which cannot be conveniently packed in a column. By providing large surface area, fine resins can adsorb metal more efficiently from dilute effluents. While the metal uptake with conditioned resins appears to compare favorably that using unconditioned resins, overall kinetics with dilute effluents is not entirely satisfactory. It appears, much higher resin to solution ratios are required. Also, some desorption of the metal occurs during flotation.

4.3. Solvent Extraction

In the separation technique of solvent extraction a solute is transferred from one liquid phase to another immiscible or partially miscible liquid, which is in contact with the first phase. The aqueous phase contains the metal which is to be concentrated into the organic phase. The principle was originally applied in analytical chemistry where dilute aqueous solutions were concentrated using an extractant in the organic phase. A well known example (in chemical analysis) is that of extracting copper in low concentration using 8-hydroxy quinoline, represented by



Another significant application of solvent extraction was in nuclear industry to separate uranium as uranyl nitrate in diethyl ether. Presently, solvent extraction is used for a wide range of metals including copper, nickel, cobalt, chromium, uranium, vanadium, molybdenum, tungsten, tantalum, niobium, hafnium, zinc, zirconium, rare earth elements and platinum group metals (PGM). (Flett, 1977, 1979; Flett and Spink, 1976; Hudson, 1982; Ritcey and Ashbrook, 1984).

Solvent extraction comprises three steps: extraction, scrubbing and stripping. In the extraction stage, the aqueous feed is brought in contact with the organic solvent phase. In most cases, an extractant is put into a diluent to promote extraction process. The extractant is a compound which chemically combines with the metal in the aqueous phase to give a complex which is soluble in the diluent, usually a hydrocarbon, aliphatic, aromatic or a mixture of the two. The extractant must form an electrically neutral species with the metal ion. In addition, a catalyst or accelerator may be used to increase the rate of transfer into the organic phase without altering the equilibrium. Modifiers are sometimes added to improve the properties of the organic phase to increase the solubility of the extractant or to change interfacial properties.

By extraction the organic solvent is loaded with the metal to be recovered, and the aqueous phase called raffinate, which is either disposed off as waste or can be further processed. The loaded solvent from the extraction may be scrubbed by treatment with a fresh aqueous phase to remove the contaminating impurities. The scrubbed organic solvent is then stripped, usually by a strong acid like sulfuric acid, to remove the metal to be recovered. After stripping, the organic solvent is recirculated back into the extraction process.

The principles governing separation of metals by solvent extraction will be briefly discussed. Full details describing derivations of different concepts and how they apply to various solvent extractant systems can be found in the book by Ritcey and Ashbrook (1979) and several reviews (Hudson, 1982; Laing, 1994).

A measure of the efficiency of separation by solvent extraction is the distribution ratio of a metal between an aqueous phase and an organic phase. This is called extraction coefficient, designated E , or the distribution coefficient, D . It is defined as

$$E = \frac{\text{concentration of metal in the organic phase}}{\text{concentration of metal in the aqueous phase}}$$

Metal concentrations in each phase are determined by quantitative chemical analysis of the metal, in whatever form, simple ionic form or complexed with the extractant compound. Both phases are separately analyzed to check mass balance. All solvent extraction studies are based on this basic principle.

In addition to recovering metal values from effluents, solvent extraction has also been applied for separating metals from a complex mixture. Feasibility of such separation depends upon the ratio of distribution coefficients E_1 and E_2 of two metals in a solvent. This is called separation factor denoted by $SF = E_1/E_2$. The principal factors determining separation will be discussed with specific examples in the following section.

4.3.1. Chemistry of the Extractant

Ideally, an extractant should have the following features:

- (1) Ability to extract the metal at the required pH.
- (2) Selectivity for the metal to be recovered and to reject undesired components.
- (3) Acceptable rates of extraction, scrubbing and stripping.
- (4) Solubility in the organic phase and very low solubility in the aqueous phase.
- (5) Stability throughout the three principal stages.

In practical reality, these criteria are often incompatible and it becomes necessary achieve a balance between them. This is illustrated by a few examples.

4.3.1.1. Examples of Extractants and Separation of Metals

There are mainly two classes of extractants: acidic and chelating extractants.

Acidic extractants are those in which hydrogen ions or protons of the extractant are exchanged for metal ions, as per the following equation:

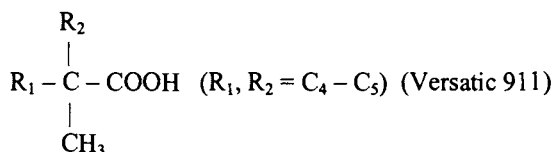


The equation implies, the reaction is governed by the pH of the system. As will be discussed further, pH is the principal control variable, which influences both extractability of metals as well as separation of two metals by acidic extractants. The percent extraction of metals is usually given at the equilibrium pH of the solution. In addition, for the purpose of comparing the extraction of various metals by a specific acidic extractant, the order of extraction is expressed in terms of $pH_{1/2}$, (also denoted by pH_{50} or $pH_{0.5}$) which is defined as the pH at which 50% of the metal in the aqueous phase is extracted into the organic phase. This is derived from dissociation equilibria of acidic extractants (see Ritcey and Ashbrook, 1984, p. 20).

4.3.1.2. Extractants Based on Carboxylic Acids

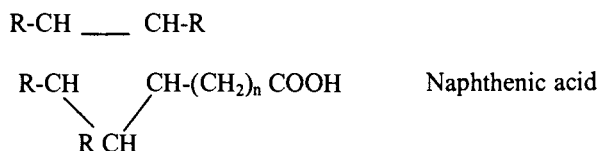
Several carboxylic acids with long branched hydrocarbon chain have been used as solvent extractants in hydrometallurgical separations. Two prominent members are versatic acids, which are synthetically produced and naphthenic acids obtained from distillation of crude petroleum.

Versatic acids are represented by the general formula,

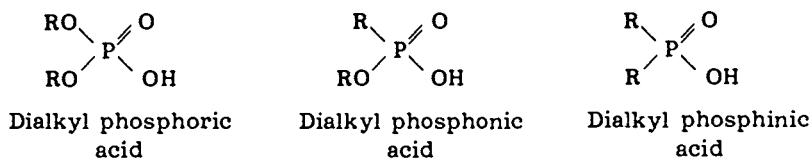


They are highly branched aliphatic monocarboxylic acids. Other members with similar structures are Versatic 10, 13, 1519 and SRS-100 (De, 1971).

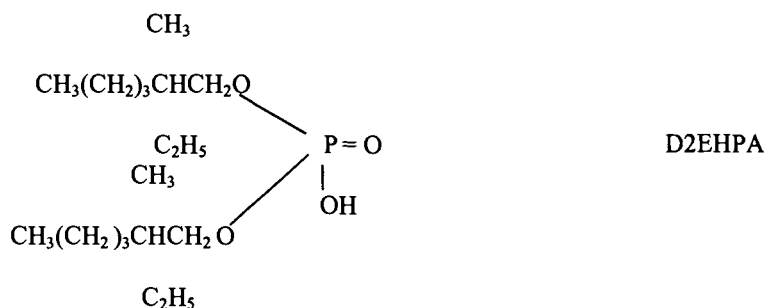
Naphthenic acids are a group of cyclic monocarboxylic acids having the general chemical structure, The product from crude petroleum has a molecular weight of about 170-330 (Fletcher and Wilson, 1961)

**4.3.1.3. Extractants Based on Phosphorus Acids**

Phosphinic, phosphonic and phosphoric acid derivatives extract many metals depending upon the equilibrium pH. The acids have the formulae:

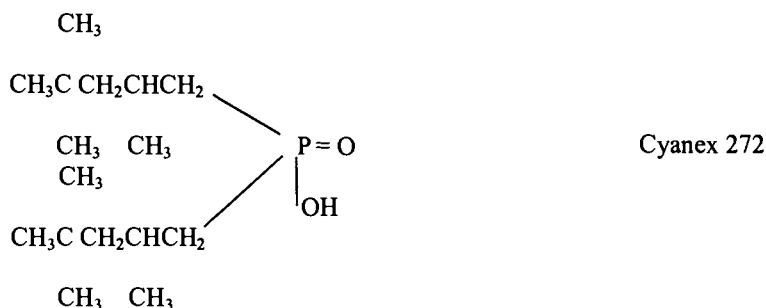


The most useful and widely used acidic extractants are organic derivatives of phosphorus acid. The group includes esters of orthophosphoric, phosphonic and phosphinic acids. One of the most widely used of these, because of its versatility, is di(2-ethylhexyl) phosphoric acid, abbreviated as D2EHPA. The 'R' group has the formula, $\text{CH}_3(\text{CH}_2)_4\text{CHCH}_3$. The O atom connects to CH group and P atom as shown the structure:



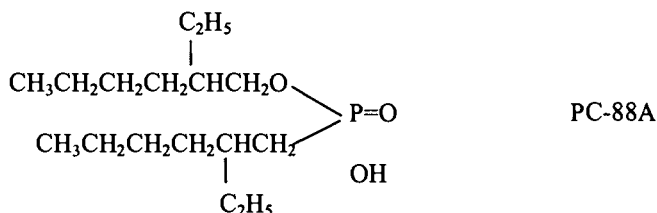
Its special advantages are chemical stability and good kinetics of extraction, good loading and stripping characteristics, low solubility in the aqueous phase, selectivity in the extraction of many metals, and its availability on a large scale.

Another widely used solvent extractant is di(2,4,4-trimethylpentenyl) phosphinic acid, with the structural formula,



This is a phosphinic acid derivative and is commercially sold with the name Cyanex 272.

Phosphonic acid derivatives are available under the name PC-88A. An example is 2-ethyl hexyl phosphonic acid mono-2-ethylhexyl ester,



This is a selective extractant for cobalt and has been used to recover cobalt from spent batteries; see Chapter 10.

4.3.1.4. Extractability of Metals and Basic Mechanisms

Table 4.6 shows the extractability of several metals according to pH.

Table 4.6. Equilibrium pH and Extraction with Cyanex 272 (Ritcey and Ashbrook, 1984)

Metal	Equil. pH	Percent Extracted.	Metal	Equil. pH	Percent Extracted
V(III)	1.81	85.1	Mn(II)	5.66	99.8
Fe(III)	4.31	98.7	Mg(II)	5.81	97.4
Zn(II)	3.08	99.4	Co(II)	5.98	99.8
Al(III)	4.14	97.2	Ca(II)	6.52	99
Cu(II)	4.08	94.8	Ni(II)	7.47	94.8

Extraction of metals by D2EHPA from a sulfate system, as a function of pH is shown in Figure 4.9. The data show significant variation in pH between metals and provides an indication of the potential for selective separation by pH control. It should, however, be noted that comparisons of these curves for any metal ion extractant are useful only as an indication of the pH range over which metal extraction occurs. Metal and extractant concentrations, the phase ratio and contact time should be known for useful conclusions to be drawn. From sulfate solutions the order of extraction as a function of $\text{pH}_{1/2}$ is: $\text{Fe(III)} < \text{Zn(II)} < \text{Cu(II)} < \text{Co(II)} < \text{Ni(II)} < \text{Mn(II)} < \text{Mg(II)} < \text{Ca(II)}$. In practice, however, considerable overlap in individual metal extraction curve occurs.

The order of extractions of metals for the three phosphoric acid derivatives, at a given pH, is as follows: (Rickelton *et al.*, 1984):

D2EHPA: $\text{Fe(III)} > \text{Zn(II)} > \text{Ca(II)} > \text{Cu(II)} > \text{Mg(II)} > \text{Co(II)} > \text{Ni(II)}$

PC 88A : $\text{Fe(III)} > \text{Zn(II)} > \text{Cu(II)} > \text{Ca(II)} > \text{Co(II)} > \text{Mg(II)} > \text{Ni(II)}$

CYANEX 272: $\text{Fe(III)} > \text{Zn(II)} > \text{Cu(II)} > \text{Co(II)} > \text{Mg(II)} > \text{Ca(II)} > \text{Ni(II)}$

The relative shift in the position of Co and Ni in these three extraction orders is reflected in the separation factor ($\beta_{\text{Co/Ni}}$) as shown in Table 4.7. For nickel and cobalt to be extracted in D2EHPA, PC 88A and CYANEX 272, they have to transform from octa to tetrahedral complexes. That occurs with cobalt, but not readily with nickel. As a result, nickel is less extracted resulting in higher separation factor. Further, in comparison to D2EHPA, separation factor improves sharply for PC 88A and CYANEX 272 on account of their lesser acidity. The separation factors suggest that if the feed solution carries significant quantity of nickel, one should prefer PC 66A, if not CYANEX 272 over D2EHPA. However, for economic reasons, D2EHPA could still be the choice as CYANEX 272 is a more expensive reagent.

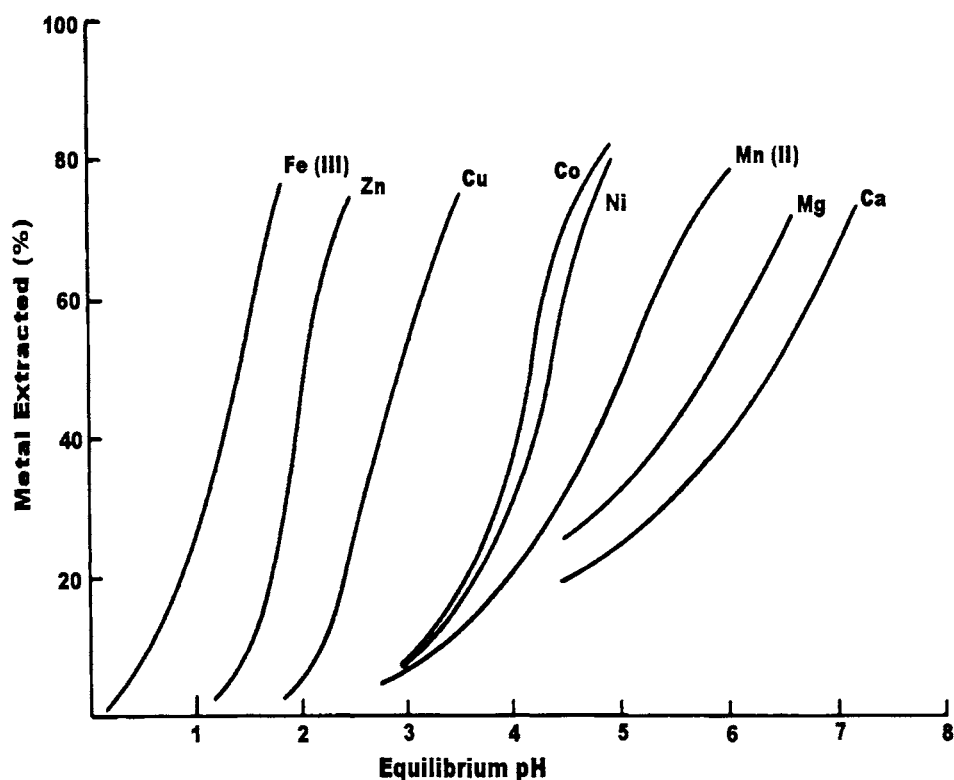
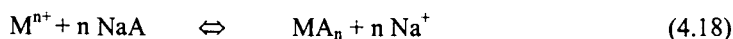


Figure 4.9. Extraction of some metals by D2EHPA from sulfate solutions (Ritcey and Ashbrook, 1984)

Table 4.7. Comparison of Organophosphorus Extractants for Co-Ni Separation (Rickelton *et al.*, 1984)

Extractant concentration 0.1 M		Equilibrium pH 4	
Metal concentration: 0.0025 M		Temperature 25° C	
<u>Extractant</u>		<u>Separation factor (Co-Ni)</u>	
D2EHPA		14	
PC 88A		280	
CYANEX 272		7000	

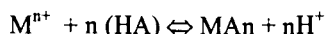
As the extraction of metals by any of these three reagents is pH sensitive and the exchange process liberates equivalent quantity of acid (Equation 4.17) it becomes necessary to neutralize the acid generated to achieve high degree of extraction. This is done by either inter stage addition of alkali or more conveniently by saponification (neutralization) of the acid before it enters the extraction circuit. A fully saponified acid (NaA) produced by neutralizing it with concentrated sodium hydroxide solution, reacts according to the Equation:



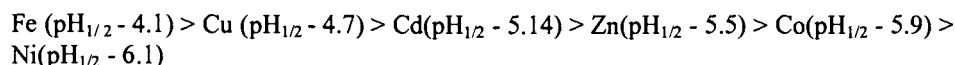
The degree of saponification, however, depends on the metal to be extracted, its concentration, nature of the extracted species as well as type of extractant. For cobalt, for example, D2EHPA can be 100 % saponified, but if PC 88A is used not more than 80 % saponification is recommended as its viscosity increases significantly. In case of zinc, 100 % saponification is not necessary as extraction can take place at pH much lower than that required for cobalt. Further, 100 % saponification of both D2EHPA and PC 88A for zinc raises the viscosity to a level not favorable for smooth running of the solvent extraction contactors. Therefore, the degree of saponification for any specific metal-solvent system could depend on various operating conditions and optimization is possible after detailed investigations.

Although the main mechanism in the action of acid extractants is that of cation exchange, coordination bond formation through the phosphoryl oxygen is also known to occur in some cases. Other factor to be considered are the solubility of the reagents in aqueous phases and steric effects. In most cases, long alkyl chain length decreases solubility, but it may also result in lower metal loading due to steric effects.

For mildly acidic solutions, a large number of acidic extractants in the categories of carboxylic and organophosphorus acid have been evaluated. The acidic reagents (HA) extract metal cations (M^{n+}) according to the following reaction:



This equation indicates that the thermodynamic efficiency of such exchange reaction of any specific cation would depend upon the pH of the aqueous solution, which in turn is related to the acidity of the organic reagent, stability of the metal complex and extraction constant. Thus the higher the values for acidity of the extractant (pK), stability of metal complex and extraction the lower will be the value of $pH_{1/2}$, which is defined as the pH at which 50 % of the metal value present in the aqueous phase is extracted in the organic phase. The $pH_{1/2}$ value for different metals is used to determine the metal extraction order. For example, in the case of naphthenic acid, the position of cobalt with respect to other metals is as follows:



This extraction order suggests that if cobalt is associated with unwanted elements such as Fe, Cu, Cd, and Zn, these elements will get extracted prior to cobalt and their separation can be achieved by suitable control of pH. However, separation of impurity like nickel will be a more difficult proposition based on pH control alone. Carboxylic acids, in general, are therefore not widely used in the separation of cobalt on account of higher pH (5-6) requirement for cobalt extraction, poor separation factor with respect to nickel, poor extraction kinetics and loss of solvent due to its higher solubility in the aqueous phase.

The difference in $pH_{1/2}$ values for two metals in the same oxidation state is useful measure of the extent of separation of the two metals. For example, if it is desired to separate >99% of metal M_1 from metal M_2 , with <1% contamination in a single extraction using equal aqueous and organic volumes, the ratio M_1/M_2 should be 10^4 . This

corresponds to a value 4 for $pH_{1/2M1} - pH_{1/2M2}$. The best separation of the two metals is achieved at a pH intermediate between the two $pH_{1/2}$ values.

The $pH_{1/2}$ values of metal atoms has been correlated with stability constants of the metal complexes and, in the case of trivalent rare earth metal atoms (called lanthanides) with the cationic radii of the metal. Other physico-chemical factors associated with the chemistry of the metal atom also influence the parameter. An excellent discussion, with experimental results has been presented by Preston (1985).

4.3.1.5. Solvating Extractants

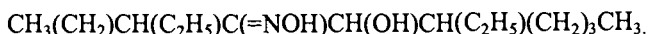
Phosphoric acid esters, for example, tributyl phosphate, $(CH_3CH_2CH_2CH_2O)_3PO$ are used for the separation of nuclear fuel elements, uranium, zirconium and hafnium, and rare earth elements. Trioctyl phosphine oxide (TOPO), R_3PO where R is C_8H_{17} is another solvating extractant used to recover uranium from wet process phosphoric acid liquors (Hudson, 1982). It is also used as a constituent of supported liquid membranes to recover rhenium from hydrometallurgical effluents (to be described in Chapter 12). Some long chain ketones, for example, methyl isobutyl ketone, $CH_3CO, CH_2CH(CH_3)_2$ have been used for separation of niobium and tantalum (described in Chapter 10).

4.3.1.6. Basic Extractants

There are very few examples of the application of basic extractants in metal separations. These are based on secondary alkyl amine, R_2NH or tertiary alkyl amine R_3N . One widely used for uranium, cobalt, tungsten, vanadium extraction is alamine 336, which is a tertiary amine where $R = C_8-C_{10}$.

4.3.1.7. Chelating Extractants

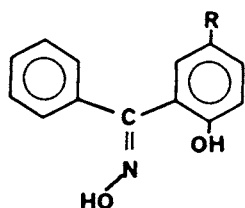
The action of chelating reagents is based on coordination bond formation with the metal ion, similar to that discussed for chelating ion exchange resins. Chelating agents contain donor groups, which form bidentate complexes (two ligands bound to one metal atom). Based on the chemistry, selective chelating extractants have been synthesized. As an example, extraction of copper has been done by 8-hydroxy quinoline for many years as the nitrogen atom in the cyclic structure donates a pair of electrons to form coordinate bond with cupric ion. Another widely used chelating extractant is 5,8-diethyl-7-hydroxy-6-dodecanone oxime, known as LIX extractant.:



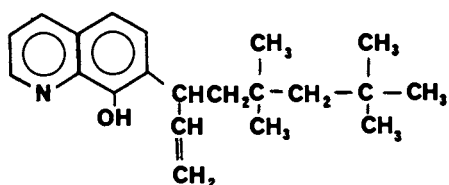
It is an oxime derived from a ketone, by reaction with hydroxylamine, NH_2OH . This original LIX was not very selective for copper over nickel. It was also too expensive to be used for recovering small concentration of metal ions from effluents. However, derivatives of LIX which were synthesized in subsequent years show much greater selectivity. An example is LIX 64, which is a substituted o-hydroxybenzophenone oxime.

Another group of chelating extractant is derived from 8-hydroxy quinoline and is known as Kelex 100. Its formula is as follows: The formulae are shown above

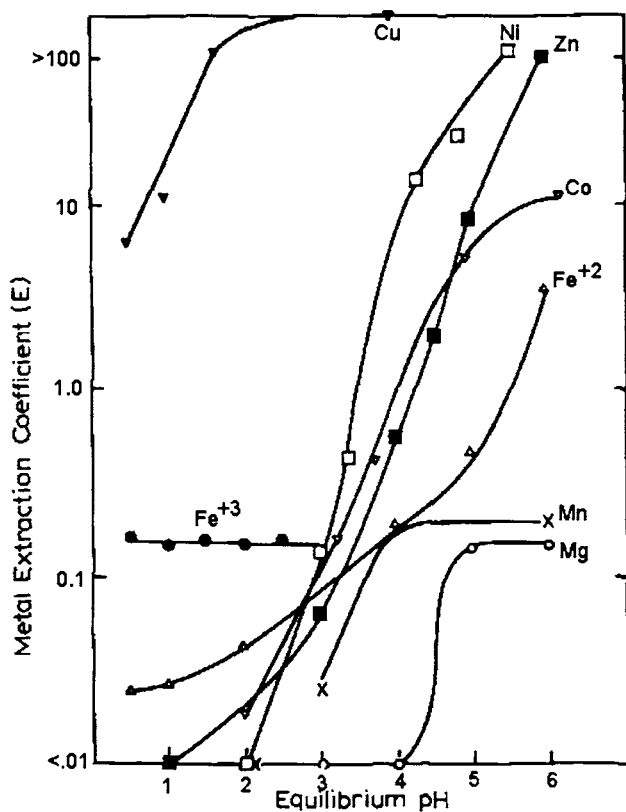
The order of extraction of metals by Kelex 100 is given by Ritcey and Lucas (1974): $Cu(II) > Fe(III) > Ni(II) > Zn(II) > Co(II) > Fe(II) > Mn(II) > Mg(II) > Ca(II)$, in the pH range 0-6. The data are represented in Figure 4.10.



LIX 64



Kelex 100



Feed Solutions 5 g/L metal
Solvent 0.5 M Kelex 100
Phase Ratio 3/1 A/O
Time 5 minutes

Figure 4.10. Order of Extraction of Metals by Kelex 100 (Ritcey and Ashbrook, 1984)

A new class of chelating extractants, N-alkyl hydroxamic acids, developed at Monsanto show very strong complexing capability with high selectivity, shown by

extraction curves, Figure 4.11. They function over a wide operating range, show good kinetics and are biodegradable.

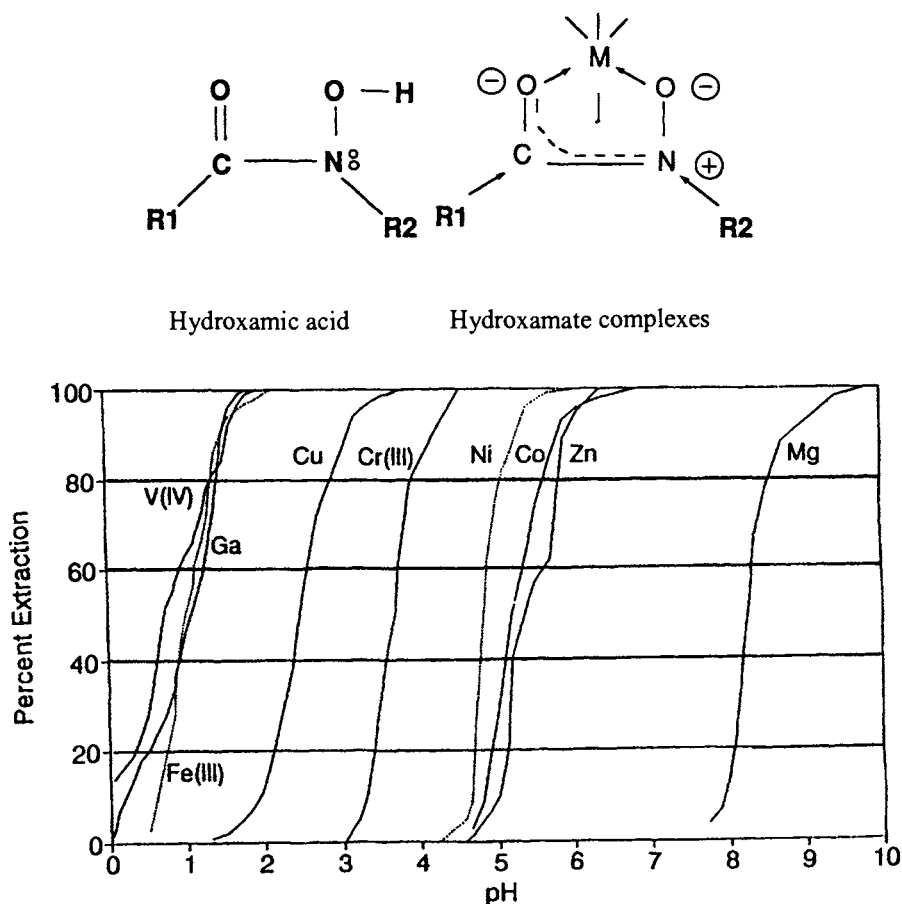


Figure 4.11. pH-Extraction curves for N-alkyl hydroxamic acids (Lakshmanan and Rathie, 1996)

Many other formulations of solvent extractants of different classes are listed in the book of Ritcey and Ashbrook (1984).

4.3.2. Stripping, Diluents and Accelerators

The stripping process is the reverse of extraction and carried out using strong sulfuric acids solutions. The first stage of extraction is the protonation of acid solutions. This results in the recovery of metals as a concentrated sulfate solution.

The extractant is often dissolved in an organic solvent called diluent, usually a hydrocarbon. The nature of the diluent has a great influence on the extraction process as it can change such factors as the ratio of extraction, scrubbing and stripping, the metal ratios and the rate at which the aqueous and diluent phases separate after extraction. The choice of the diluent depends upon the metals which are to be extracted. A diluent which strongly solvates the extractant probably tends to remove this reagent from the interface.

That would affect the rate of attainment of the equilibrium (Equation 4.17). However, a diluent, which does not solvate the extractant probably cannot dissolve sufficient reagent for a large scale extraction process. It is, therefore desirable to select a solvent which allows a reasonable concentration of the extractant at the interface while dissolving sufficient of the extracted complex.

Accelerators are catalysts added to accelerate the rate of attainment of equilibrium. The mechanism of their action is not fully understood. Many of the accelerators have groups, which rapidly react with the metal ion. The complex formed between the metal and the accelerator may be readily transferred from the interface to the organic phase. Further details may be found in the review by Hudson (1982); and the book by Ritcey and Ashbrok, (1984).

4.4 Electrochemical Processes

Many metals are recovered from effluents by electrochemical process, based on the principle of cathodic reduction of metal ions at the cathode of an electrolytic cell. The process can produce a coherent solid or be obtained in the form of a powder using high current density. The equilibrium or reversible potential of a metal ion/metal system is expressed by the Nernst equation: $E = E^0 + RT/zF \ln a_{M^{z+}}$ where E^0 is the standard redox potential (see Table 4.8) for the metal/metal ion system, E is the measured potential at metal ion activity $a_{M^{z+}}$ at temperature T (Kelvin scale), z is the charge on the metal ion (or valence of the metal), R gas constant (in $J \text{ deg}^{-1} \text{ mol}^{-1}$) and F Faraday constant (in Coulomb mol^{-1}). Relationship between the potential and molal ion activity for some commonly occurring metals in effluents are shown in Figure 4.12.

Table 4.8. Standard Redox Potentials of Some Metals (from a compilation by A. J. deBethune, T. S. Licht and N. Swendeman, 1959, *J. Electrochem. Soc.* **106**, 616)

Electrode	Electrode reaction	E^0 , V
Hg Hg^{2+}	$\text{Hg}^{2+} + 2 e = \text{Hg}$	+0.851
Ag Ag^+	$\text{Ag}^+ + e = \text{Ag}$	+0.799
Cu Cu^{2+}	$\text{Cu}^{2+} + 2 e = \text{Cu}$	+0.337
Pb Pb^{2+}	$\text{Pb}^{2+} + 2 e = \text{Pb}$	-0.126
Sn Sn^{2+}	$\text{Sn}^{2+} + 2 e = \text{Sn}$	-0.136
Ni Ni^{2+}	$\text{Ni}^{2+} + 2 e = \text{Ni}$	-0.230
Co Co^{2+}	$\text{Co}^{2+} + 2 e = \text{Co}$	-0.280
Cd Cd^{2+}	$\text{Cd}^{2+} + 2 e = \text{Cd}$	-0.403
Fe Fe^{2+}	$\text{Fe}^{2+} + 2 e = \text{Fe}$	-0.440
Cr Cr^{3+}	$\text{Cr}^{3+} + 3 e = \text{Cr}$	-0.744
Zn Zn^{2+}	$\text{Zn}^{2+} + 2 e = \text{Zn}$	-0.763
Mn Mn^{2+}	$\text{Mn}^{2+} + 2 e = \text{Mn}$	-1.180
Al Al^{3+}	$\text{Al}^{3+} + 3 e = \text{Al}$	-1.662
Mg Mg^{2+}	$\text{Mg}^{2+} + 2 e = \text{Mg}$	-2.363
Ca Ca^{2+}	$\text{Ca}^{2+} + 2 e = \text{Ca}$	-2.866
Li Li^+	$\text{Li}^+ + e = \text{Li}$	-3.04

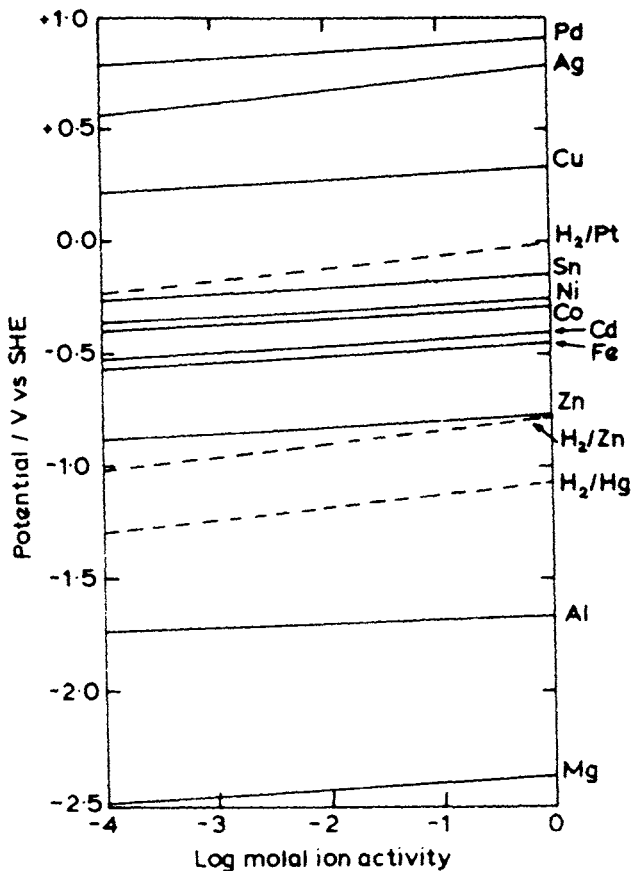


Figure 4.12. Potential/molal ion activity relationships for some metal/metal ion systems (Jackson, 1986)

At equilibrium, the anodic and cathodic current densities are equal. For the cathodic process to occur, the potential of the cathode must be more negative than the equilibrium potential of the specific metal/metal ion system. This decreases the activation energy for the cathodic process allowing that to take place. This results in a net flow of cathodic current. The increase from the equilibrium potential required to bring about the deposition is known as **activation overpotential** denoted by η_{act} . It may be cathodic or anodic depending upon if it refers to cathodic reduction (for metal deposition) or anodic oxidation (dissolution of metal).

For systems, which establish their reversible potentials rapidly the activation overpotential is usually small. Such systems include metals in the first and second group of the Periodic Table like copper, silver, cadmium and zinc. Most transition metal systems are considered irreversible. In such cases, greater activation overpotentials are observed.

A consideration of redox potential values for various metals can help to determine the feasibility of selective deposition of metals from a complex effluent. In practice, it is

usually achieved where potentials of two metals are well separated and where the activation overpotential associated with the depositing metal is small. For example, silver ($E^\circ = 0.79$ V) usually present in small concentrations can be separated from copper ($E^\circ = 0.337$ V) which may be present in high concentration. Similarly copper can be selectively separated from iron (Fe^{++} , $E^\circ = -0.44$ V). By contrast, selective electrodeposition of nickel from cobalt is impracticable as the redox potential values of the two metals are very close to each other.

Another factor to be considered in electrodeposition is hydrogen evolution. On a platinized platinum surface hydrogen overpotential is negligible; that is the basis of the standard hydrogen potential 0 V. but it can be very significant and the hydrogen discharge potential moves to negative values. This fact is very important in the deposition of many metals from aqueous solutions. It favors efficient deposition of several metals because hydrogen evolution would occur at negative potentials. On the same principle, more reactive metals like aluminum and magnesium cannot be effectively deposited from aqueous solution because their deposition potential is more negative than the hydrogen discharge potential; as a result, hydrogen is evolved preferentially.

4.4.1. Electrowinning of Metals

In electrowinning process cathodic reduction is used to recover the desired metals from electrolyte solutions. In most effluent systems the electrolytic solution is an aqueous effluent. In these cases, the anodic reaction is usually oxygen evolution:



If the metal salt dissolved is sulfate, as is usually the case with most mineral and metallurgical effluents, the sulfate ions get discharged at the anode, the sulphate radical rapidly reacts with water and oxygen is evolved at the anode:



Chlorine may also be evolved if the effluent metal salt is a chloride:



4.4.1.2. Electrodes

The anode in aqueous electrowinning should be a completely insoluble metal. Lead alloys containing 5-10 % antimony have been widely used. They get corroded to a small extent by anodic oxidation, which causes some contamination. This is not usually a problem with dilute effluents, but it could be serious in higher acid concentrations. It can be minimized by the addition of anodic depolarizers to the electrolyte, which decreases the anodic overpotential of the oxygen evolution reaction. Co(II) ions have been used for this purpose (Cooke *et al.*, 1981). More stable lead-based alloys have been developed. A silver/lead alloy (0.5 -0.75 % Ag) serve better as they become coated with a protective layer containing manganese dioxide and lead dioxide.

Titanium-based anodes coated with a range of materials have been investigated. Platinized titanium and titanium coated with iridium oxide and ruthenium oxide have been used as anodes.

The cathodes used in aqueous electrowinning are often made of thin sheets of the same metal that is being deposited. Where this is not feasible as for example in zinc electrowinning, pure aluminum cathodes are used. The zinc deposited is stripped either manually or by automatic stripping machines. The technique, referred to as *total production stripping*, has also been introduced for copper electrowinning (Jacobi, 1981).

In each electrolytic cell, cathodes are arranged alternately with anodes. The cathodes and anodes are electrically connected together, but separately in parallel. The cells are connected in series, the cathodes of one cell being linked to the anodes of the adjacent cell; see Figure 4.13. The size of cells and the number of cells in a row varies from plant to plant.

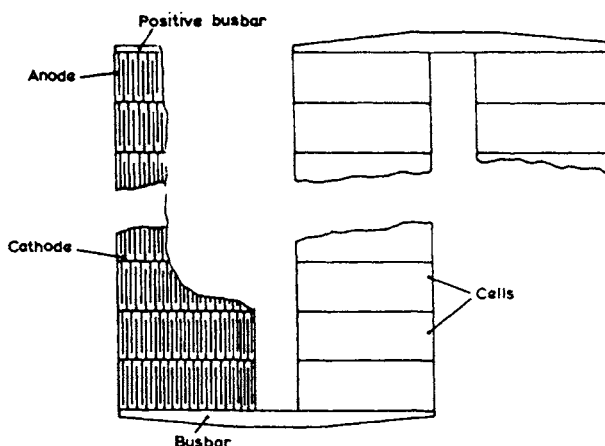


Figure 4.13. Typical arrangement of electrowinning cells and electrodes (Jackson, 1986)

4.4.1.3. Energy Requirements

Energy consumption is determined by various factors associated with the electrolytic process. First one is *current efficiency* (CE), which is the ratio of the actual extent of electrode reaction to that expected theoretically. It is usually expressed as a percentage. For a cathode metal deposition the current efficiency is the ratio of the mass of metal actually deposited to the quantity that is calculated from Faraday's law. Current efficiency is decreased by factors such as hydrogen evolution reaction and the reduction of oxidized species of other redox systems.

The *decomposition potential* or *applied potential* (V_1) is the potential that must be applied to an electrolytic cell to produce current, I , through the cell. The nominal potential difference between anode and cathode which must be exceeded for a cell reaction to occur is the difference between the reversible potentials of the anodic and cathodic reactions, E_A and E_C respectively. This is also termed *reversible decomposition potential*, V_0 . The actual reversible decomposition potential is calculated from the formula:

$$V_1 = (E_A - E_C) + \eta_A + \eta_C + (IR)_{\text{electrolyte}} + (IR)_{\text{contacts}} \quad (4.21)$$

In this equation, the η terms refer to overpotentials at cathode and anode and the IR terms denote the potentials required to overcome the resistance of the electrolyte and the various electrical contacts. The energy consumption per unit mass of metal reduced may be expressed in kWh/kg of metal deposited by the formula,

$$\text{Energy consumption} = \frac{V_L F}{(A/z) \times 3600 \times 0.01 \text{ (CE)}} \quad (4.22)$$

where F is the Faraday constant, A the relative atomic mass.

By putting the numerical value of F, this equation can be simplified to

$$\text{Energy consumption} = \frac{26.8 V_L}{(A/z) \times 0.01 \text{ (CE)}} \text{ kWh/kg} \quad (4.22a)$$

The energy consumption per unit mass of the metal recovered is an important factor in assessing and comparing economics of electrolytic processes.

4.4.1.4. Innovative Cell Designs

An electrowinning cell of novel design has been described by Treasure (2000). Named as EMEW^R cell, it consists of a cylindrical in place of planar electrodes. The outer tube is the cathode and the inner one is anode. The diameters of the electrode tubes are sized according to the particular application to minimize cell voltage for a given solution chemistry. Both ends of the cell are fitted with plastic closure caps with liquor inlet and outlet ports. Liquor is pumped through a series of up to 30 cells at up to 135 L/min. Current is applied to the anode and cathode by cable connections on the outside of each cell.

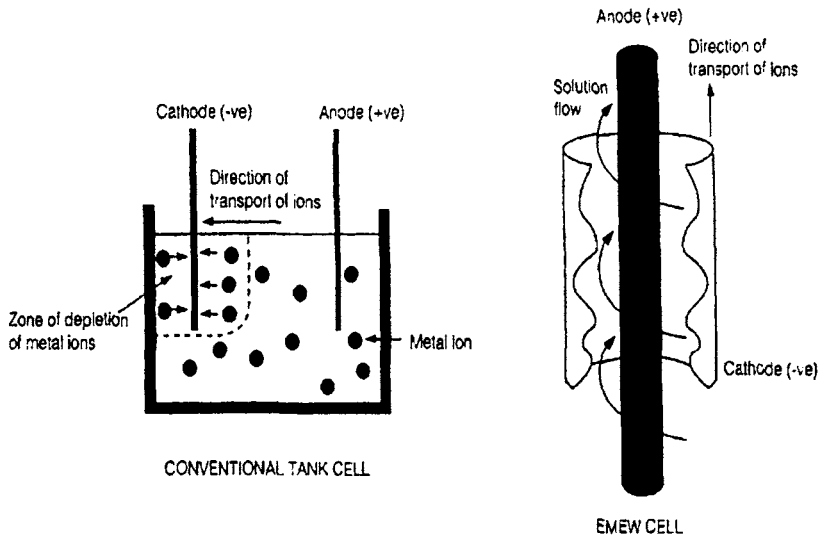


Figure 4.14. Comparison of EMEWR and conventional electrowinning cells (Treasure, 2000)

The operation of a conventional electrowinning cell is limited by mass transport of ions. When plating from a 'bath' of solution commences, the migration of ions to the cathode surface creates a 'zone of depletion' of metal ions in the solution close to the electrode as the ions are plated onto the cathode surface. For further plating to occur, ions have to move greater distances to reach the cathode. This causes 'competing' reactions at the cathode, such as reduction of hydrogen, which, in effect, makes less current available for its primary purpose. Unless the solution has a high concentration of the target metal, recovery will be significantly lower than is theoretically possible, that is, lower current efficiency and high consumption of power per unit of metal recovered. In the EMEW^R cell, operating at high continuous rate, sufficient metal ions are supplied to the cathode surface to satisfy the demand imposed by the operating current even at very low concentrations of the metal. This high mass transport of ions to the cathode surface enables the EMEW^R cell to operate outside of the mass transport limited regime of conventional electrowinning cells. The increase in efficiency of mass transport leads to a high grade product from a mixed metal solution, due to the distinct plating properties of metals in the electrochemical series.

Thus far, this new design cell has been applied for the electrowinning of zinc from acid and alkaline solutions. High grade product is obtained in a single step. Many other advantages have been claimed, including production of high surface area powder, ability of the cell to be operated in a wide variety of acid or alkaline electrolytes, lower decomposition potential for zinc in zincate than sulfate solutions, ability to handle chlorides, which is difficult for conventional zinc plants due to cathode corrosion and chlorine gas evolution and high current density (500-600 A/m²).

4.4.1.5. Electrolytic Reduction

Electrochemical principles are applied to oxidize or reduce ionic components of an electrolyte where the ions exhibit variable oxidation states and oxidation or reduction could be a step to recover desired metal or an anionic species. For instance, extraction of iron from reclaimed battery acid is done by electrolytic reduction of iron from the +3 oxidation state (ferric iron) to +2 oxidation state (ferrous iron). This facilitates ion exchange recovery as ferrous lasts are more soluble and ferrous iron does not get precipitated as hydroxide at pH below 8. A circular design cell for this purpose has been described (Leiby *et al.*, 2000); see Figure 4.15.

The cell consists of two compartments, a cylindrical outer anode compartment containing a lead anode and an inner cathode compartment, also containing a lead electrode. The two compartments are separated by a semipermeable anion selective membrane, which prevents the transfer of iron to the anode, which would cause re-oxidation. Granulated graphite is introduced into the cathode compartment for improved current distribution and increased contact area, which improves current efficiency.

The same investigators have developed a cell for industrial operation. This is a three-compartment cell consisting of a central flow through cathode compartment and two stationary anode compartments, separated by anion selective membrane. The electrodes are solid lead plates. Larger cells can be constructed consisting of a series of alternate anode and cathode compartments separated by anion selective membranes.

The principle of this technique may also be considered for the electrolytic reduction of metals where they occur in their higher oxidation states. For example, permanganate (Mn⁷⁺) may be reduced to manganese (Mn²⁺), and dichromate (Cr⁶⁺) to chromium (Cr³⁺).

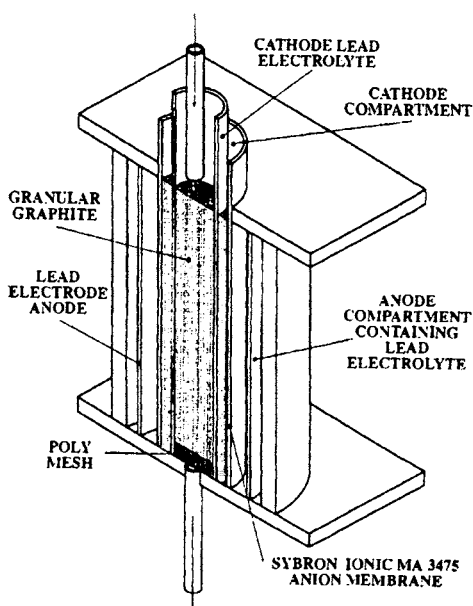
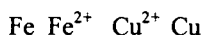


Figure 4.15 Laboratory design of cell for electrolytic reduction (Leiby *et al.*, 2000)

4.4.2. Cementation

In the process of cementation a dissolved metal in effluent is displaced by another metal, which should be more electropositive than the one to be displaced. A typical example (which is also used in effluent treatment) is displacement of copper by iron metal. The reduction of cupric ion to copper metal with simultaneous oxidation of iron to ferrous ion takes place as the redox potential of Cu^{2+}/Cu is more positive than that of Fe^{2+}/Fe ; see Table 4.9. The two metal/metal ion couples constitute an electrochemical cell represented by



With the cell potential, $E^{\circ} = 0.337 - (-0.440) = 0.777 \text{ V}$ the standard free energy change for the cell reaction is $\Delta G^{\circ} = -zFE^{\circ} = -149.5 \text{ kJ mol}^{-1} \text{ Fe}$. (where F is Faraday constant and z denotes number of ions per atom transferred. The high negative value of free energy change implies that the reaction is thermodynamically favored. With progress of the reaction, however, the Fe(II) concentration increases with precipitation of copper, and the cell potential steadily falls until an equilibrium is reached where the potentials of the two metal/metal ion couples becomes identical in accord with the Nernst equation (see Section 4.4):

$$E^{\circ}_{\text{Cu}} + 0.0591/2 \log a \text{ Cu}^{2+} = E^{\circ}_{\text{Fe}} + 0.0591/2 \log a \text{ Fe}^{2+} \quad (4.23)$$

(where 0.0591 was obtained by putting in the Nernst equation, the numerical values of R (gas constant) in $\text{J deg}^{-1} \text{mol}^{-1}$, Faraday constant (C mol^{-1}), temperature (298°K) and the factor 4.303 to convert natural logarithms ($\log_e$) to Napierian logarithms ($\log_{10}$).

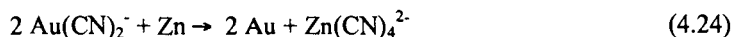
Introducing the numerical values of the standard potentials (Table 4.10) the ratio $a\text{Cu}^{2+}/a\text{Fe}^{2+} = 4.0 \times 10^{-27}$. The very low value indicates that the displacement of copper by iron would be virtually complete at equilibrium.

For a cementation process to be practical the cell potential should be at least 0.3 V. The cell potentials and standard free energy changes for a number of cementation processes are listed in Table 4.9.

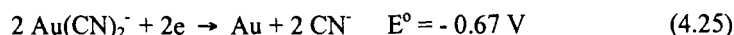
Table 4.9. Standard cell potential and free energy changes for some cementation reactions (Jackson, 1986).

System	Reaction	$E_{\text{cell}}^\circ/\text{V}$	$-\Delta G^\circ/\text{kJ.mol}^{-1}$ reductant
Pd-Cu	$\text{Pd}^{2+} + \text{Cu} = \text{Pd} + \text{Cu}^{2+}$	0.583	112.5
Ag-Cu	$2\text{Ag}^+ + \text{Cu} = 2\text{Ag} + \text{Cu}^{2+}$	0.462	89.2
Pt-Fe	$\text{Pt}^{2+} + \text{Fe} = \text{Pt} + \text{Fe}^{2+}$	1.64	316.5
Pd-Fe	$\text{Pd}^{2+} + \text{Fe} = \text{Pd} + \text{Fe}^{2+}$	1.36	262.4
Ag-Fe	$2\text{Ag}^+ + \text{Fe} = 2\text{Ag} + \text{Fe}^{2+}$	1.24	239.3
Cu-Fe	$\text{Cu}^{2+} + \text{Fe} = \text{Cu} + \text{Fe}^{2+}$	0.777	149.9
Ni-Fe	$\text{Ni}^{2+} + \text{Fe} = \text{Ni} + \text{Fe}^{2+}$	0.19	36.7
Co-Fe	$\text{Co}^{2+} + \text{Fe} = \text{Co} + \text{Fe}^{2+}$	0.16	30.9
Au-Zn	$2\text{Au}^{3+} + 3\text{Zn} = 2\text{Au} + 3\text{Zn}^{2+}$	2.21	426.5
Pt-Zn	$\text{Pt}^{2+} + \text{Zn} = \text{Pt} + \text{Zn}^{2+}$	1.96	378.2
Pd-Zn	$\text{Pd}^{2+} + \text{Zn} = \text{Pd} + \text{Zn}^{2+}$	1.68	324.2
Ag-Zn	$2\text{Ag}^+ + \text{Zn} = 2\text{Ag} + \text{Zn}^{2+}$	1.56	301.0
Rh-Zn	$2\text{Rh}^{3+} + 3\text{Zn} = 2\text{Rh} + 3\text{Zn}^{2+}$	1.46	281.7
Cu-Zn	$\text{Cu}^{2+} + \text{Zn} = \text{Cu} + \text{Zn}^{2+}$	1.10	212.3
Ni-Zn	$\text{Ni}^{2+} + \text{Zn} = \text{Ni} + \text{Zn}^{2+}$	0.51	98.4
Co-Zn	$\text{Co}^{2+} + \text{Zn} = \text{Co} + \text{Zn}^{2+}$	0.48	92.6
Cd-Zn	$\text{Cd}^{2+} + \text{Zn} = \text{Cd} + \text{Zn}^{2+}$	0.36	69.5
Cu-Al	$3\text{Cu}^{2+} + 2\text{Al} = 3\text{Cu} + 2\text{Al}^{3+}$	2.00	386.0

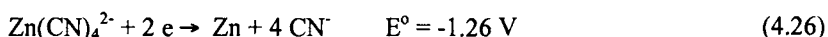
The electrode potentials are very different in complex ionic systems (as compared to the simple systems listed in Table 4.10). An example of such a complex system is the displacement of gold from aurocyanide solutions by zinc metal:



The two electrode systems are



and



The standard potentials of complex cyanide systems are much more negative than the corresponding cation systems listed in Table 4.8. This is related to the high stability of the cyanide complex.

The possibility of impurity contamination in cementation reaction should be considered. When the cell potential is high, there could be contamination by the metals which are less electropositive than copper, but more electropositive than iron. For example, if the solution also contains nickel ions, the copper deposit may be contaminated with nickel as some of this metal would also be displaced by iron. Such possible contamination can be minimized by controlling the quantity of iron metal mixed to the stoichiometric level.

A kinetic study of cementation reactions of several metal ions by aluminum has been described by Singh (2000). The cementation of three metal ions, cobalt, nickel and manganese, follow a first order rate of kinetics. The values of rate constants are 0.018 min^{-1} for cobalt, 0.0076 min^{-1} for nickel and 0.0045 min^{-1} for manganese. The rate of cementation of cobalt is about 2.4 times greater than that of nickel and 4 times greater than that of manganese. This has been taken advantage of to separate cobalt from cobalt process effluents containing nickel and manganese impurities.

4.5. Leaching Processes

By leaching a soluble component from a solid is extracted using a solvent, called leachant. In waste processing and recycling it is the process by which a metal compound (e.g., hydroxide, oxide, carbonate, etc.) occurring in a waste rock or sludge is chemically dissolved producing a concentrated solution of the metal compound, from which the metal may be recovered by one of the techniques described in Sections 4.2 and 4.3, or, in some cases, the compound may have direct use as an industrial product. The material to be leached should be finely ground in order to liberate the component to be leached. In addition, fine particle size enhances the rate of leaching reaction.

Some of the principal factors to be considered in leaching operation are the following:

1. Chemical and physical character of the material to be leached.
2. Corroding action of the reagent on the materials of construction of leach vessels.
3. Selectivity for the desired constituent to be leached.
4. Feasibility of regenerating the leaching agent. This is very important both from economic as well as environmental points of view.

Selectivity of a leaching agent toward a specific component in a waste material depends upon several factors including concentration of the leaching agent, temperature and contact time. The importance of each will be considered.

Concentration of the leaching agent: In some cases a certain minimum concentration of the leaching agent is adequate and no benefit is derived by increasing the concentration. For example, most carbonates can be dissolved by acid at moderate concentration. However, in many other cases the dissolution rate can be enhanced by increasing the concentration of the leaching agent; for example, most of the heavy metal oxides and hydroxides require higher concentration of acids.

Temperature plays a role in enhancing the rate of leaching in the case of oxides and hydroxides. However, it should be carefully controlled in materials containing several components, not all of which are desired to be leached. Exceeding an optimum temperature may result in poor selectivity as undesired components are also leached.

Contact time also has to be regulated and optimized for selectively leaching a desired component. Extended contact period between the solvent and the solid may result in an increased percentage of undesired components in solution. For example, in the leaching of a metal oxide from a waste rock, the oxide is preferentially leached, but extended contact time would cause leaching of silicates, which will introduce aluminum and alkaline earth metals in the leach solution.

4.5.1. Leaching Agents

Leaching agents are chosen based on the chemical reactivity of the components occurring in the waste rock or sludge. The following are the most commonly used leaching agents for treating waste rocks and sludges.

4.5.1.1. Water

Water alone is adequate to leach the water soluble components like sulfites or other sulfoxyl salts (sulfate, thiosulfate). Sulfoxyl salts are produced by the atmospheric oxidation of sulfides present in the waste material. Water also dissolves some sulfides in the presence of air or oxygen under pressure and at about 150 °C converting them to soluble sulfates, for example,



4.5.1.2. Acids

Sulfuric acid is the most commonly used leaching agent. It is the least expensive of all mineral acids and has only minor corrosion problems when it is used, and is effective to leach most oxides, hydroxides, carbonates and sulfides. It is used dilute, moderately concentrated or concentrated depending upon the leachability characteristic of the component to be leached.

Selective leaching by sulfuric acid is possible in the treatment of sludges containing different metal hydroxides. This is done by pH control. In this context leaching is opposite of precipitation of metal hydroxides. The metal hydroxide with highest solubility is leached at highest pH, that is it requires lowest concentration of sulfuric acid, whereas the hydroxide with least solubility requires low pH and higher concentration of the acid. The hydroxide precipitation diagram (Figure 4.1) is useful to select the pH range for selective leaching of specific hydroxides. For example, from a mixture of hydroxides of zinc and iron (Fe^{3+}) the hydroxide of zinc which is precipitated at pH 5-6 can be leached at pH below 6. By controlling the pH at 4-4.5, zinc hydroxide is selectively leached as ferric hydroxide remains insoluble at this pH. .

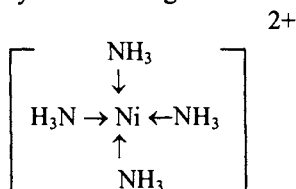
Titanium minerals dissolve at high acidity, and if dissolved they also hydrolyze when the acidity decreases. Other refractory material such as zirconium, niobium, and tantalum oxides and siliceous minerals are not dissolved. If carbonates are present in the material they should first be removed with a dilute acid as they cause frothing problem with concentrated acid.

4.5.1.3. Bases

Sodium hydroxide is one of the common bases used for leaching amphoteric hydroxides or oxides; for example, alumina which is commonly present in silicate waste rocks. Ammonium hydroxide is used to leach hydroxides of certain transition metals which form metal ammines. Cobalt and nickel are the most well known examples. Ammines are formed by the transfer of lone pair electrons of nitrogen atoms to the 'd' orbital of the transition metal, as shown by the following equations and chemical structure:



Nickel ammine ion is represented by the following structure:



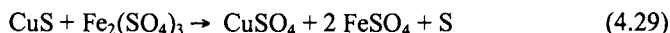
The arrows represent co-ordinate bond formed by a lone pair of electron of nitrogen donated to the nickel atom. This does not affect the two positive charge of the nickel ion. Cobalt ammine has a similar structure except that there are 6 ammonia groups co-ordinated with a Co atom.

In place of ammonia organic amines have been used as the organic ammines have greater stability. Ammines are soluble compounds with the metal dissociated as cation. Metal can be recovered by electrodeposition explained in Section 4.4.1.

A great advantage of solubilizing as ammines is that nontransition metal hydroxides (like magnesium and calcium hydroxides and ferric hydroxide) are not solubilized since those metals do not form ammines. This makes it possible to selectively leach cobalt and nickel hydroxides. Some examples will be described in the Chapter Metal Recycling

4.5.1.4. Aqueous Salt Solutions

Some base metal salts are used as leaching agents to dissolve sulfides. For example, ferric sulfate reacts with a metal sulfide producing soluble metal sulfate:



The leaching is based on the oxidation of sulfide sulfur to sulfate by ferric ions. Ferric salt is reduced to the ferrous state. It can be regenerated by oxidizing by air and recycled.

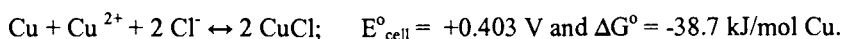
4.5.2. Electrochemical Aspects of Leaching

The example described in Section 4.5.1.4 shows a redox reaction leading to dissolution of sulfide. It is a charge transfer reaction, electron transferred from sulfur (II) (sulfur as sulfide) to Fe(III) resulting in the reduction to Fe(II) and oxidation of sulfide to sulfate. (The oxidation state of sulfur in sulfide is -2; in sulfate it is +6).

When electron transfer is involved, the reactions are electrochemical in nature. An oxidative leaching process may be regarded as an electrochemical cell in which the

anodic process is sustained by a suitable cathodic reaction in which a species at higher oxidation state is reduced to a lower oxidation state. The reduction of the oxidized species should have a potential more positive than that of the anodic process;. For the reaction to be effective the difference is usually at least 0.2 V. This may be ascertained from Table 4.10, which lists standard potentials of selected redox systems.

Another example is leaching by cupric chloride. From Table 4.9, Cu(II) - Cu(I) equilibrium potential E° in chloride solution is +0.54 V (for the reaction, $\text{Cu}^{2+} + \text{Cl}^- \leftrightarrow \text{CuCl}$). For the reduction, Cu(I)-Cu(0) ($\text{CuCl} + e \leftrightarrow \text{Cu} + \text{Cl}^-$), $E^\circ = +0.137$ V. The dissolution of copper by cupric chloride can be written as



Cuprous chloride is sparingly soluble under these conditions, but its solubility increases with chloride concentration as complex ions CuCl_2^- and CuCl_3^{2-} are produced. The solubility also increases with temperature. This principle is used to leach copper metal from scrap and recover copper as cupric chloride.(Langer *et al.*, 1977). Ferric chloride can also be used for the same purpose, but cupric chloride is preferred as it does not introduce objectionable metal ions. If ferric chloride is used it will produce ferrous chloride and cuprous chloride in equimolar proportion.

Table 4.10. Standard Potentials of Some Redox Systems (from a compilation by A. J. deBethune, T. S. Licht and N. Swendeman, 1959, *J. Electrochem. Soc.* **106**, 616)

Redox system	E°/V
$\text{S}_2\text{O}_8^{2-} + 2e = 2\text{SO}_4^{2-}$	+2.00
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e = 2\text{H}_2\text{O}$	1.77
$2\text{HClO} + 2\text{H}^+ + 2e = \text{Cl}_2 + 2\text{H}_2\text{O}$	1.63
$\text{MnO}_4^- + 8\text{H}^+ + 5e = \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$2\text{BrO}_3^- + 12\text{H}^+ + 10e = \text{Br}_2 + 6\text{H}_2\text{O}$	1.50
$2\text{ClO}_3^- + 12\text{H}^+ + 10e = \text{Cl}_2 + 6\text{H}_2\text{O}$	1.47
$\text{Cl}_2 + 2e = 2\text{Cl}^-$	1.359
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$2\text{HNO}_2 + 4\text{H}^+ + 4e = \text{N}_2\text{O} + 3\text{H}_2\text{O}$	1.29
$\text{MnO}_2 + 4\text{H}^+ + 2e = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$\text{O}_2 + 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$	1.229
$2\text{IO}_3^- + 12\text{H}^+ + 10e = \text{I}_2 + 6\text{H}_2\text{O}$	1.195
$\text{Br}_2 + 2e = 2\text{Br}^-$	1.087
$2\text{Hg}_2^{2+} + 2e = \text{Hg}_2^{2+}$	0.92
$\text{Fe}^{3+} + e = \text{Fe}^{2+}$	0.771
$\text{Cu}^{2+} + \text{Br}^- + e = \text{CuBr}$	0.64
$\text{Cu}^{2+} + \text{Cl}^- + e = \text{CuCl}$	0.54

It should, however, be noted that the values in Table 4.9 are standard redox potentials. They relate to unit activities or unit activity ratios of the oxidized and reduced components. At the beginning, the activity ratio oxidant/reductant is high and thus may raise the potential significantly above the standard redox value. The potential at a given stage of the reaction may be expressed by the Nernst equation:

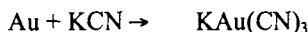
$$E = E^{\circ} + \frac{RT}{zF} \ln (a_{\text{ox}}/a_{\text{red}}) \quad (4.30)$$

If the ratio $a_{\text{ox}}/a_{\text{red}} = 100$, at 25°C , $E = E^{\circ} + 0.118 \text{ V}$

As the reaction progresses the potential will decrease leading to the reaction slowing down and eventually coming to equilibrium. One way of maintaining the required potential is reoxidize the reduced species as it forms. This may be done by anodic reoxidation, that is by applying an anodic potential or by an oxidant such as oxygen. Bubbling in air may be adequate in some cases.

4.5.3. Microwave Treatment of Tailings

Microwave pretreatment has been used to make it easier to leach some of the tailings, which contain minerals that are not readily leachable. By this treatment some of the minerals are chemically transformed. For example, in gold tailings, goethite is converted to hematite by microwave treatment (Haque *et al.*, 1998). That enhances the leaching rate of gold tailings by cyanide to recover gold by the cyanidation reaction:



Microwave assisted leaching has been applied for the processing of metallurgical slag. Details will be described in Chapter 8.

4.5.4. Methods of Leaching

There are several methods practiced in hydrometallurgical leaching. The choice of the method mainly depends upon the value of the metal content in the material and cost factors. The principal cost for leaching metallurgical waste is preparing the feed to a satisfactory degree of particle size to facilitate ease of leaching. When the material is already ground, as in the case of sludges, this is not an issue as the material is already in the finely ground state. In the case of waste rocks, grinding is often required. An often used method of leaching for finely ground material involves agitation. In addition to sludges and finely ground rocks, it is also applied to granulated alloy scrap, alloy turnings and borings. The large surface area of the feed material ensures high rate of leaching. The agitation minimizes the thickness of diffusion layer and maximizes the gas-liquid interfacial area in the case of gaseous reactants. Leaching can be carried out at elevated temperature up to 100°C for rapid rate. High pressure leaching is sometimes chosen where the cost is justified by the economic value of the product.

Several forms of autoclaves are available for high temperature, high pressure leaching. A horizontal pressure vessel (Figure 4.16) is shown as an illustration. This is a pressure reactor, 3-5 m diameter and 8-17 m long with their long axis laid horizontally. It is constructed of mild steel with all internal surfaces and parts made of suitably resistant materials. The most common corrosion-resistant material is stainless steel. Where the acid concentration is high, titanium, special alloy, or acid-resistant brick lining has to be used. The autoclave is generally divided into three or four compartments each containing an impeller for agitation. Pulp is pumped under pressure into one end of the autoclave and flow as through the vessel from one compartment to the next. Injection of live steam is usual source of heat. If the reaction is exothermic (as is the case in most leaching processes) steam injection is discontinued. It may be necessary to control the temperature

by cooling; this is done by internal circulating by water introduced through cooling coil nozzles. For high pressure leaching, air or oxygen is introduced through the air nozzle. A pressure of 500-1000 kPa at 120° C.

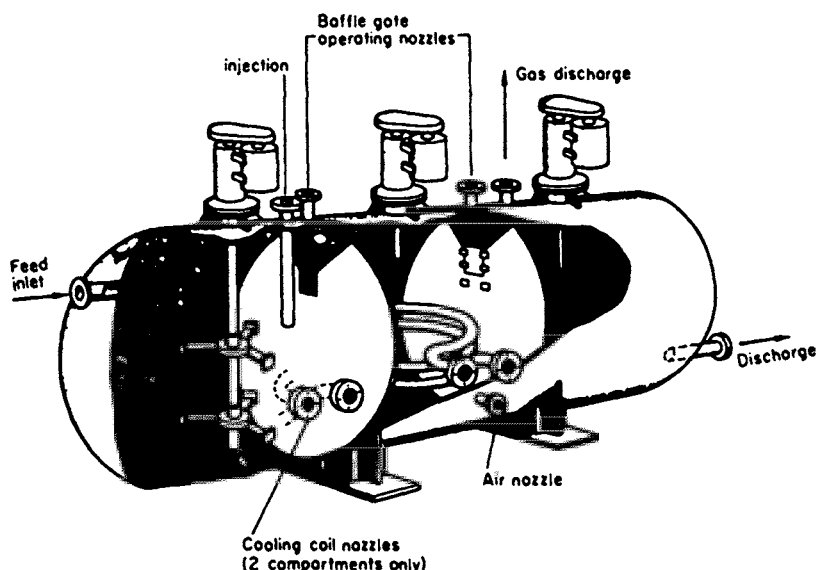


Figure 4.16. Typical autoclave for pressure leaching (Habashi, 1969)

4.5.5. Factors Influencing Leaching Kinetics

Six principal factors governing the rate of a leaching process have been listed by Habashi (1970).

1. Rate of leaching increases with decreasing particle size of the material since the smaller the particles, the larger is the surface area per unit weight. In the leaching of sludges the particles are already ground to a fine size, therefore, this factor is not of concern. It applies to waste rocks as they have to be ground to a satisfactory degree of liberation.
2. If a leaching process is diffusion controlled it will be influenced by the speed of agitation. If, however, it is chemically controlled, it will not be influenced by agitation, provided that enough agitation is done to prevent the solids from settling.
3. Increasing temperature increases leaching rate. However, temperature effect is much less significant for a diffusion- controlled process than for a chemically controlled process.
4. Rate of leaching increases with increasing concentration of the leaching agent. The concentration should, however, be controlled to an optimum level to maximize selectivity; see Section
5. Rate of leaching increases with decreasing pulp density, that is, when a large volume of leaching agent is added to a small volume of solids.
6. If an insoluble product is formed during leaching, the rate depends on the nature of this product. If it forms a non-porous layer, the rate greatly decreases. If, however, the solid product is porous, the rate is not affected.

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Chapter 5

BIOTECHNOLOGICAL PROCESSES

Certain natural materials of biological origin can retain large quantities of metal ions by one of the different possible mechanisms including sorption and complexation. The biological material of such properties is called **biomass** and the phenomenon is called **biosorption**. It has been exploited for the separation and recovery of metals from effluents as well as for toxicity removal. This chapter will describe the sources of biomass, possible mechanisms of metal uptake and their potential in metal recovery from metallurgical effluents. Specific applications will be described in Chapters 7- 10.

5.1. Sources of Biomass

An economical source of biomass for the production of biosorbents is spent biomass from a fermentation process for manufacturing of biochemical products like antibiotics, enzymes, organic acids and possibly vitamins. This material, however, contains extraneous insoluble matter like the medium components or product recovery chemicals, which do not participate in biosorption. Even with such drawback, the spent biomass is far more cost effective than production of designed fermentation to produce biomass specifically for biosorption purposes. Conversion of a "waste" biomass to a biosorption agent also results in reclaiming the biomass material that would otherwise be disposed off as a waste. This is done by appropriate treatment procedures.

An abundant source of mixed microbial biomass is the activated sludge (AS) wastewater treatment process. The ability of AS biomass to remove and accumulate heavy metals has been known for many years. In a sewage treatment facility, metals such as Cd, Cu, Cr, Mg and Pb are removed largely by filtration and adsorption. Evidence has been put forward, which indicates that the principal mechanism of metal uptake by AS is passive biosorption (Nelson *et al.*, 1981) However, the biosorbent studies with AS, both living and dried, suffer from the mixed population nature of AS whose composition is largely unknown and is difficult to reproduce. The metal-sequestering performance of a biosorbent derived from a mixed culture is often unpredictable.

Another inexpensive source of biomass is marine algae. Specifically cultured fresh water algae also serves as a continuous biomass source for the biosorbent family. These are more expensive, but considered to be competitive with ion exchange resins (Kuyucak, 1990).

The following main advantages of biosorption technology are listed by Kuyucak (1990).

1. Metals at low concentrations can be selectively removed.
2. Biosorbent has very low affinity for calcium and magnesium ions (which makes it specially advantageous for the separation of heavy metals).

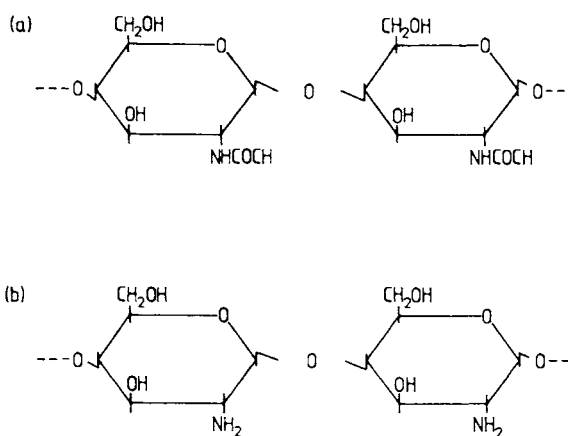
3. Effluent concentrations meet environmental regulations.
4. The system operates over a broad pH range 3-9.
5. The system is effective over a temperature range of 4 to 90 °C.
6. The system offers low capital investment and low operation costs.
7. The cost and liability of toxic sludge disposal are eliminated by converting pollutant metals to a metal product.

While algae have been known to concentrate heavy metals, including radioactive metals like radium (Kalin, 2005), and in some instances the application of algal populations to purify low concentration industrial wastewater in open air natural systems may be practicable, a combination of specific climate and geographical conditions, including sunshine, temperature, land availability, etc. is required for success. The metals accumulated in the algae settle in sediment, which, in course of time, could become a metal recycle source. It will be discussed in Chapter 10. Becker (1983) has reviewed the limitations of using living algae to remove heavy metals.

Another natural source of biomass is fungi. They are a nonphotosynthetic (those which are not synthesized by the action of sunlight) group of microorganisms relying on organic substrates as their sole source of carbon and energy for growth. Many large scale industrial fermentation processes produce copious quantities of mycelia (a group of fungi) as an unwanted byproduct. The potential use of this product as a biomass source for producing bioadsorbents is therefore specially attractive.

The principal active species in the fungal cell wall are **polysaccharides**. Two such molecules of interest are chitin and chitosan. Chitin is a polymer of N-acetyl-D-glucosamine. It is a completely substituted polysaccharide carrying one amine or amide group per glucose ring. Chitosan is deacetylated chitin; see structure in the formula:

Uptake of metals such as Fe, Zn, Cu, Pb, Hg, U, etc. are taken up by chitin by coordination binding with the nitrogen atoms of amine and amide groups. (Muzzarelli, 1972). Metal uptake is dependent on the solution pH; the optimum pH range is 3-4. Ion exchange has also been suggested as a process that may be active in certain metals' uptake by chitin or chitosan (Ainsworth and Sussman, 1965).



Chitin and chitosan structure

A class of bacteria belonging to a family known as *Enterobacteria* excrete copious quantities of polysaccharide coatings. Such organisms provide extensive adsorption sites which are additional to the cellular material. With certain species metal tolerance is increased by these excretions as they help protect the bacteria from excessive internal accumulation by concentrating metals externally (Scott and Palmer, 1990; Scott and O'Reilly, 1991)

5.1.1. Granulation Procedure

In order to be useful in recovering metals, biomass has to be employed in equipment used to contact the wastewater to be treated with the biosorbent. The agent must be easy to transfer, or separate, from the contactor device, and it must have good physical and chemical stability for extended treatment of wastewater and for regeneration (metal recovery). These requirements are met by granulating or immobilizing the biomass. The use of individual microbial cells substantially increases the complexity of the application as metal-loaded cells have to be separated from the wastewater through a solid-liquid separation technique, centrifugation, filtration, or sedimentation.

A procedure for the granulation of a biomass is schematically represented in Figure 5.1. It is similar to immobilization of industrial enzymes. The process essentially comprises concentration of the biomass recovered from the fermentation process, mixing of the reagents selected for granulation, extrusion of the biomass with subsequent granulation, and final drying of the product.

The biomass from the fermentation process may have to be passed through a sieve to remove particulate material. This material can be present as an insoluble component of the fermentation medium and adds nothing to the biosorption agent. The biomass may be concentrated by centrifugation or filtration to reduce water, which can adversely affect binding characteristics. The concentrated biomass is then mixed with the granulating agents. This is a critical step in the process as it ensures a homogeneous product, which is cross-linked to provide a granule of desired stability and activity. The quantity of cross-linking reagent has also to be optimized. Excessive amount results in a granule of low activity because of slow diffusion of the metals to the biosorption sites. Too little reagent results in a granule which may be too quickly break down in the contacting equipment.

The cross-linked biomass is then processed to form the granule product. This is done by extrusion. The granules are produced from the extrudate by a process called **marumerization** (Brierley, 1990). In this a rapidly spinning plate within a spinning cylinder converts the extruded biomass of a given length to the spherical shape. Further detwatering of the cross-linked biomass may be required and is done by using a belt press. The granule size is controlled at the extrusion step by the diameter of the orifices of the die used to form the extrudate. The granule is then dried, which provides an indefinite shelf life to the product.]

5.1.2. Biomass Supported on Activated Carbon

Activated carbon has been used as a support for biomass during contacting phase (the stage when the biomass comes in contact with metal-laden effluent). This provides good surface to liquid contact and aids subsequent recovery of the particles as they become metal saturated. The biomass is now heat treated which fixes the metals onto the substrate and the carbon is recovered and can be reused to grow more biosorbent (Scott *et al.*, 1992).

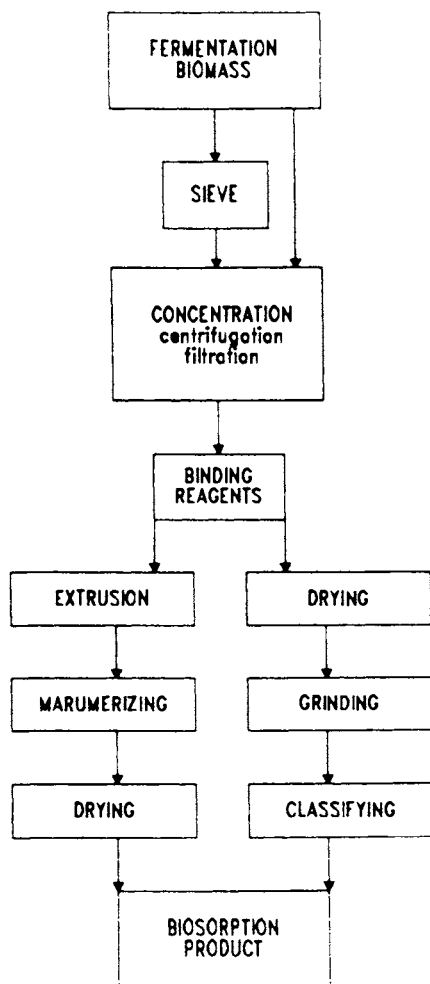


Figure 5.1. Process steps in converting a *Bacillus* biomass from fermentation to a granular product used for biosorption of metals (Brierley, 1990)

5.2. Process of Biosorption

The term biosorption refers to many modes of nonactive metal uptake by microbial biomass which may even be dead (Brierly et al., 1986) (ref. 16, p.41, Volesky). Metal sequestration by different parts of the cell. Mechanism of the uptake will be discussed in Section 5.2.3. An understanding of the cell wall structure is useful to analyze biosorption process.

5.2.1. Description of Cell Walls

A simple diagram of a bacterial cell is presented in Figure 5.2. The shape of bacterial cells can vary from a rod-shaped cylinder (called bacilli), to spherical cells (called cocci),

to corkscrew-shaped cells (called vibrio or spirochetes). The cellular shape, and location of spores and flagella are used to identify a particular organism.

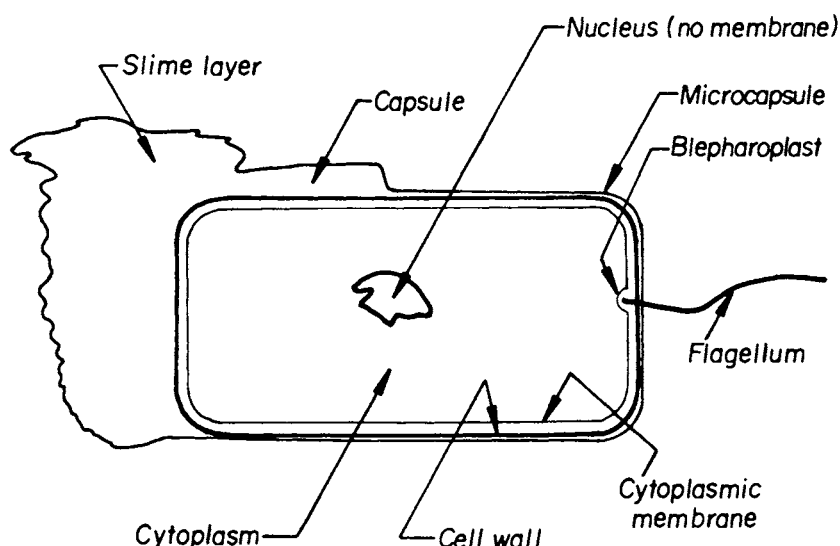


Figure 5.2. A bacterial cell

On the external side of the cytoplasmic membrane is the cell wall. Bacteria are divided into two groups, based on the structure and chemical composition of the cell wall, that are reflected in their staining characteristics. The first group is the **gram-negative** organisms that have cytoplasmic membrane surrounded by a cell wall called peptidoglycan layer, which in turn is surrounded by the outer membrane; Figure 5.3. The second major group is the **gram-positives**. They have no outer membrane and the cell wall is a complex of N-acetyl glucosamine (NAG) and n-acetyl muramic acid (NAM), which are cross-linked by a penta-amino acid chain. Cell walls are generally 10-25 nm thick and represent about 25 % of the cellular dry weight. The cell wall provides structural and, to a lesser degree, selective permeability, since the entrance of nutrients and excretion of wastes are controlled somewhat by the molecular weight of the material. The cell wall is resistant to most chemical reagents except strong inorganic acids and alkalis.

The cell wall of gram-positive bacteria is composed of several layers bearing anionic groups. Two main wall constituents covalently attached to the peptidoglycan contribute to the anionic property of the wall, the teichoic acids and the teichuronic acids. The teichoic acids are composed of 30-40 molecules of either glycerol or ribitol (a polyhydric alcohol) phosphate residues. Ester (glycosyl and D-alanine) are bound to the teichoic acid linear chain which is linked to N-acetylmuramic acid of peptidoglycan by a phosphate group. The teichuronic acids are free of phosphate and made up of hexuronic acid linear chains. The proportion of teichoic and teichuronic acids depends on the culture conditions, especially on the phosphate supply. (See Section 5.2.2 for media and growth requirements). The teichoic and lipoteichoic acids are mainly known to play a physiological role by supplying magnesium to the plasma membrane.

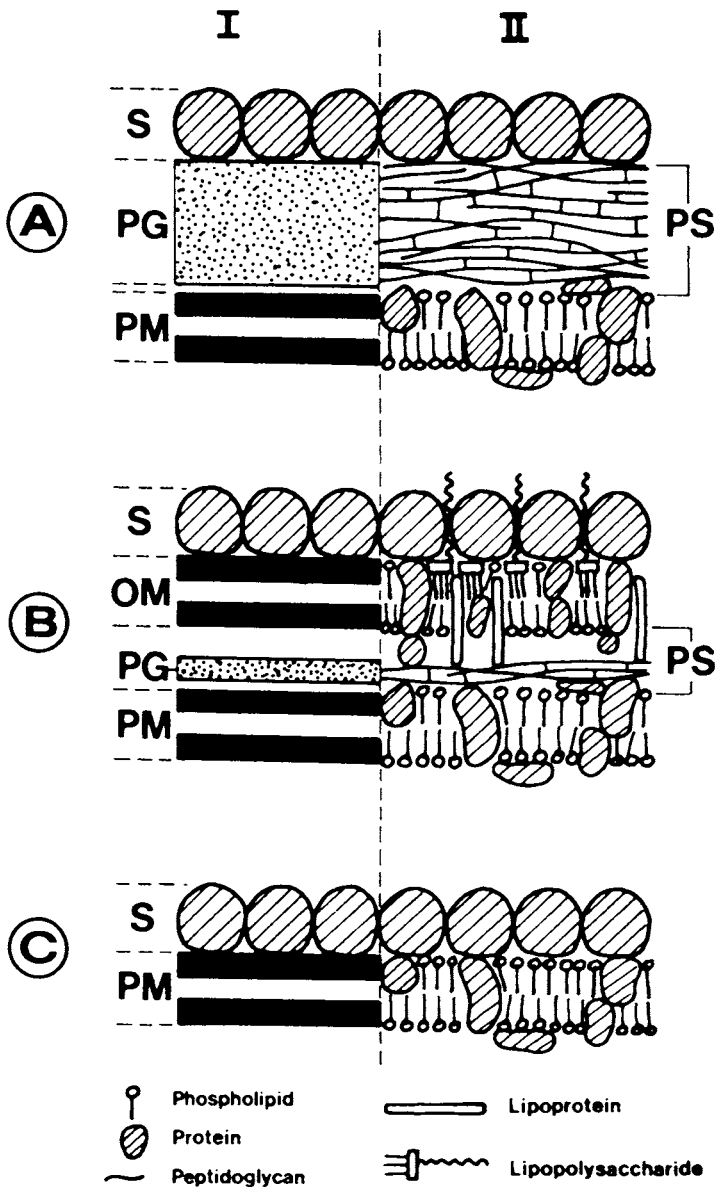


Figure 5.3. Schematic diagram of main categories of bacterial cell envelopes (Sleyter, 1981)

The fungal cell wall consists of various polysaccharides complexed with proteins, lipids and other substances (e.g., pigments). The algal wall is structurally similar to fungal wall and is made of a multilayered microfibrillar framework generally consisting of cellulose and interspersed with amorphous material.

5.2.2. Media and Growth Characteristics

All biological systems require nutrients for their growth. They are used to build cellular material or to obtain energy. Almost any material can nourish one microorganism or other. No one organism is capable of utilizing all nutrients. Some nutrients can be utilized by a limited number of species.

The selection and transport of nutrients into the cell, and disposal of the waste products are the main functions of the cell membrane. In most instances the nutrients are transported across the cell membrane by a process called **active transport**. It is the ability of an organism to accumulate substances within the cell in high concentration, from an external environment, where the substances are in low concentration.

It is thought that some 35-40 elements in the Periodic Table are essential nutrients for bacteria and fungi. Six non-metals (C, O, H, N, P, S) and two metals (K, Mg) constitute over 95 % of the dry weight of bacteria and fungi. These eight elements are referred to as **macronutrients**, the concentration needed in growth media being greater than 10^{-4} M. All other elemental nutrients are usually required at concentrations less than 10^{-4} M and are called **micronutrients**.

One class of microorganisms, known as **autotrophic bacteria**, grow solely on inorganic materials, with carbon dioxide as the carbon source, and sunlight (photosynthesis) or the oxidation of inorganic compounds (chemosynthesis), as the energy source. All autotrophs incorporate carbon dioxide into the cell material. Chemosynthetic autotrophs constitute the vast majority of bacteria used in biotechnology. Among the chemosynthetic microorganisms, the thiobacillii are of practical significance. An example is organism *Thiobacillus ferrooxidans* used in the oxidative leaching of sulfide minerals (see Chapter 4). The chemical composition of the medium for their growth is called 9K medium and has the following composition (Silverman and Lundgren, 1959): FeSO_4 , 9.0 g; $(\text{NH}_4)_2\text{SO}_4$, 3.0 g; K_2HPO_4 , 0.5 g; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g; KCl , 0.05 g; $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.01 g; distilled water, 1 liter. The media used for cultivation of other autotrophs are very similar to the 9K medium, except that certain other specific chemicals may have to be added or substituted. For full details on media for autotrophs and heterotrophs (those that live on organic matter), manuals of microbiology should be consulted; (Buchanan and Gibbons, 1974; *Difco manual*, 1984.)

5.2.2.1. Physical Conditions Required for Growth

In addition to supplying the proper nutrients, it is also necessary to provide the proper physical conditions for optimum growth. As their nutritional requirements vary greatly, bacteria exhibit diversity in their response to changes in the physical conditions of their environment. The following principal conditions should be paid special attention.

Gaseous Atmosphere: Most bacteria can grow under ambient oxygen atmosphere. Certain types, however, can derive their oxygen requirement from various substrates. Aerobic organisms require the free admission of air, while anaerobes grow only when atmospheric oxygen is excluded. Between these two groups are the microaerophiles, which develop best under partial aerobic conditions (< 0.1 atmosphere), and the facultative anaerobes, which can grow under both aerobic and anaerobic conditions. A complete description of various methods for maintaining anaerobic conditions in cultures can be found in the book Dowell and Hawkins (1977).

Temperature: As all growth processes are dependent on chemical reactions, and as reaction rates are dependent upon temperature, the growth of bacteria is influenced by

temperature. It affects the rate of growth and the total amount of growth (yield of biomass) of the organism.

pH: The pH of the medium is extremely important for growth of microorganisms. The majority of microorganisms prefer approximately neutral culture media. However, there are organisms, which can withstand highly alkaline or highly acidic conditions. It should be noted that pH rises as the temperature falls and allowance must be made if the pH is measured when the medium is hot, but subsequently cools to room temperature. When heated in an autoclave, solutions that have been adjusted to be a little on the alkaline side of neutrality tend to fall about 0.1 pH unit.

Other environmental factors affecting growth of microorganisms will be discussed in the next section.

The media in which microorganisms are grown must be sterile, that is, free from possible contamination with other organisms, which might influence or prevent the normal growth of the inoculated type. Sterilization can be done by heat, (dry or moist), by ultraviolet or ionizing radiation or filtration. Heat treatment is most often employed since it is generally the simplest and most reliable. Sterilization in an autoclave for 15 min at 121° C and a pressure of 103 kPa is recommended for quantities of liquid media up to 1 liter. For larger volumes, longer time of treatment is necessary. The medium is prepared, distributed in tubes or flasks plugged with non-absorbent cotton, and placed in the autoclave. After sterilization, the autoclave is returned to atmospheric conditions. Pressure should be reduced gradually to prevent the media from boiling over.

5.2.2.2. Media for Yeasts and Fungi

Molds obtain their nutrients by diffusion or transport of soluble matter across the cell membrane using relatively simple substrates. Most molds derive carbon and energy from carbohydrates, and some can utilize alcohols or organic acids. They can also satisfy their carbon requirements from protein or from products of protein digestion. Sources of nitrogen include organic compounds such as peptones, peptides and amino acids. Some species can utilize ammonia or nitrates.

Yeasts require the same chemical elements as other forms of life: carbon, hydrogen, nitrogen, oxygen, phosphorus, etc. carbon is commonly obtained from sugars, organic acids, aldehydes, or glycerol. Nitrogen is derived from products of protein hydrolysis (such as proteoses, peptones, amino acids and ammonia) or from urea or amides. In the laboratory and in industrial processes, ammonium sulfate, phosphate, or chloride is often used as the source of nitrogen. Phosphorus is essential for growth as it plays an important role in carbohydrate metabolism. It is usually supplied as a phosphate salt. Yeasts also require growth factors, such as biotin (which has a significant role in nitrogen metabolism), pyridoxine, thiamin, niacin and inositol (which is apparently built into the cell structure).

Molds grow more slowly than bacteria. Acidic media with a relatively high concentration of sugar would be tolerated by molds, but would be inhibitory or unfavorable to most bacteria.

The most common types of media used for growth of molds and yeasts are:

1. Natural media, such as pieces or infusions of fruits, vegetables, or animal tissues.
2. Complex media consisting of peptones, plant extracts, agar, and other compounds of unknown or variable composition.

3. Synthetic media from defined chemicals to obtain a medium of known composition and one which is exactly reproducible.

There are two broad groups of media: liquid and solid. Many liquid media containing different nutrients have been devised and most bacteria grow in one of them. All large scale fermentation is carried out using liquid media. They have two disadvantages:

1. Cells do not have a characteristic appearance in liquid media and, except when used in a medium designed for a specific biochemical test, liquid media are of limited use in identifying the organisms.
2. Organisms cannot be separated with certainty from mixtures by growth in liquid media.

These disadvantages can be overcome by preparing the media as a gelatinous solid.

Solid media are advantageous for identifying bacterial colonies as each has a characteristic appearance. Solid media are indispensable for the isolation of pure culture.

5.2.3. Metal Binding Mechanisms

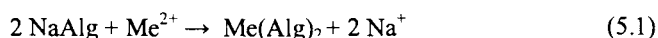
The binding of metal to the biomass has been incompletely understood. Part of the difficulty occurs from the complexity of the cell wall and its characteristics which determine interaction with metals and metal uptake. Three principal mechanisms of metal sequestration by the cell walls have been identified. They are, adsorption, metal precipitation and metal nucleation.

Metal uptake can occur by one or more of the following routes (Volesky, 1990):

- Complexation
- Coordination
- Chelation of metals
- Ion exchange
- Adsorption
- Inorganic microprecipitation

Any one or a combination of these routes results in various degrees of immobilizing one or more metallic species on the biosorbent. Metallic cations are attracted to negatively charged sites at the surface of the cell. Several anionic ligands participate in binding the metal. They include carboxyl, sulfhydryl, and hydroxyl groups of membrane proteins.

The mechanism followed depends upon the functional groups present in the cell walls of the biomass from which the biosorbent has been prepared. Many cell walls contain different polysaccharides as basic building blocks. They possess ion exchange properties. An example is alginic acid. Bivalent metal ions exchange with counter ions of this polysaccharide by the reaction (Volesky, 1990, p. 20):



Evidence has been put forth to show that ion exchange plays an important role in efficient sequestering by the biomass of several microorganisms even when they are dead. (Beveridge, 1986; Marquis *et al.*, 1976).

Charge at the surface of organisms has been established by electrophoretic mobility measurements. For example, dissociation of phosphodiester groups probably gives rise to negative surface charge of *Saccharomyces cerevisiae*. *Escherichia coli* has carboxyl groups and *B. egaterium* has a mixture of phosphoryl and carboxyl groups (Neihof and

Echols, 1973). Adsorption is determined by affinity of metal to biomolecules, which contain specific functional groups or ligands with which bind metal atoms by ionic or covalent bond. Based on their atomic properties and solution properties metal ions have been classified into three categories by Nierboer and Richardson (1980). They distinguish metal ions which are oxygen seeking, nitrogen- and sulfur-seeking and an intermediate class. The scheme has been related to the Periodic Table of elements as shown in Figure 5.4.

Note. Electrophoretic mobility refers to the mobility of a particle possessing a surface charge under the influence of an electric field. When an electric field is applied, between two electrodes, the charge particles move towards the electrode with opposite charge. The mobility can be measured and, for a given electric field, is related to the surface charge of the particle. Details are described in text books on Colloid Chemistry or the book by S. R. Rao and J. Leja (2004) mentioned under "Selected Readings" in Chapter 3.

Legend:

- Class A (diagonal lines)
- Borderline (horizontal lines)
- Class B (vertical lines)

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac†															
Lanthanides * Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu																	
Actinides † Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr																	

Figure 5.4. The Periodic Table of elements showing the disposition of the Class A, intermediate, and Class B metal and metalloid ions. (Nierboer and Richardson, 1980)

The affinity of the three metal ion classes for ligands is inferred from thermodynamic consideration. The preference of the three metal ion groups for the most common ligands in biological materials is shown in Table 5.1.

Table 5.1. Ligands Encountered in Biological systems (Nierboer and Richardson, 1980).

I. Ligands preferred by Class A metal ions	II. Other important ligands	III. Ligands preferred- by Class B metal ions
F^- , O_2^{2-} , OH^- , H_2O , CO_3^{2-} , SO_4^{2-} , $ROSO_3^-$, NO_3^- , HPO_4^{2-} , PO_4^{3-} , etc. ROH , $RCOO^-$, $-CO-$, ROR	Cl^- , Br^- , N_3^- , NO_2^- , NH_3 , RNH_2 , SO_3^{2-} , R_2NH , R_3N , $=N-$, $-CO-N-R$, O_2^- , O_2^{2-}	H^- , I^- , R^- , CN^- , CO , S^{2-} , RS^- , R_2As , R_3As

The symbol R represents an alkyl group; in a few cases, it may also represent an aryl (e.g., phenyl) group. Class A metal ions have an absolute preference in aqueous solution for the types of ligands in column I, all of which bind through oxygen. Class B metal ions show a high affinity for ligand types in column III, but can also form strong complexes in aqueous solutions with the ligands in Column I.I. Borderline metal ions can interact with ligands in all three columns, but may show preferences (Nierboer and Richardson, 1980)..

It should, however, be noted that cell walls contain a mixture of monovalent and divalent cations and the displacement of one cation by another (e.g., H^+) is dependent on the strength of the individual ligand complexes. Additionally, the relative strength of different complexes in the solution should be considered.

Metal uptake by polysaccharides has also been related to coordination bonding. These and other mechanistic studies on various metals have been discussed by Macaskie and Dean (1990).

Metals can also be adsorbed by electrostatic mechanism. Many microorganisms are found to possess negative surface charge originating from the molecular functional groups like carboxyl acids, which in alkaline pH generate carboxylate anions. The surface charge has been estimated by electrophoretic mobility measurements by van Loosdrecht and coworkers (1987).

The possible precipitation of insoluble metallic compounds is another mechanism that should be considered in biosorption. Nonhydrolyzed metallic species can form insoluble metal phosphate by combining with the phosphate groups in the cell wall. In other cases, the metal ions are hydrolyzed forming polynuclear metal hydroxy species. For example, depending upon the pH of the medium, thorium ion undergoes extensive hydrolysis in the solution in accord with the following reactions:



The metal hydroxy species are known to undergo polymerization forming, for example, $Th_2(OH)_2^{6+}$. This forms an extremely insoluble complex with phosphate (Cotton and, Wilkinson 1988; p. 1002).

External factors such as temperature, pH, and the presence of other anions, cations, or organic compounds can all affect the chemistry and availability of both the binding sites on the biosorbent, as well as of heavy metals in solution, thus affecting the biosorption process. The same applies for generalized models for the biosorption process. As comprehensive information is not available, the optimum conditions for each biosorbent system have to be determined experimentally.

5.2.4. Techniques for Metal Recovery from Biomass

Once the metal is bound by biomass, it has to be separated and recovered in a form from which it can be processed further to the desired final product (either single metal or metal compound). Various schemes have been put forward to this end, to utilize organisms, living or dead, to remove and recover metal ions from solutions. In one process developed at the U.S. Bureau of Mines (which ceased to exist in 1996), killed organisms are immobilized in porous polysulfone beads, which can be handles much like ion exchange resins (Jeffers *et al.*, 1991, 1993). Extracted metals are recovered from the beads by elution with a dilute acid yielding a concentrated eluate. The beads named BIO-FIX effective in removing very small amounts of heavy metal ions from solution and they perform well in the presence of Ca(II) and Mg(II) ions in high concentration.

Another scheme studied by Smith and Misra (1991) is to harvest microorganisms that have accumulated heavy metal ions by froth flotation (see Section 3.6), taking advantage of the flotability of microorganisms using a cationic collector like dodecylamine chloride. The cationic reagent is chosen as the microorganisms possess negative surface charge. Some microorganisms exhibit sufficient natural hydrophobicity and in such cases use of collector will not be necessary.

5.3. Techniques of Bioprocessing

The metal recovery process by biosorption is essentially a solid-liquid contact process comprising the metal uptake (sequestering) cycle and the metal desorption (elution) cycle, very similar to ion exchange process described in Chapter 2 (Section 2.2). The metal-laden effluent is contacted with the solid sorbent phase in a batch, semicontinuous, or continuous flow arrangement. A batch stirred tank contactor or continuous flow stirred tank contactor may be employed for this purpose. Contactors of different designs and details of the operation have been described by Volesky (1980).

Following the metal uptake the metal recovery from the biosorbent is achieved by one of the following alternatives.

Elution: Similar to ion exchange the elution cycle is based on eluting the metal by a small volume of an appropriate solution which will release the biosorbed metal by its chemical affinity for the metal. In general, the eluting solution should be able to wash out the metal in small volume so as to achieve its highest concentration, without damaging the capacity of the biosorbent, which will make it reusable for another metal uptake cycle. The efficiency of the eluant is expressed by solid to liquid ratio, S/L. The solid represents the amount of solid sorbent by weight; the liquid represents the amount of eluant applied, also by weight. High values of S/L indicate complete elutions.

Elution also helps to enhance selectivity. The selective uptake of the metal by biosorbent is important. However, the overall selectivity of the combined uptake-release process is the one of technological importance. While the uptake selectivity may not be necessarily impressive in some cases, it could be enhanced in the elution cycle by an appropriately chosen eluting solution with high desorption efficiency for the metallic species of interest.

Regeneration of the biosorbent material is an important factor for the success of the biosorption process as an industrial operation. The eluting solution should be able to effectively uncouple the bonds by which the metal is sequestered on the biosorbent material. The choice of the eluant is, therefore, governed by its chemical affinity to the metal resulting in the formation of a soluble compound. For example, uranium separated

by biomass is recovered by elution with sodium bicarbonate with high S/L ratios resulting in eluates with uranium concentrations in thousands of milligrams per liter (Tsezos and Volesky, 1982). Gold sequestered on biosorbent material is recovered by elution with a solution consisting of 0.1 M thiourea and 0.02 M ferric ammonium sulfate (Volesky and Kuyucak, 1988). The ferric ions oxidize gold to the +3 state (auric) and the auric ions form a soluble complex with thiourea. Another example is recovery of cobalt by elution with 0.1 M CaCl_2 solution (Kuyucak and Volesky, 1988).

Ashing: An alternative to elution is ashing of the metal-laden biosorbent. The biosorbent is not recovered in this process. Waste biomass applied as a biosorbent, in some cases, may be so inexpensive and abundant that its recycling is not considered worthwhile. This generally applies to bioadsorbents, which consist of raw biomass supplied either as a waste material from industrial operations (e.g., industrial fermentation) or as a naturally abundant renewable biomaterial (e.g., algae) which can be cheaply harvested.

5.4. Industrial Biosorption Processes

Biological treatment systems where live microbial sludge or biofilms serve the function of metal sorbers have been used in many places for collection and removal of heavy metals from industrial metal-containing effluents. Such systems, however, operate on the principle of *bioaccumulation* and are not geared to the recovery of metals.

Biosorption systems use the biosorbent materials derived from metal-sequestering biomass. They can operate at elevated metal concentrations which could be toxic to a living system. Industrial biosorbents are either reusable or those which can be disposed off after they are fully loaded and saturated with the sequestered metals. The metal-laden biosorbents can be shipped to a metal recovery facility where they are either regenerated for reuse or destroyed by ashing with simultaneous metal recovery. In some cases they may be simply disposed off if the sole purpose of the biosorption is remediation. Regeneration of biosorbents with subsequent metal recovery can also be done on the location of the sorption plant.

In commercial operations different types of biomass materials are processed into suitable biosorbents by more or less proprietary procedures. The design and operation of the biosorption process equipment and system do not differ much from that used in the technology of ion exchange adsorption (see Section 5.2). The process operation is usually based on a contactor system with a bed of either fixed using a normally downflow stream of liquid or fluidized by a normally upflow stream of liquid. Pretreatment of the liquid mainly to remove suspended solid particles may be necessary in some operations. The choice of the biosorption system depend mainly on the amount of the flow to be handled and on its continuity and composition as well as on the conditions for regenerating the biosorbent. The solid-liquid contact sorption system can be scaled up on a modular basis. Good metal uptake performance and selectivity of new biosorbents coupled with their physical characteristics allow great flexibility in application design, thus facilitating ease of operation ease of operation in a variety of metal-removal situations.

Biosorbents are usually made as granular materials (see Section 5.1.1) for direct sorption of metals from effluent streams. This eliminates the costly and cumbersome chemical pretreatments, which usually generate metal-enriched sludges for either disposal or reprocessing. Specific data on the performance of individual biosorbents are usually not available as most are proprietary items; but this is not a serious handicap as a choice

can be made on the basis of published information on systems which are comparable with those required for treatment. Specific operating parameters are then determined by experimental studies.

Regeneration of biosorbents is accomplished in a two-step process consisting of metal elution stage, resulting in a highly concentrated solution of the specific metal and a simple washing stage to complete the regeneration of the biosorbent for recycle.

Volesky (1990) has listed the following major interesting features to be considered in newly developed biosorbent materials:

High versatility: Most operate under a wide range of pH, temperature, and other conditions specific for solution and process.

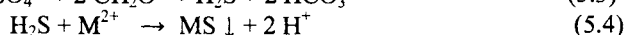
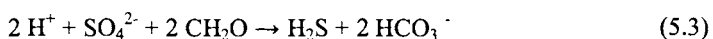
Metal selectivity: If required, a wide range of heavy metals can be sequestered without interference from common alkaline earth metals.

No dependence on concentration: there is high heavy metal uptake for a wide range of metal ion concentration, < 10 ppm to > 100 ppm.

High tolerance for organics: Low levels (< 5 g/L) of organic contamination do not affect metal uptake.

5.5. Sulfate Reducing Bacteria

Sulfate ions are a common occurrence in many mining and metallurgical effluents. In sulfide mining regions and also in regions where coal containing pyrite is mined and processed the waste rocks generate an acidic effluent as they decompose by a process of oxidation under atmospheric conditions. It is called acid mine or acid rock drainage (AMD or ARD). It often carries with it significant concentration of several metals, in particular, zinc and copper, of economic value. One of the methods of treating AMD is by using microorganisms called sulfate reducing bacteria (SRBs). During the process, SRBs utilize a carbon source and generate alkalinity (Kuyucak *et al.*, 1991) in accord with the following reactions:



(CH₂O represents the organic compound used as nutrients and M represents metal ions.)

A mixed culture of sulfate reducing bacteria can be isolated from mine sediments. The specific name of the pure culture is *Desulfovibrio desulfuricana*. The work by Kuyucak *et al.* (1991) and Kuyucak and St.Germain (1994) has led to a procedure for harnessing these bacteria for the treatment of AMD. The substrate chosen consists of limestone and sand in 1:1 proportion. Gravel sediment serves the same purpose. It is inoculated with SRB from mine sediment. The inoculum is 1 % of the working water volume. Organic carbon is derived from cellulosic wastes consisting of wood pulp, sawdust, bark, maple leaves, oat straw fuel peat or horticultural peat or organic wastes. Nitrogen is derived from organic wastes like cow manure, distillers' dried grains, brewers' dried grains, dehydrated whey and molasses. The process is conducted in a reactor for a 35-day period.

The effect of treating sulfate containing effluents with sulfate reducing bacteria is shown in Figure 5.5. The trend in the pH curve is closer to the trend in the alkalinity generation curve as opposed to the sulfide ion curve. This implies that the influence of alkalinity generation on pH is predominant over sulfate reduction.

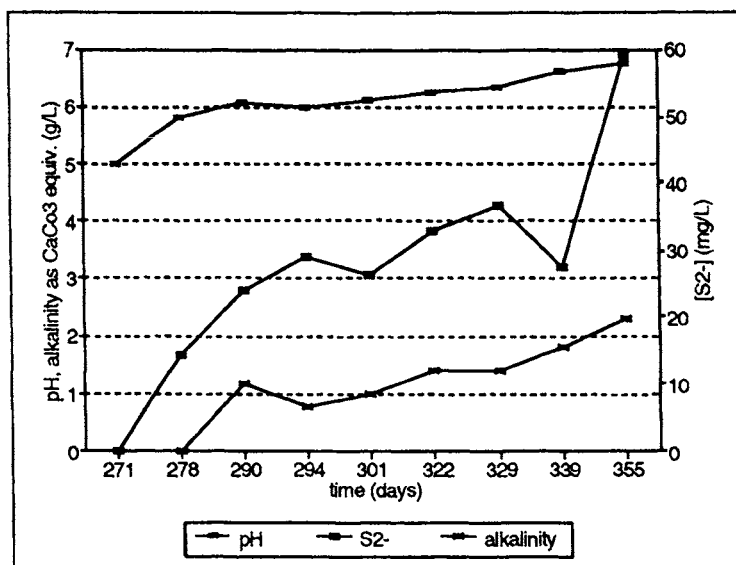


Figure 5.5. The relationship between pH, alkalinity and sulfide generation in the treatment of sulfate containing effluents by SRBs (Kuyucak and St. Germain, 1994).

5.5.1. Factors Affecting the Performance of Sulfate Reducing Bacteria

In the industrial application of SRBs, the effect of several chemical and engineering parameters have to be understood as most such systems from which metal recovery is sought are very complex containing ionic species like sulfur oxyanions (SO_x^{y-}) and metal ions, which could inhibit the growth of SRBs and diminish their sulfate reduction efficiency.

A fundamental study by Saleem and coworkers (2001) has explored the effect of some of the parameters on the growth of SRBs. They arrived at following conclusions.

1. Effect of metal ions. The presence of dissolved heavy metal ions, such as Cu and Co, can be inhibitive. A complete inhibition of SRB occurs for a 5-day span at 80 mg/L cupric sulfate. With cobalt compound, the growth rate is the highest with 40 ppm Co, dropping with increasing concentration. Apparently, cobalt is essential to many bacteria, but becomes toxic at higher concentration. The mechanism of such toxicity has not been fully understood. It may be related to the transition metal ion's ability to bind with the organic ligands of the bacteria producing deleterious effect.
2. Effect of sulfide ions. There is practically no effect with initial sulfide ion concentration up to 150 mg/L. However, when the concentration is increased to 300 mg/L or above, no growth and no activity of the bacteria is observed.
3. Effect of sulfur oxyanions. The rate of reduction differs for the various oxyanions. The highest rate is found with thiosulfate, followed by sulfite and is lowest with sulfate. This sequence parallels the oxidation state of sulfur in these anions (it is maximum, +6 in sulfate) and free energy values of the corresponding reduction

reactions. Gibbs free energy values for the reduction of sulfate, thiosulfate and sulfite are estimated to be 166.4, 145.5 and 65.9 kJ/mole respectively.

4. **Effect of pH.** As the equilibrium of aqueous sulfide species is affected by pH, the SRB growth is also dependent upon pH. At lower pH, greater proportion of sulfide occurs as H_2S , a weak acid and sulfide ion concentration is relatively low. With increasing pH, however, leading to neutralization of hydrogen sulfide the concentration of sulfide ions rises, causing decline in bacteria growth and SRB activity.

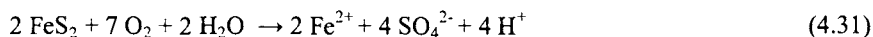
The use of sulfate reducing bacteria to recover metals from AMD and other sulfate effluents will be discussed in Chapter 10.

5.6. Bacterial Leaching

Microbiological degradation process leading to oxidative leaching of sulfides brought about by certain specific bacteria has long been known (Waksman and Joffe, 1922). Bacteria are microscopic organisms, 0.5-2 μm in size, which reproduce by binary fission. They occur widely distributed in soil, air and water. As described in Section 5.2, the bacteria which live on inorganic matter are called autotrophic; those that live on organic matter are called heterotrophic.

The bacteria of importance in leaching are autotrophic. They use carbon dioxide for the generation of cellular tissue. They live and grow in acidic environment (pH 1.5-3) and in the presence of many heavy metal ions including those which are highly toxic to other forms of life. Table 5.2 lists four principal bacteria in this class and the oxidation reactions which provide energy for their growth.

The first two are the most common in leaching. In mineral waste treatment bacterial leaching is specially useful for leaching pyrite from waste rocks. It is essentially an oxidative reaction producing ferrous and sulfate ions according to the following reaction:



followed by

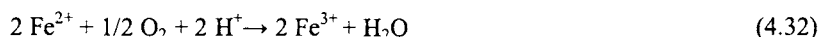


Table 5.2. Bacteria of importance in leaching (from Habashi, 1969)

Bacterium	Source of energy
<i>Thiobacillus thiooxidans</i>	Oxidation of sulfur, sulfur dioxide, thiosulfate ions
<i>Thiobacillus ferrooxidans</i>	Oxidation of ferrous ions, thiosulfate ions
<i>Ferrobacillus ferrooxidans</i>	Oxidation of ferrous ion
<i>Ferrobacillus sulfoxidans</i>	Oxidation of sulfur, ferrous ions

Under normal atmospheric conditions these reactions are very slow; the enzymes present in *thiobacillus ferrooxidans* catalyze the second reaction. The reaction is a source of energy for the bacteria and they utilize carbon dioxide to build cell by a process similar to photosynthesis. The ferric ions produced promote the dissolution of other sulfide minerals by reaction similar to the reaction (4.29) described in Section 4.5.1.4. (Tuovinen and Kelly, 1974). The sulfur produced can be oxidized to sulfuric acid:



As noted from Table 4.13, this reaction is catalyzed by *thiobacillus thiooxidans*.

It should, however, be mentioned that while separation of pyrite from waste rock is a desirable objective as that mineral has the potential of generating acid when it is left to wither in moist atmosphere, the reaction has to be controlled to minimize the production of sulfuric acid. As is evident from Equation (4.33) the catalyzation of the reactions by the two bacteria produces sulfuric acid resulting a strongly acidic effluent, which is called **acid mine drainage (AMD)** or **acid rock drainage (ARD)**. As will be discussed in Chapter 10, huge amounts of ARD accumulated has been a serious environmental problem, especially in sulfide mining regions. In order to reduce the production of AMD it is necessary to hinder the bacterial action by minimizing contact with atmospheric oxygen. Details of such preventive measures are described from time to time; some of the principal ones are described in the book by Ritcey (1989).

Selected Readings

- Cotton, F. A. and Wilkinson, G., 1988. *Advanced Inorganic Chemistry*, John Wiley, New York.
- Habashi, F., 1969. *Principles of Extractive Metallurgy*, volume 2, Gordon & Breach, London.
- Ritcey, G. M., 1989. *Tailings Management*, Elsevier, Amsterdam.
- Volesky, B., editor, 1990. *Biosorption of Heavy Metals*, CRC Press, Boca Raton, FL.

Chapter 6

PYROMETALLURGICAL PROCESSING

Many metallurgical residues containing valuable metals occur as oxides. The recovery of metals from them is usually done by direct reduction of the oxides at elevated temperatures exceeding 1000 °C. This is done using carbon (or any carbonaceous material like coal, coke, etc.) as reducing agent. In addition, to facilitate the melting process, a *flux* is usually added with the high-melting components. Its function is to combine with and neutralize the gangue and products of decomposition, apart from gases, making a product that is fusible and easy to handle and separate from the metal at the operating temperature. The flux forms the *slag* with lower melting point. For example, lime is added as flux to combine with silica (which has melting point of 1728 °C) present in the recycle material. It forms calcium silicate whose melting point is around 1500 °C.

The oxides and other insolubles separating from a molten metal are referred to as *dross*. Refining operations such as cooling to allow separation of insolubles and blowing with air or steam (sometimes the metal is poled with green timber) of lead and tin are called *drossing*. It may also include addition of other elements (like aluminum to separate antimony, arsenic and copper from tin), to produce insolubles, or to increase insolubility. The basic feature of drossing is that the solubility of the constituent being removed decreases with decreasing temperature.

Both slag and dross are inevitable products generated in metal extraction processes and were considered to be “wastes” to be disposed off. Growing environmental concerns and the recognition that they contain components of value or could be converted into useful products have led to the development of technologies for processing these materials. They are now mostly regarded as by-products. In addition, metallurgical residues of pyrometallurgical operations, include large quantities of metallurgical dust, which is also becoming a secondary source of metals. The subject will be discussed in Chapter 9 and 10.

Pyrometallurgical processing involves high temperature reactions, roasting, smelting and converting (for example, metal oxide to metal). A variety of high temperature furnaces are used in metallurgical industry. Some of those, which are used in recycling processes will be described.

6.1. Furnace Technology

A furnace is an apparatus for conducting reaction at high temperature, which is necessary for the processing of non-ferrous scrap. A number of technologies are applied

at different scales of operation. Furnace designs are influenced by different operating parameters like heat input, melt rate, mixing and temperature uniformity. The principal technical factors will be discussed in the following sections. Most of these have been used in extractive metallurgy to recover metals from their minerals and have been adopted for recycling operations.

6.1.1. Melting

In melting, energy (latent heat of fusion) has to be applied to the structure of the solid to increase internal energy to the point where all atoms vibrate leading to disintegration of the solid structure. In most pure metals, the range of temperature through which the metal becomes liquid, occurs within a very narrow range. Impurities in the metal, such as alloying elements, widen this temperature range. By phase diagrams, the composition of the liquid and the solid phases at different temperatures and elemental concentrations is estimated. Such diagrams indicate, large changes in liquid composition can occur within very narrow temperature range.

Mechanical agitation can also affect the composition of the solid and liquid phase. Severe agitation is often unavoidable in large scale melting operations and, in some circumstances, is desirable. Therefore, the equipment that can take advantage of this property of alloys is not a simple melting furnace, but a carefully designed holding furnace to which the liquid metal has been transferred after it has been melted.

6.1.2. Oxide Growth

A metal is usually oxidized at the beginning of melting and continues to oxidize as temperature increases. In some metals a protective film of metal oxide forms on the surface and it thickens with rising temperature. The growth of the oxide film is due to the transport of oxygen from the outside of the film to the metal substrate., and from the transport of the metal atoms from the substrate to the film. The two factors combine in the film to form a highly resilient and stable coating on the piece being heated. If there is no diffusion through the film, there is no oxidation.

As an example, diffusion of oxygen in alumina is dependent on temperature. The structure of the oxide changes sufficiently to allow for greater transport of oxygen atoms through the film as temperature increases. For solids the diffusion coefficient is given by the approximate formula:

$$D = D_0 \exp(E_A/RT) \quad (6.1)$$

where E_A is the activation energy of the process, D_0 is diffusion at temperature T and R gas constant.

This is a physical process, which is not controllable. The flux of oxygen atoms transported through the film is dependent on the difference in the oxygen concentration from one side to the other, which is called the diffusion rate. It is a function of temperature and time and is governed by the relationship:

$$m = - DA \cdot dc/dx \quad (6.2)$$

where m is mass transfer, A area, dc/dx is change in concentration with thickness of the oxide film.

If it is possible to reduce the time during which a surface is subjected to a high temperature environment, the thickness of the oxide film formed on the surface of the liquefying particle can be reduced. The shorter the time the particle is in its solid phase the thinner will be the skin of oxide, which forms on the surface and the smaller will be the loss from oxidation. Rapid liquefaction can be facilitated by reducing particle size and therefore area of the surface accepting heat. The heat flux applied to the particle is a function of the surface area of the particle.

6.1.3. Heat Transfer and Melting Rate

The basic equation governing heat transfer Q is

$$Q = hA (T_s - T_a) \quad (6.3)$$

where h is heat transfer coefficient, A area, and T_s and T_a denote temperature of the surface and ambient temperature respectively.

A high surface area has an impact on the loss from oxidation as the total volume of oxide produced is obtained by multiplying the thickness of the film by the surface area of the particles. The maximum diameter of the particles is chosen to allow the melting time to be calculated. This is done by a procedure called lumped heat capacity method. It assumes, the internal resistance of the body is negligible in comparison with the external resistance. At greater size the internal thermal resistance will increase the time required to melt larger blocks. (For a detailed analysis of *lumped heat capacity system*, see *Heat Transfer* (chapter 4) by J. P. Holman, 1990).

Another method for high heating rates is to increase the average speed of the flow of hot gas to which the particle is being subjected. The heat transfer coefficient (h) is a function of the Reynolds number of the flow and may be calculated with reasonable precision using a commercially available numerical model.

Heat exchange by radiation can also be promoted, but there are a number of practical limitations. To generate high heat fluxes from radiation it is necessary to drive furnace temperatures extremely high. When metal is an extremely good reflector, (like, for example, aluminum), and with a low coefficient of emissivity, it is a very difficult surface to heat with radiant heat alone. It may not be a severe problem when the load is still in its loosely charged solid phase, radiant heat exchange may become difficult as the batch melts.

A batch melting furnace, when charged by a solid load that gradually collapses into a liquid pool in the hearth as the temperature is raised, exhibits many different radiation properties. Many processes are employing sophisticated methods to determine the moment when the bath flattens. This enables the burner systems to be adjusted to reduce the radiant contribution to the overall internal heat exchange.

The third mode of heat transfer is conduction. The very high thermal conductivity of most non-ferrous metals, particularly aluminum, is a great advantage to achieve very high heat fluxes. The first method is to produce a kind of furnace, which uses molten metal as the heat exchange fluid. In this case the convection boundary between the metal particle and liquid metal is extremely small and the thermal resistance between the liquid and the particle is negligible. The problem of heat transfer is thus reduced to the rate at which heat is applied via conduction from the liquid to the particle. Liquid to solid melting has the added advantage that the melting occurs anaerobically.

6.1.4. Liquid Metal Pumping

Melting particles can be submerged using technology based on linear motor, which generates a flow pattern. A series of electromagnetic coils are wrapped around a silicon carbide tube. The coils are energized in sequence and induce an alternating magnetic field. The magnetic fields induce a force on liquid metal inside the tube. This force can then be directed to accelerate the liquid in the direction of the next field being induced in the next inductor. By varying the frequency and current of each coil it is possible to pump liquid metal with no moving parts at rates up to 8 m/s. These pumps are in use on large some large furnaces where they are used to suck the liquefying metal down into the body of the melt. This technology is, however, very expensive and is currently used only in large scale processors.

6.1.5. Furnace Design

In batch type processing or in smaller designs it is not practical to use the melt by pumping as described before. A furnace can still be designed taking advantage of conduction. This technique is usually applied to small scale melting requirements and is characterized by a number of burners firing below a refractory shelf or in a more modern design over a bridge. The shelf supports material through which the flue gas from the furnace is vented. Solid material is loaded into the furnace with careful consideration to prevent from being subjected to excessive pressure. Incoming metal receives some pre-heat from the products of combustion leaving the melting chamber; however, the load takes a significant proportion of the heat via conduction through the shelf. Control of the average particle size, particularly, the volume to surface ratio, is therefore a critical consideration when trying to achieve a good yield from the process. The choice of equipment becomes self-evident depending on the constraints of operation. It is important to be able to communicate (with the furnace designer) accurately, the type of process, the material to be processed, the normal operating parameters and the extremes of operation that may be encountered during service of the new furnace.

6.1.6. Thermal Desorption

In most practical operations, the load is often contaminated. It may contain engineering oils, cutting fluids, materials added as part of another process. lubricating oils, fats, greases applied during service, paint, plastics, etc. Of all such contaminants, hydrocarbons break down and generate noxious, reducing or combustible gases when they are heated to high temperature. It is dangerous to take a wet or heavily contaminated scrap stream and add it directly to a furnace which has been designed to allow liquid metal as the main transfer fluid. The safest way to deal with such a scrap stream is to raise its temperature long enough to ensure that all volatile compounds evaporate. A pre-heating step serves the purpose.

The vapors from the preheating step would contain a significant quantity of hydrocarbons often mixed with the products of combustion from the furnace. In Canada, most provinces require the off stream gas stream to be processed via some type of thermal destructor and collection of the particulate solid. An after burner has been used in Ontario province to operate at approximately 1000° C, which gives off gas a residence time of at least 1 hour measured from the tip of the flame. Air flow through the total system thus becomes of vital importance to the overall efficiency of the process as air mass can represent a significant heat load.

In a medium to large scale installation a batch furnace or load preheater is fitted with fume extraction, which vents into the chamber of an after burner. The off gas then discharges into some kind of dilution or cooling section prior to the waste gas being treated in a bag house.

Entry of air into the system should be minimized as extra air requires extra heat to raise it to the required incineration temperature. Poorly fitted seals, defective pressure control systems, leaking auxiliary vents, broken sight holes can all be uncontrolled sources of air entry. The furnace seals have to be well designed and maintained .

Gas volumes from the burner system can be reduced by improving the efficiency of the furnace, either by recuperation or regeneration of the waste heat. Some of the waste heat from the furnace off gas can be extracted and applied to the combustion air. Heat can also be reclaimed by pumping some of the waste gas into the solid prior to it being placed inside the melting chamber. The very lowest gas flows from the furnace can be achieved by making the process continuous, by heating indirectly and using small amounts of nitrogen to wash the volatile gas from the system. This method achieves the lowest flow rates from the furnace and therefore requires the smallest after burner.

The advantage of continuous processing is that the after burner required is quite small. It does not have to be designed to cope with the surges in the flow of hydrocarbons that occur when furnaces are charged. Hydrocarbons volatilize usually over a very narrow temperature range. The indirect fired furnace must be purged with nitrogen as a dangerous condition may arise if the system is purged with air. The addition of nitrogen has the added benefit of keeping the level of oxygen down, which may help to decrease the overall metal loss.

In normal practice the after burner is sized to cope with the absolute maximum off gas flow rate and maximum hydrocarbon load; consequently, it has a very poor thermal tumdown. In order to obtain acceptable efficiencies the heat from the after burner is returned back to the process. This is usually achieved by using a preheater. Unless the atmosphere inside the preheater is controlled, there is usually more heat available from the after burner than that which can be usefully imparted to the incoming load and therefore the control of the after burner has an important role in the operational processing costs.

In batch processes, the after burner is only operated during preheating cycle when the volatile material is evaporating. At certain predetermined temperatures the after burner is shut down and some method can usually be contrived to make the heat from the after burner useful for either part of the process or for some other process in the facility.

6.2. Burner Selection

The choice of burners for gas fired melting and holding furnaces depend greatly on the application and the duty cycle. High velocity burners emit gas streams at speeds of up to 300 fps. The high speed flow inside the furnace is advantageous for the convective component of total heat exchange inside the furnace to be maximized, Figure 6.1. High velocity burners may be a little aggressive for small chambers especially when they are at an angle. The constant movement of hot gas at the surface of the melt can cause excessive oxidation loss by ensuring that clean metal is continually exposed to the furnace atmosphere.

Flared tile burners may not take full advantage of gas firing. There is the possibility that the oxide may thicken and insulate the surface of the metal. This would cause a gradual deterioration in the amount of heat that is being exchanged to the melt.

Large melting furnaces require a much greater mass flow inside the furnace, which may be accomplished by using the so-called high momentum burners. They operate at slightly lower velocities than the high velocity burners and are characterized by much longer and wider flames. They generate a less localized flow pattern inside the furnace than small high velocity burners. Such burners are able to alter the radiosity of the flame by changing the way gas and air are mixed at the burner. This property can be used to mitigate the radiation trap that can prevent the roof of the furnace from transmitting all of its radiation to the melt. As a side benefit, the high momentum burner operating with a more luminous flame will be quieter than equivalent high velocity or high velocity burner. Burner placement is very important and can dramatically affect the operational efficiency.

6.2.1. Regenerative Burners

The main advantages of regenerative burners are, very low specific energy consumption and a very high flame temperature. This is desired benefit in areas where fuel is considered a precious commodity. They have been extensively used in Europe and to a lesser extent in North America.

The high flame temperature results in higher nitrogen oxide content in the off gas, which could be a drawback. However, the burners produce less mass of polluting gas for a given process. As an interesting side benefit, the characteristic cycling from the cold regenerator to the hot regenerator causes the waste gas stream from the furnace to undergo extremely rapid cooling. Most systems can subject the waste gas stream to a temperature drop of over 800 °C/s at full fire. This would have the benefit of preventing recombination of halogen hydrocarbons and therefore would be an acceptable way of cooling off gas from an incinerator.

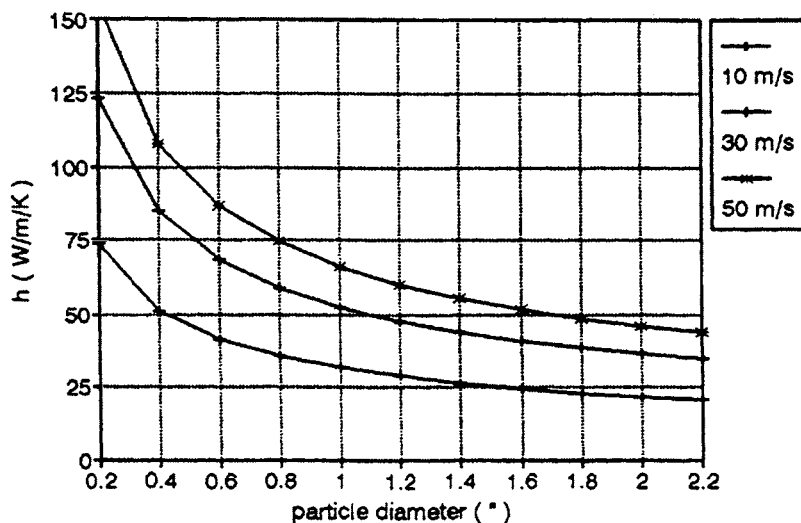


Figure 6.1. Graph showing heat transfer changes with particle size. (Burns, 1995)

6.2.2. Flat Flame Burners

Flat flame burners can be used in holding furnace applications. They spin the flame from a curved tile. The flame hugs the wall of the furnace and has very little forward velocity. These burners can be used to produce an even roof temperature over the melt and are common in most holding furnace applications. The radiant heat from the roof often causes stratification of the temperature in the melt. It is necessary to engineer the furnace such that the flow rate of metal through the furnace exceeds a minimum value. Failure to observe this ratio can result in composition problems.

6.2.3. Immersion Burners

In immersion burners a ceramic tube is inserted vertically into liquid metal bath. The tube is closed at one end and is capped by a burner at the other. Inside the tube an intense gas flow is promoted by the burner. The flow field generates very high internal heat fluxes. All the heat that can be transferred to the wall of the ceramic tube is adsorbed by the melt. The surface of the ceramic stays very close to the operating temperature of the furnace. The use of the ceramic sheath enables all combustion products to be vented from the furnace without the need to come into contact with the melt. The immersion burner is a closed system. It helps to minimize hydrogen pickup and prolong the time between melt treatments, particularly for grain refining operations. Because of the low thermal mass of the silicon carbide tube, when the control system begins to respond to temperature changes, heat is almost instantly available.

Conventional reverberatory furnaces require a significant temperature lead in the roof before the heat flux begins to make an impact on the bath temperature. Conversely, once the melt is up to temperature the roof can still radiate heat to the metal surface and continues to raise the temperature of the melt pool. Immersion burner systems are capable of controlling melt temperature within 2-3 °C in aluminum and a little better in zinc. Melt temperature uniformity from top to bottom is often better than 15 °C depending on the volume of the bath and the number of burners fitted.

Relatively high capital cost of the equipment has been a drawback in the application of immersion burners. They do, however, work very well in the right applications and could have a positive impact on the non-ferrous recycling industry.

6.2.4. Oxy-Fuel Burners

In every burner, combustion occurs by chemical reaction between fuel and oxygen leading to the generation of heat. Air contains 20.9 %oxygen, the rest being mostly nitrogen, which is inert in the combustion process. The oxygen concentration can be raised to produce oxygen-enriched air. Doing so increases the thermal efficiency as the amount of inert nitrogen gas flowing through the combustion process is greatly reduced. The flame temperature is estimated to increase from 1760 °C with air-fuel to 2300-2500 °C with oxygen-fuel (Hewerston, 2000). Oxygen may be mixed with the combustion air stream, injected through a lance on the underside of the flame, or be used in burners designed especially for high oxygen concentrations. The choice generally depends upon the type and the size of the furnace, the operating benefits desired, and capital cost considerations.

Oxy-fuel combustion technology has been applied in melting aluminum. This has resulted in operation improvements, including production increase of over 30 %, fuel savings of 20-30 %, reduced smoke emissions, lower baghouse temperatures (10-65 °C)

and reduced dust carryover (50 %). Newer innovations have been developed for the processing of electric arc furnace dust and sludges. Its applications will be described in Chapter 8.

6.2.5. Waterless, Non-Consumable Oxygen Lance

This is a new innovation developed at McGill University (Montreal, Canada) and is designed to increase the efficiency of the process (Yuan *et al.*, 2004). It is a new heat transfer device called thermopump. It is based on heat pipe technology, heat pump technology, and basic heat transfer principles.

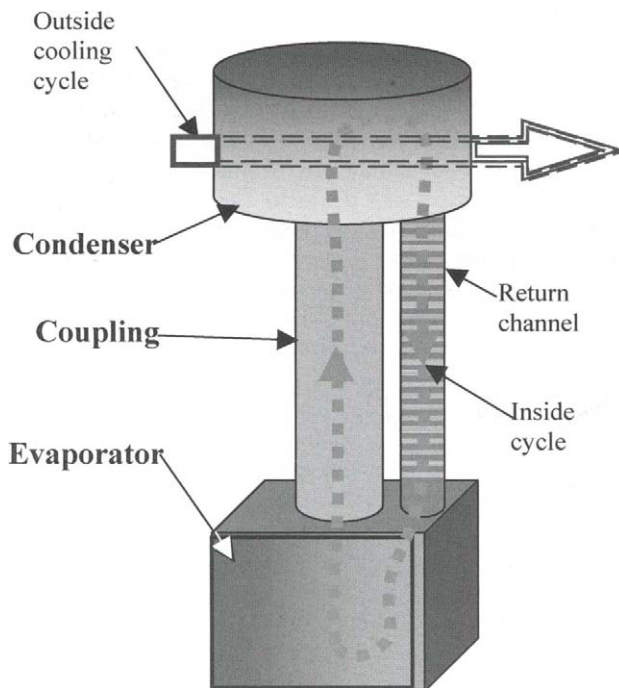


Figure 6.2. Concept of thermopump; Yuan *et al.* 2004

A Thermopump (I), like a loop Thermosyphon, is a heat transfer device which can transfer heat at high heat fluxes efficiently and with extremely small temperature drops. Figure 6.2 shows the concept of a Thermopump. It has an evaporator, a coupling section, a condenser and a working substance sealed inside its chamber. There are at least four differences between a Thermopump and a conventional heat pipe. Firstly, a Thermopump replaces the wick in a heat pipe with a return channel to overcome the countercurrent flow of vapor and the return liquid in a conventional heat pipe. This countercurrent flow is the cause of the entrainment limitation in a conventional heat pipe. Secondly, it incorporates flow modifiers in its evaporator section to improve the film-boiling limitation of a heat pipe. Thirdly, the area of the condenser section of a Thermopump is larger than that of its evaporator' section. By changing condensing mechanism and

packaging a heat exchanger, if needed, in the condenser, a Thermopump can overcome the condensing limitation existed in a conventional heat pipe when it works in a high heat flux environments. Fourthly, the Thermopump has a liquid reservoir which is integrated together with its condenser and becomes part of the condenser. By this design a Thermopump could operate at its optimal amount of working substance.

The flow mechanism between a heat pipe and a Thermopump is also different. In a Thermopump, the working substance in the evaporator section absorbs heat from the heat source through the wall of the evaporator. The working substance thus cools the wall, and becomes a two-phase (vapor and liquid) fluid and flows from the evaporator to the condenser. The working substance dissipates the heat in the condenser, flows back through the return channel to the bottom of the evaporator. The circulation in a Thermopump makes it possible to use the most efficient heat transfer mechanism: flow boiling mechanism to transfer heat. In a heat pipe, only vapor (one phase) goes to condenser and the condensate (another phase) flows back along wick. Thus, the vapor and liquid flow in a countercurrent manner in one channel. A thermopump lance can be made by packing a pipe inside a thermopump.

A schematic diagram of the oxygen lance is shown in Figure 6.3.

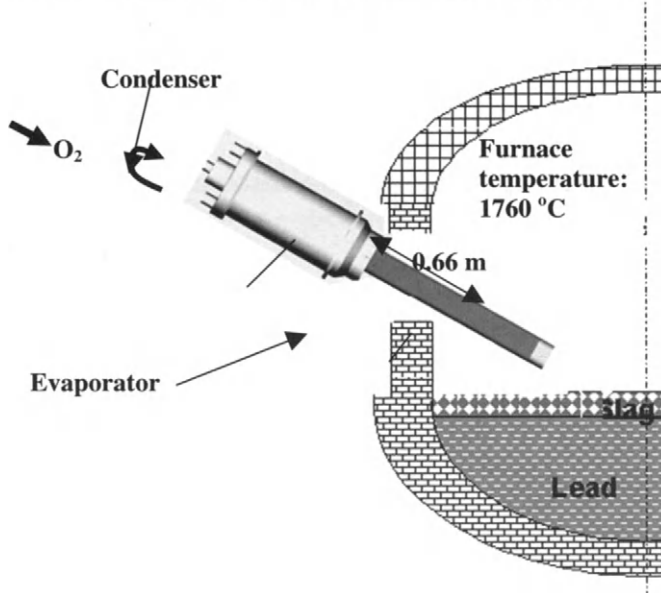


Figure 6.3. Thermopump oxygen lance, schematic (Yuan *et al.*, 2004)

The plant trials have shown many valuable results pointing to potential benefits from their application. Some of them are described in the following:

Potential of increasing productivity and saving energy: The plant tests show the potential of increasing productivity and saving energy by injecting oxygen to the surface so that the oxygen stirs the melt, burns 'fuels' in the melt or in the freeboard, and heats the melt directly. Figure 6.4 shows how oxygen lancing by the first TP lance influenced battery charge rate and the burner's gas and oxygen consumption before, during and after oxygen lancing. The curves in the figure, from top to bottom, are burner's oxygen flow

rate, burner's natural gas flow rate, battery charge rate (being shown on right axis) and lance oxygen flow rate respectively. The figure shows that by blowing about 65 m³/hr of oxygen on the melt surface, the burner's gas and oxygen could be reduced 10%, and the overall productivity could be increased by about 18%. This is done without increasing the total oxygen blown into the furnace.

Blowing pre-heated oxygen: In another application, the lance is operated at around 700 °C. The lance absorbs heat from furnace freeboard, transfers the heat to the oxygen it is blowing, and blows the hot oxygen onto the melt surface. The estimated exit temperature of the oxygen is as high as 350 °C, from a starting point of about 20 °C. The lance does not use any extra cooling (water or air). After the test, an examination of the lance tip shows it to be in good shape with no visible sign showing that the hot oxygen had consumed the lance. This shows that the lance can preheat oxygen and not be consumed by the hot oxygen. These lance characteristics, specifically no extra cooling and preheating of the oxygen, can benefit users if they replace their water-cooled oxygen lances with the Thermopump lances.

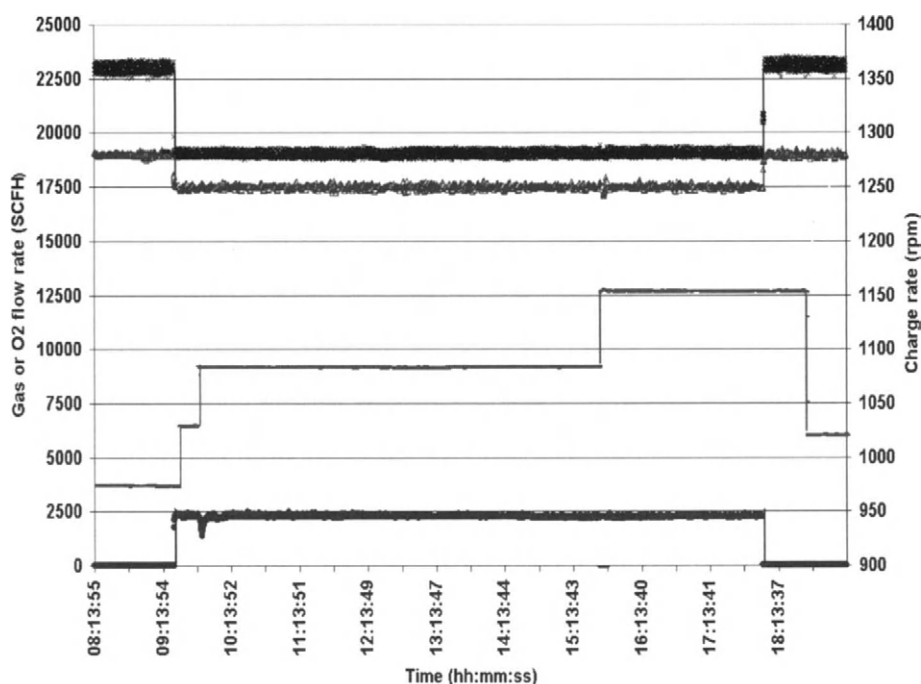


Figure 6.4. Battery charge rate and gas flow rate during oxygen lancing (Yuan *et al.*, 2004)

Several advantages of the heat pipe lance over a conventional water-cooled lances are: first, the Thermopump oxygen lance has limited safety concerns while the water-cooled oxygen lance has; second, Thermopump oxygen lance needs no water, so it can

save the cost for infrastructure and maintenance of the cooling water circulating system; third, by preheating and blowing hot oxygen, the flame temperature will be proportionally increased, and this also means a higher efficiency for energy utilization.

Easier furnace operations: With oxygen lancing, the slag fluidity is improved and this decreases the operator's labor work. So oxygen lancing is very welcome by the personnel of the furnace.

No safety problem or other negative effects: Although the two lances eventually failed and some sodium leaked out, they did not cause any safety problems during the failures or afterwards. This means the sodium-based Thermopump lance is safe in application. During the tests no any other negative effect, such as higher NO_x emission or higher temperature off gas, was detected. This means that the Thermopump oxygen lance gives users a number of gains with limited loss.

6.2.6. Refractories

Refractory materials are used to line smelting furnaces. The most usual lining configuration in North America is one that consists of a thin layer of insulation castable protected from the liquid metal by a monolithic material with nonwetting additives. European practice is to use fired bricks and bricks. These materials are often easier to bring into service and form a more durable lining. They can be manufactured within very tight dimensional tolerances giving 1-2 mm average joint thickness.

Installation of excessive insulation at the back of the dense refractory materials should be avoided as penetration of metal through the joints can push the bricks out of position. That can cause heat loss at a higher rate than occurring in a furnace lined with monolithic material. The advantage is a longer campaign life and less lining damage when the furnace is cleaned.

The type of fluxes used in the process has an effect on the life of the furnace refractories. For example, a flux developed to dissolve corundum will probably dissolve other materials and could severely damage the furnace lining.

6.3. Smelting Furnaces

Several processes require melting of the feed material. This is done in smelting furnaces.

Note. The term 'smelting' is used for a variety of processes to mean melting of an ore or a concentrate (See Habashi, 1985, p. ix). In the present context, and in the following chapters, it is used for processes where the charge consisting of the secondary material to be processed is melted for metal recovery by reduction.)

6.3.1. Brief History of Primary Smelting Processes

Smelting processes were developed initially for fusing high grade lump ore either as produced by the mine or obtained by hand, or in the case of nickel pyrrhotite ores by magnetic cobbing. Such lump ores were suited to smelting in a low shaft blast furnace with coke. The shaft furnace was simple and low cost to construct and could be readily expanded to accommodate higher tonnages. It comprised a hearth, water-cooled boiler plate jackets with entry ports for low-pressure air injection and a spout for discharge of combined matte and slag to a settle chamber. Off gas was released through to permit settling of coarse dust before exhausting to atmosphere through a brick lined stack that provided the draft to pull the furnace exhaust gas through the flow system. Such shaft

furnaces were widely used in copper, nickel and lead smelters and some are in full operation.

The trend to lower grade ores and increasing use of flotation to concentrate metal-bearing sulfides prior to smelting necessitated development of agglomeration processes (to be described in Section 6.6) to maintain the gas permeability of the charge column in the furnace. This led to introduction of sintering lump charge from fine flotation concentrate. The charge was also often delivered hot to the furnace increasing thermal efficiency and smelting rates. Concentrate pelletizing and briquetting techniques were also investigated as an alternative or supplement to sintering. Industrial use was limited.

A limitation of blast furnace capacity was the need for the low-pressure blast air to reach the centre of the column. This limited the width of the column to about 1.5 m. There was no absolute limit to the length of the furnace. Multiple units were normally operated to permit production to be maintained when one unit was taken off line usually to replace a leaking jacket. Blast furnace had high smelting capacity per unit cross-sectional area, were thermally efficient due to heat exchange between combustion gases and the charge column, were low in capital cost, accommodated in a small building and were relatively simple to operate. The blast could accommodate limited oxygen enrichment increasing smelting capacity and reducing coke consumption. ,

The increasing use of flotation, eliminated lump ore production, and processes were developed to avoid the need for agglomeration of the charge by sintering and to permit higher production with fewer smelting units. The mostly widely adopted of these alternative processes was the reverberatory furnace usually fed with fine partially roasted concentrate produced in multi-hearth roasters. Reverberatory furnaces had high throughput capacities. Off gas temperatures were much higher than for blast furnaces. And this heat was usually extracted in an off gas boiler whenever a steam supply could be beneficially used.

The sinter blast furnace and multi-hearth roaster reverberatory furnace combinations were labor intensive, dusty operations that were dependent on the abundant supplies of low cost fossil fuels. Competitive forces led to development of alternative smelting approaches to increase productivity, improve working conditions and reduce dependence on fossil fuels

In recent years there has been a proliferation of oxygen smelting devices developed in an attempt to improve the flash furnaces and electric furnace operations. Among the more successful have been the Kivcet furnace for producing a clean slag in lead operations and the Noranda reactor for digesting high-grade copper concentrate and copper bearing electronic scrap.

Primary smelting operations have a high capacity and a tolerance for the fine powdered materials containing minor impurities and for mixed metallic scrap unsuitable for direct recycling to the foundry industry. This makes them competitive for a range of recycle products that are available in limited tonnage or are available in too limited quantities or variable composition to merit development, construction and operation of separate independent recycling facilities.

The principal furnace types will be described in the following sections.

A **film smelting furnace** is schematically shown in Figure 6.5. It has two combustion rooms called main combustion room and second combustion room. The feed is melted from the surface of it in the main combustion room by burner heating. The molten material drops through second combustion room onto water and quenched. The second

combustion room controls the compositions of the gas phase decomposition. This type of smelting furnace has been used for recovering zinc and lead from fly ash; see Chapter 8.

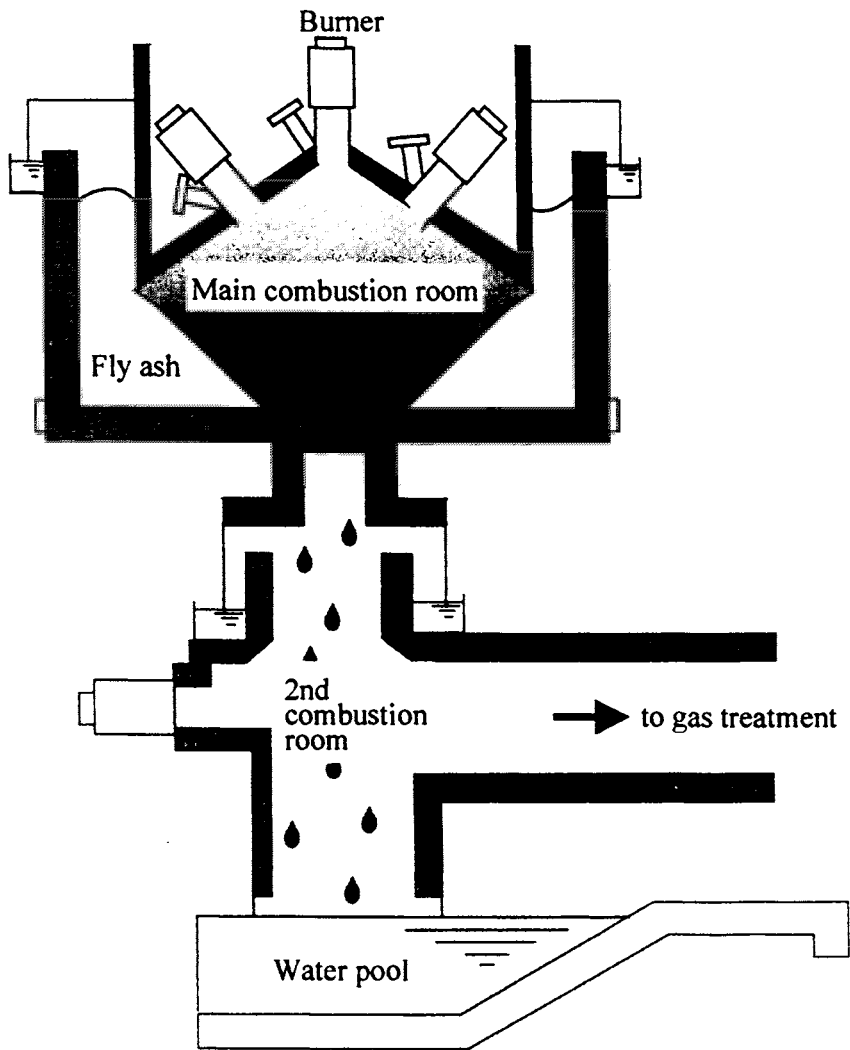


Figure 6.5. Schematic representation of a film smelting furnace for fly ash (Takasu *et al.*, 1998)

6.3.2. Rotary Kilns

These are cylindrical shells slightly inclined to the horizontal and rotating around their longitudinal axis; Figure 6.6. The usual dimensions are 6-160 m length and 1-10 m diameter.

The rotary kilns are heated by burning carbonaceous fuel (coal or charcoal) at the lower end, while the charge is fed from the upper end and moves downward on the slope. Baffles running lengthwise enable mores surface of the charge to be exposed through the stream, which improves both heat and mass transfer.

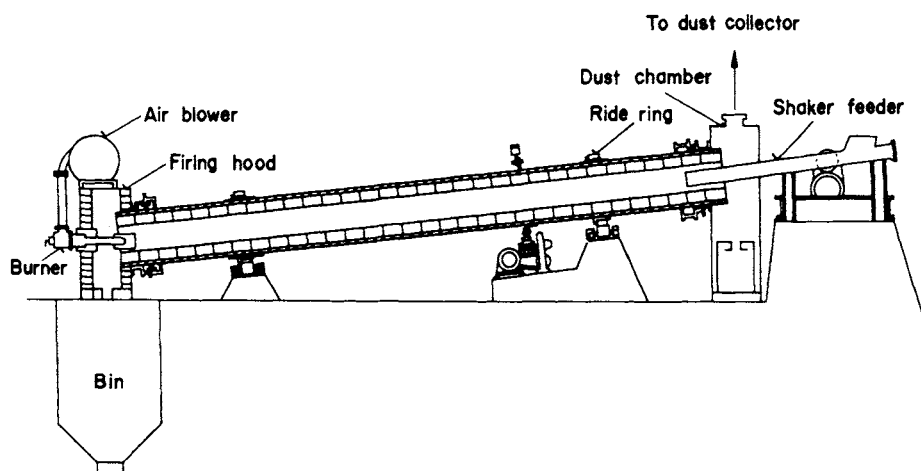


Figure 6.6. A rotary kiln (Habashi, 1969)

Many base metal oxides are reduced by carbon. The more common ones occurring in metallurgical residues are oxides of copper, zinc and lead. Various modifications have been made to suit to specific material. Some of the applications will be described in Chapters 7 and 8.

6.3.3. Waelz Kiln

Waelz kilns are specially used in the processing of metallurgical dusts for the recovery of metals, especially zinc as will be described in Chapter 8. The name 'waelz', derived from the German verb "Waelzen", describes the trundling motion of the kiln charge. A Waelz kiln is typically 50 m long with a diameter of 3.6 m. It is slightly inclined and has a rotary speed of 1.2 rpm. Figure 6.7 shows a simplified diagram of a Waelz plant.

The moist material, compact and pelletized, moves through the rotary kiln, and is dried and preheated by the concurrently flowing kiln gas. In the reaction zone, reduction of the metal oxides begins at about 1200 °C and the metals (e.g., zinc and lead) are vaporized into the freeboard. The process air is injected from the kiln end. In the kiln atmosphere, which is operated with excess air, the metals are reoxidized. Chlorine and alkalis volatilize jointly with the metals. The dust-laden off gas is treated in a down's off gas stream. In the first stage, mechanically entrained coarse particles are separated in a dust chamber and returned to the kiln. The hot, dust-laden off gas is cooled and the Waelz oxide separated in a precipitator.

The dust-free off gas is cleaned (to remove volatile hazardous components (dioxins, mercury, cadmium) and discharged to atmosphere through a fan. The retention time of the feed material in the waelz kiln is between 4 and 6 hours depending on the brick lining, length of the kiln and rotary speed. The slag is discharged through a wet deslagging system. Unreacted coke is separated from the slag by magnetic separation.

Two different reaction zones in a Waelz kiln, strongly reducing conditions in the charge and the oxidizing atmosphere in the gas space, are shown in Figure 6.8. It shows the cross-section of a rotary kiln in the reduction zone and the reactions taking place in the charge and in the freeboard. The added atmospheric oxygen reacts in the charge,

converting the carbon available there to carbon dioxide, which reacts with solid carbon to form carbon monoxide. This reduces the metal oxides.

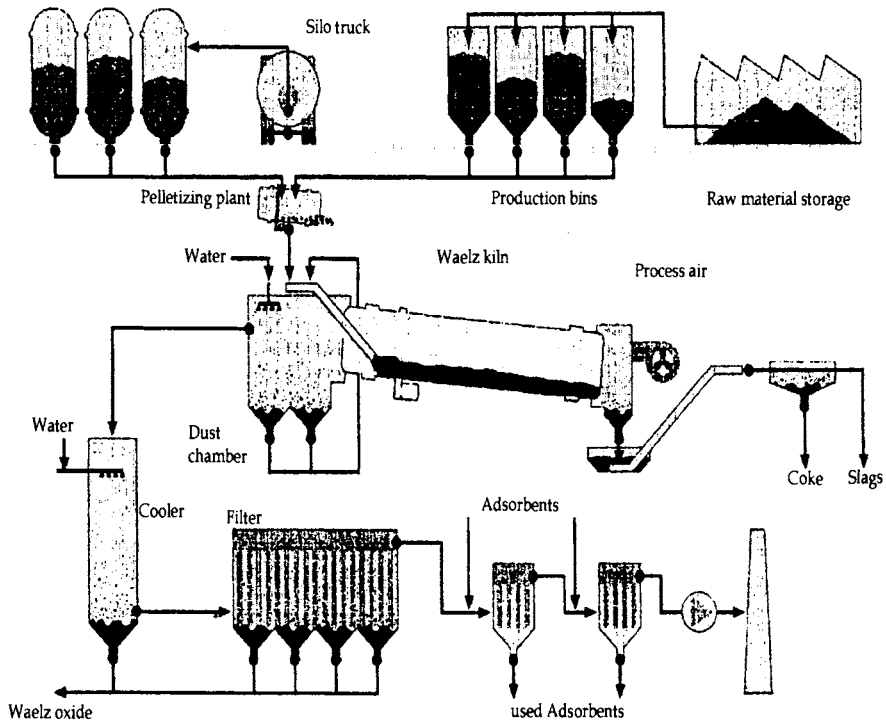


Figure 6.7. Simplified flow diagram of a Waelz plant (Mager *et al.*, 2000)

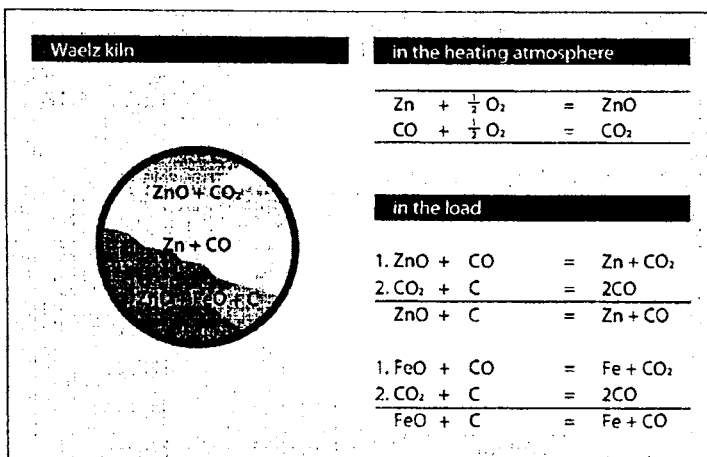


Figure 6.8. Main reactions in the reduction stage within the Waelz kiln (Mager *et al.*, 2000)

6.3.4. Reverberatory Furnace

Reverberatory furnaces are constructed with dimensions of up to six by thirty meters. They are fired by pulverized coal with multiple end-wall burners. They can also be heated by burning gaseous or liquid fuel, or by electrodes suspended from the roof; see Figure 6.9. In fuel-fired furnaces, the flame extends over the charge on the hearth, part of the heat reflected by radiation from the roof, which gives the name “reverberatory furnace”. In metal recovery from secondary sources such as electric arc furnace (EAF) dust the furnace is charged with powdered material by means of hoppers set in the roof either at middle or near the walls. Solid feed in the form of scrap metal or lumps of lime stone (as flux) is charged through the side doors by leading in boxes and carried by machines, which introduce them in the furnace. The molten bath produced is usually 1 m in depth. The resulting slag and molten material move toward the tapping end of the furnace and separate. The hearth slopes towards the pouring side to a tap hole of about 15 cm diameter.

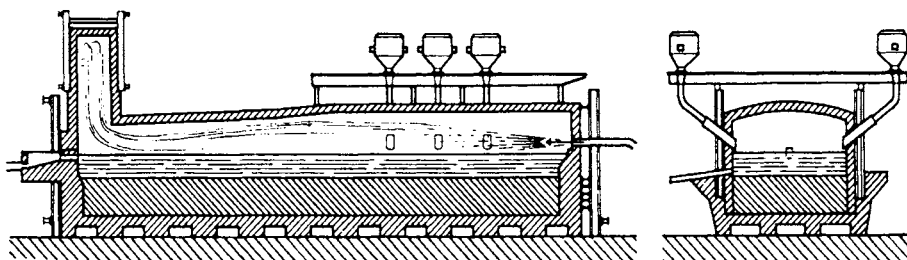


Figure 6.9. Reverberatory furnace fired by carbonaceous fuel (Habashi, 1969)

6.3.5. Fluidized Bed Furnace

This type of furnace consists of a large vertical brick-lined steel cylindrical vessel into which a gaseous reactant (usually air or oxygen) is blown under a perforated steel grate at the base. The powdered solids enter at one side by a screw conveyor, and the reaction product continuously overflows from another opening; see Figure 6.10. It is called fluidized bed as it behaves in a manner similar to a boiling liquid. Such furnaces are used for treating metallurgical wastes, which involves oxidation, reduction, chlorination, etc. The gas should have a minimum velocity to effect fluidization. As the gas velocity increases the pressure drop increases gradually until a constant value is reached when fluidization starts. This is the minimum velocity to achieve fluidization. Increasing the gas velocity would cause the solids to be blown out of the furnace. Because of the intense gas-solid contact, chemical reaction and heat transfer are extremely rapid. Reaction temperature is thus closely controlled, which prevents any local overheating or fusion of solids. An exothermic reaction has to be initiated by an auxiliary flame, which is then extinguished with progress of the reaction. For endothermic reactions, the gas is preheated to a temperature slightly above the reaction temperature by, for example, by electrical resistive heating using graphite electrodes. Temperature rise by exothermic reaction has to be controlled by, for example, inserting a cooling coil in the furnace, injecting water directly, or recycling a part of the cooled product. Details of construction and working are described text books of pyrometallurgy (Habashi, 1985). Specific areas of application will be described in Chapter 5-8.

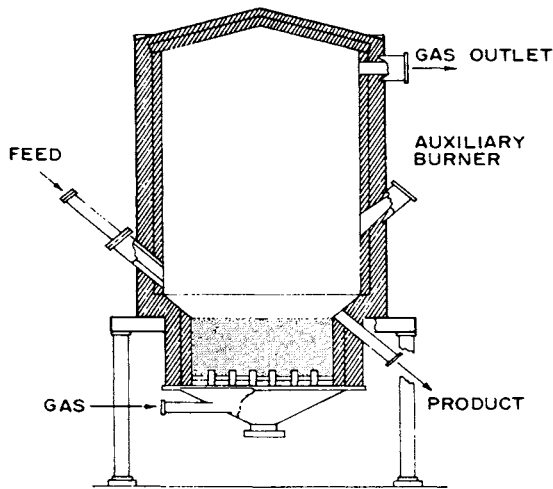


Figure 6.10. Fluidized bed furnace (Habashi, 1969)

6.3.6. Top-blown Converter

This design is made specially for oxidation processes. Oxygen at high speed is introduced into the molten bath by a water-cooled lance situated at some distance from the surface of the metal. The oxidizing action takes place in the bath in the immediate vicinity of the lance, but, due to convection currents, it spreads rapidly through the whole batch. The reaction is usually complete in about 15 minutes. The oxygen flow is then stopped, the lance is raised, and the converter tilted to empty its contents.

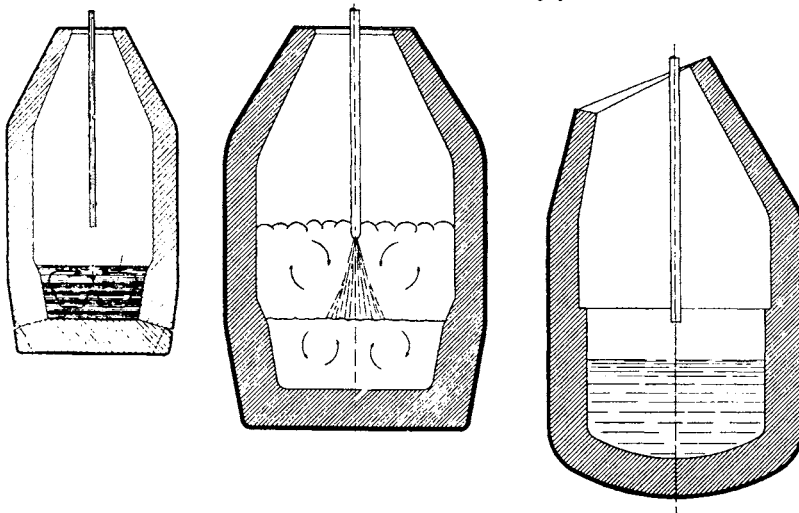


Figure 6.11. Top-blown converters of different designs (Habashi, 1969)

6.3.7. Shaft Furnace

This furnace, also known as vertical furnace, consists of a hearth and a stack on the top. It is also called blast furnace as air is blown or “blasted” through the charge. It is

heated by a carbonaceous fuel or by electric methods. Coke is often used as carbon fuel and mixed with the charge entering at the top of the stack and the products exit at the bottom. In electrically heated furnaces, the charge itself serves as the resistance developing heat. One design is shown in Figure 6.12.

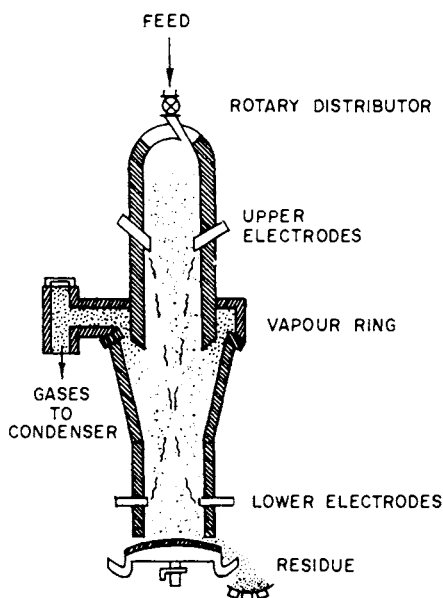


Figure 6.12. Electrically heated shaft furnace for reduction of oxides (Habashi, 1969)

6.3.8. Noranda Furnace (Themelis *et al.*, 1972)

Designed by Noranda Company in Quebec, Canada, this furnace consists of a raised hearth and settling zone. The vessel can be tilted to expose the nozzles in case the air flow is interrupted. Feed is introduced continuously while the metal and slag tapped continuously or intermittently.

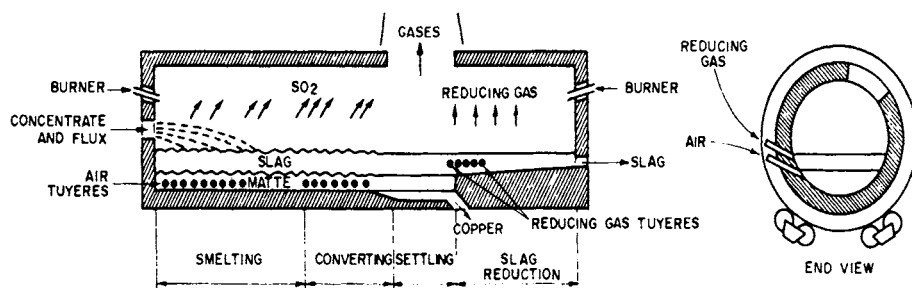


Figure 6.13. Noranda furnace used in copper recycling (Habashi, 1969)

6.3.9. Muffle Furnace.

This type of furnace, used specifically for smelting operation in the recovery of zinc, will be described in Chapter 7.

6.3.10. Sweat Furnace

The word 'sweating' is used to describe partial melting of the metal as the temperature is raised. Sweating furnace is any furnace operated at a temperature where a portion of the charge liquefies and can be drained off. Sweating most commonly applies in aluminum recycling where it is desired to separate aluminum from iron or brass. The term is also used in connection with a similar operation in the zinc and lead industries. The common design for aluminum is a vertical rectangular chamber with a sloping hearth at the bottom leading to a tap hole. The column is charged and discharged on a batch basis. The heat is supplied through burners in side ports on the walls. The aluminum is cast into ingots for refining. Sweating furnace can be of rotary or reverberatory design. Further description and applications will be in Chapter 7.

6.3.11 Flash Smelting. (Victorovich *et al.*, 1987; Kojo *et al.*, 2000)

Flash furnace (schematically shown in Figure 6.14) was first developed at INCO (International Nickel Company) for direct production of copper from sulfide concentrates.

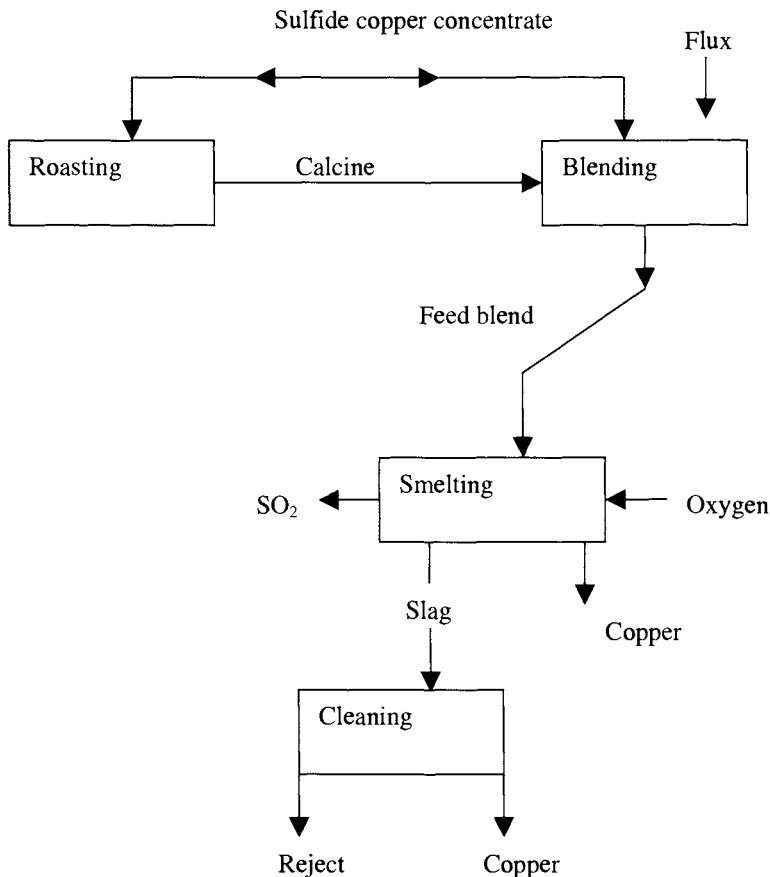


Figure 6.14. Schematic diagram of flash smelting process (Victorovich *et al.*, 1987)

The roasting is conducted in a fluid bed reactor, which leads to the release of about 1/3rd of the sulfide sulfur as a continuous stream of sulfur dioxide gas (~10% SO₂), which is suitable for fixation of sulfur for the production of sulfuric acid. The remaining 2/3rd sulfur is released from the oxygen smelting operation as a strong sulfur dioxide gas (~70% SO₂), which can be directly used for producing liquid sulfur dioxide, or in any other way designed.

The calcine produced by roasting is uniformly blended with unroasted sulfide and flux. The blend is then autogenously smelted with oxygen. This solves the problem of excess heat generated during the oxygen combustion of sulfides containing base metals. The process requires substantially less oxygen per unit weight of copper than would be required to produce the same quantity of copper from unroasted sulfide only.

The most important benefit of flash smelting is the effective containment of sulfur dioxide produced in sulfide roasting. This has resulted in waste minimization by marked reduction in sulfur dioxide emission and consequent environmental benefit. In addition, as it utilizes the exothermic properties of sulfide minerals, the process requires very little additional fuel (Warhurst and Bridge, 1996).

6.3.12. New Innovations:

The recycling operations in metallurgical industry have led to the development of several new innovations aimed at enhancing the process efficiency and to mitigate reactions leading to environmentally hazardous products and to safely contain them where such products are formed. Increasingly they are being used in recycling operations involving metal scrap, metallurgical slag and dust. Some of these new innovations will be described in this Section.

6.3.12.1. Mitsui Furnace

A new furnace design developed in Japan, called Mitsui Furnace has been successfully employed for treatment processes involving reduction of oxides by carbon or coke. It is schematically illustrated in Figure 6.15. The process flowsheet is shown in Figure 6.16.

The furnace was first used for the treatment of electric arc furnace dust to recover zinc. The raw material (e.g., EAF dust or metallurgical residues where metal occurs as metal ferrites) is dried with coal and silica. The material is ground in a rod mill and mixed with a sulfide solution as binding agent to agglomerate and the raw material in briquettes. The charge consists of the briquettes mixed with coal and flux, which are then charged to the furnace. The metal (Zn) present as ferrite (ZnFe₂O₄) is reduced and then oxidized to metal oxide by excess oxygen. The metal oxide is collected in the gas cooler and bag filter. The slag is drawn out of the tapping hole at the bottom of the furnace. It is used in cement industry. The furnace is extensively used in Japanese steel industry (Yoshida and Nagasaki, 2001).

6.3.12.2. Mitsubishi Process.

This process employed for the recovery of copper from sulfides combines three furnaces. In the first unit, the feed (metal sulfide) is smelted with oxygen-enriched air through vertical burners whose products impact on the molten bath below. Mixed matte and slag flow continuously to the second unit, which is an electrically heated slag cleaning furnace. Slag from this is granulated (by cooling in a jet of water) and discarded.

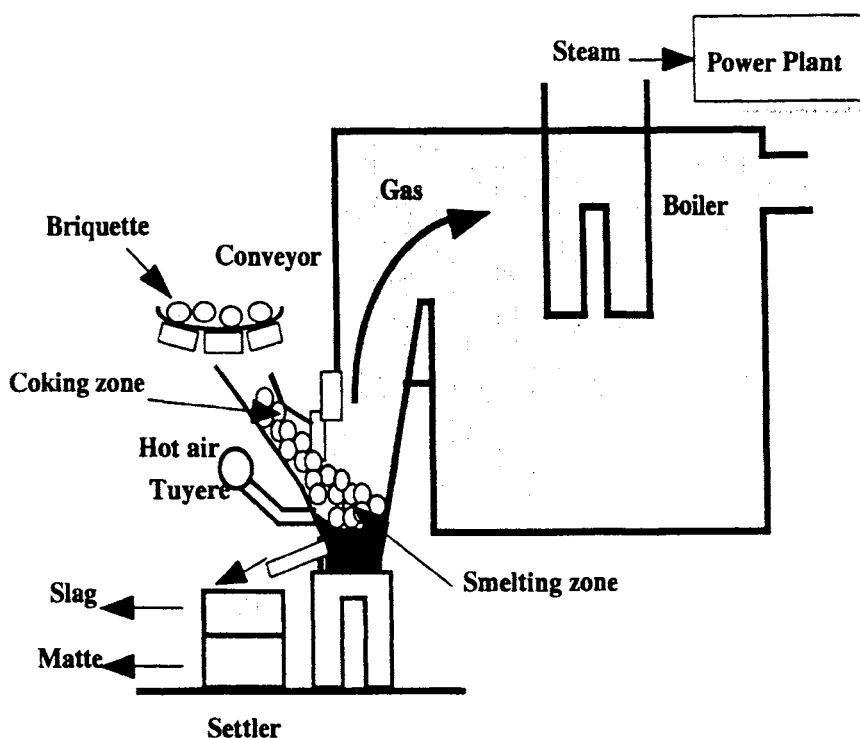


Figure 6.15. Schematic illustration of Mitsui Furnace system (Yoshida and Nagasaki, 2001)

Matte continuously flows to the converting furnace where top blowing with oxygen-enriched air produces blister copper. The slag from the converter, carrying a high level of copper, is recycled to the smelting furnace.

6.3.12.3. Imperial Smelting Furnace (Lee, 1995)

The Imperial Smelting Process (ISP) was developed for producing zinc and lead in a blast furnace. A typical layout is shown in Figure 6.17.

The furnace is charged with sinter, briquettes of secondary zinc materials or plant recycles and coke preheated to 700-800 °C. Inside the furnace coke burns with air preheated to 950-1150 °C forming carbon monoxide which reduces zinc and lead oxides in the charge to metals. Zinc is produced as vapor and travels with the furnace gas at over 1000 °C into a condenser where it is absorbed in a spray of molten lead generated by rotors. Liquid zinc is separated from the lead in an external cooling circuit and is sent to a thermal refinery.

The overall smelter process is illustrated in Figure 6.18. The first step in the process is desulfurization and agglomeration of the feed material. The gas from the machine is screened and converted to sulfuric acid. The sinter output from the machine is screened and the lump sized at 25-100 mm is sent to the storage bins while the fines are crushed to about 6 mm size and returned to the sinter plant feed section. Slag from the process is granulated with water and used for road construction (Schwab and Schneider, 2002).

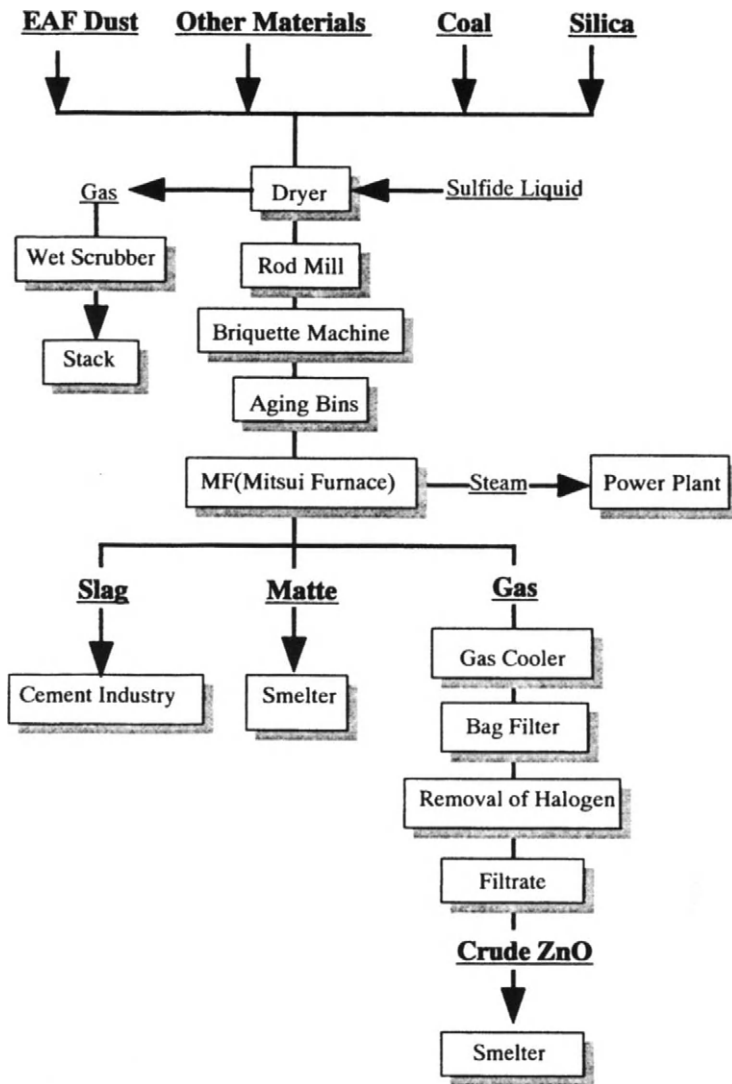


Figure 6.16. Process flow of Mitsui furnace system (Yoshida and Nagasaki, 2001)

The IS process is currently used to process electric arc furnace (EAF) dust (see Chapter 8) and to recover metal resources from spent batteries (Chapter 10) (Schwab and dioxins in EAF dust are destroyed in the IS furnace. The temperature > 2000 °C and Schneider, 2002). Organic materials like plastics from batteries or organic impurities like dioxins in EAF dust are destroyed in the IS furnace. The temperature > 2000 °C and reducing atmosphere ensure the complete destruction of toxic substances. Some other advantages are claimed for this technology are the following:

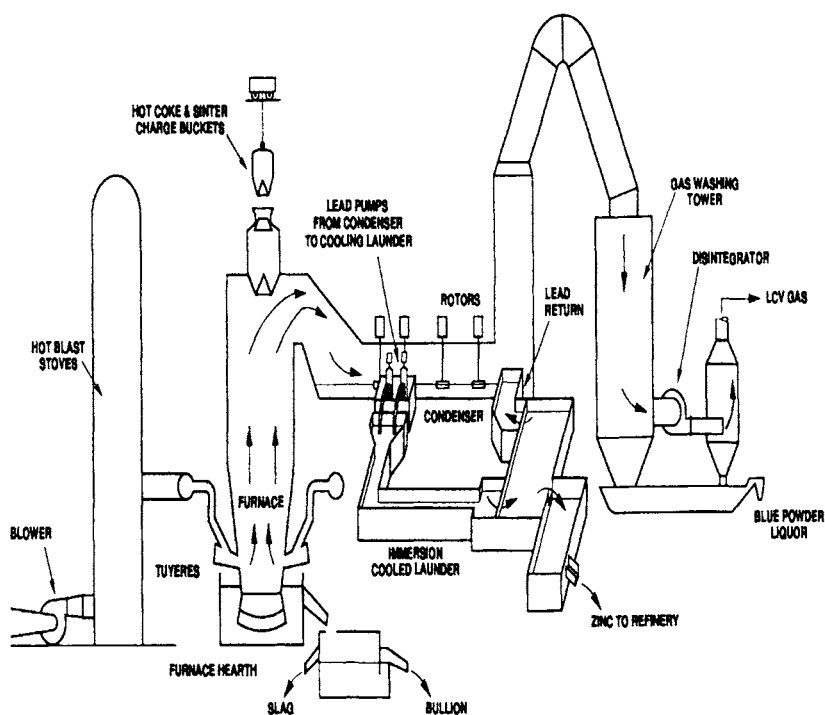


Figure 6.17. General layout of zinc/lead blast furnace (ISP system) (Lee, 1995)

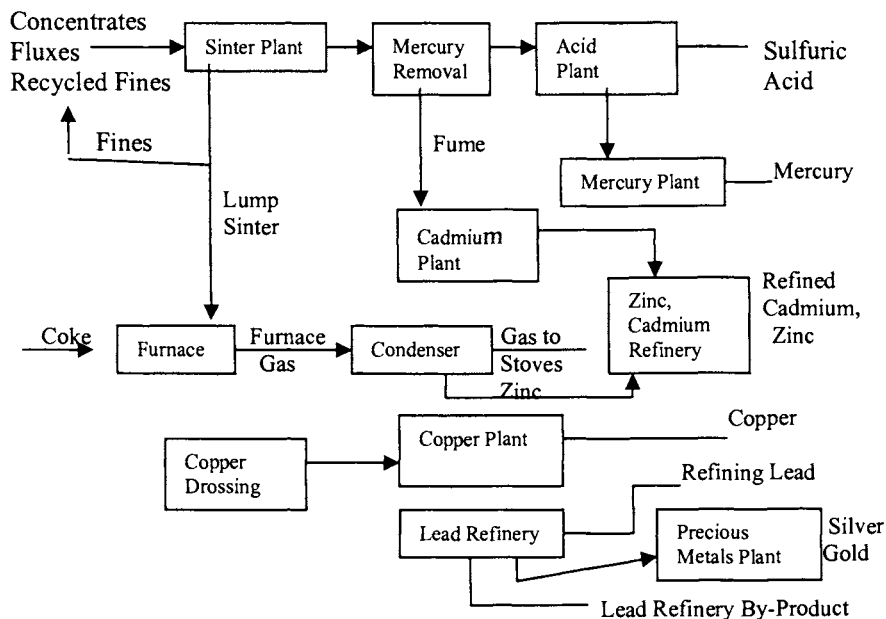


Figure 6.18. Block diagram of an ISP smelter (Lee, 1995)

- Zinc is separated via the gas phase. It is therefore almost 100% separated from associated elements.
 - Zinc and lead are simultaneously recovered.
 - Lead collects all nobler elements, including copper.
- The process withstands chemical attack by corrosive elements like chlorine

6.3.12.4. Ausmelt System

This system adopts high intensity bath smelting technology to produce a reactor to smelt and process non-ferrous, ferrous and precious metal materials. The technology utilizes a straight top submerged lance through which process air and/or oxygen and fuel are injected below the surface of a molten slag bath generating highly turbulent conditions. This turbulence promotes rapid reaction between the injectants and the molten material in the furnace, leading to high smelting capacities in a relatively small furnace volume. Fuel efficiency is enhanced by contact between the molten material and the process gases. The stainless steel lance is non-consumable and is protected from the furnace contents by a coating of frozen slag. The slag coating is established by lowering the lance into the slag with a pause above the bath to allow splash to freeze on the outer surface. The lance is then lowered into the bath to get the tip below the static level of the slag layer. The depth of lance submergence is varied to control the stirring in the bath. The lance is centrally located in the furnace, constructed as a refractory lined cylinder. Each furnace has a mild steel shell and is lined with high quality chrome magnesite refractory bricks backed with high conductivity graphite mix. The furnace shell is cooled by a thin film of water cascading down from a trough, to ensure acceptable refractory life between vessel relines. A schematic of a typical furnace is shown in Figure 6.19.

The four reaction zones in an Ausmelt furnace are:

- the Reaction Zone, in the immediate vicinity of the lance tip, which can be oxidizing, neutral or reducing.
- The Slag Zone, where smelting reactions occur under oxidizing, neutral or reducing conditions.
- The Furnace Bottom, which can be relatively quiescent with the lance raised high in the bath, or well stirred with the lance positioned deeper into the molten material.

The Gas Plume Region, where reactions between the combustion gases and the slag bath occur.

The process is controlled to allow reactant or collecting material to be added to the furnace or a product to be removed, which makes it possible for a series of operations to be carried out during a single charge. The new technology has been applied for the treatment of secondary copper material, as will be described in Chapter 8.

6.3.12.5. Ausmelt Catalytic Converter

The catalytic waste converter (CWC) is derived from Ausmelt technology for waste treatment and recycling for non-ferrous applications. The process is based on a catalytic reaction between the oxidizable components of the waste feed and ferric oxide. Mass and energy transfer occur in a slag layer, which serves to separate the metal/matte from the combustion flame and oxidizing post-combustion gases. Feed material dissolution, reaction and primary combustion all take place in the slag layer.

A schematic representation of a typical furnace is shown in Figure 6.20. The central component is a vertical suspended lance submerged in a molten slag bath. The slag is

well mixed by the injection air and oxygen. High reduction rates occur. A solid slag layer forms on the outer lance surface, which protects it from highly aggressive environment. Oxygen-enriched air and coal, gas or oil are injected through the lance and combusted at the tip to provide heat to the converter. The fuel to oxygen ratio down the lance and the proportion of reductant coal to feed are adjusted to control the degree of oxidation and reduction

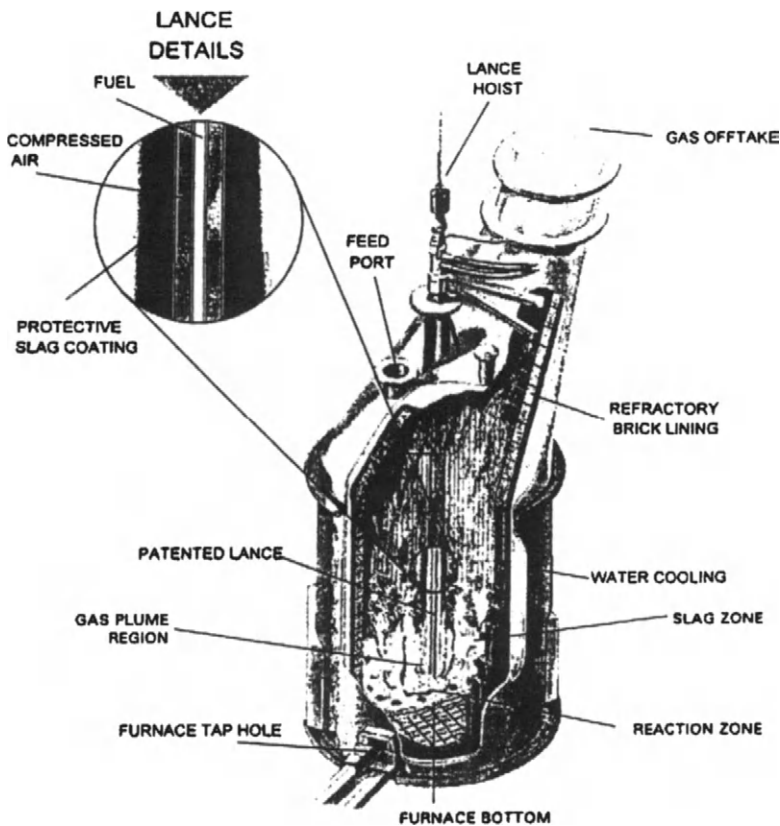


Figure 6.19. A schematic section through an Ausmelt furnace (Sofra, 1997)

The containment vessel or furnace is usually a tall, cylindrical unit operated under a negative pressure, and designed to generate slag splash. The furnace is lined with refractory materials and, depending upon the application, it is shower-cooled, insulated or incorporated with steam cooling panels to improve refractory life. Feed material, fluxes and coal are fed to the system and drop into the molten bath. Fine material can be agglomerated or injected directly into the bath to prevent any loss of dust through entrainment by rising gases.

The four reaction zones are the combustion zone, the gas rise zone, post combustion zone, and the waste reduction zone. In the combustion zone, the fuel is combusted to supply heat to the converter and help achieve the required oxygen potential for the

reaction. In the gas zone, the gaseous combustion products rise rapidly from the bath, entraining slag to produce a cascade of molten material above the surface. The cascade of slag peaks in the post combustion zone before returning to the bath, bringing with it a percentage of the heat from post combustion. In the post combustion zone air or oxygen is introduced above the bath to combust plastics and oxidize carbon monoxide generated by the process reactions, incomplete fuel combustion products and the volatile compounds from coal. In the waste reduction zone, the major metal components contained in the waste chemically react with the oxide components of the slag. The reducible components are recovered from the slag by reaction with a reductant (carbon or a sulfidizing agent) in the feed materials to form a slag.

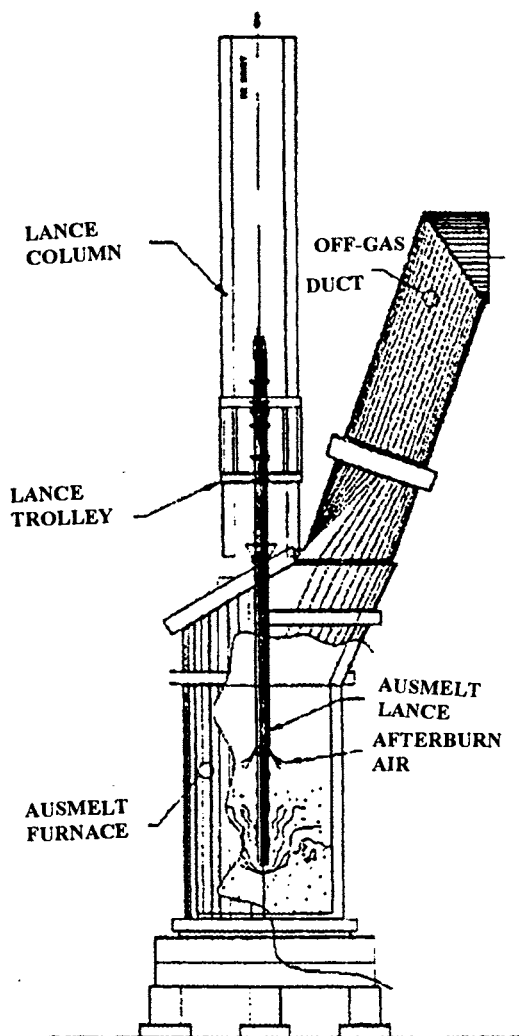


Figure 6.20. Schematic of Ausmelt furnace system in catalytic waste converter (Sofra and Fogarty , 2000)

6.3.12.6. CONTOP Smelting Cyclone

The CONTOP smelting cyclone is a cooled, upright, high-intensity smelting reactor. A double-walled cyclone is applied for smaller sizes. The cyclone is designed in tube-tube wall construction for larger feed rates. In a tubular cyclone the heat to be discharged may be used for the generation of saturated steam. Figure 6.21 is a schematic view of the cyclone type. A process flow sheet of CONTOP plant is shown in Figure 6.22.

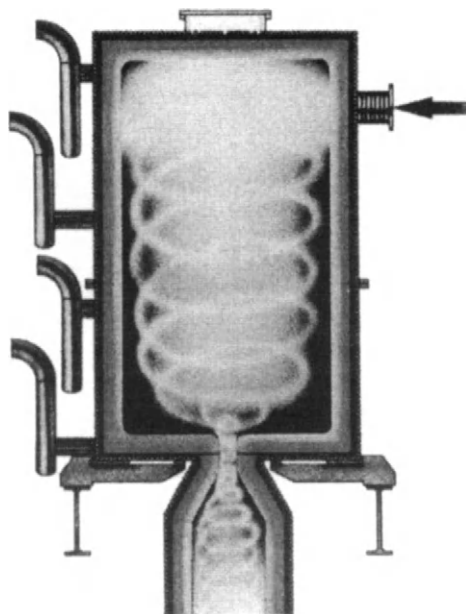


Figure 6.21. Schematic drawing of a tubular CONTOP^R smelting cyclone (Sauert *et al.*, 2000)

The pneumatically transported feed material is blown tangentially into the cyclone together with fuel and oxygen needed for combustion. Depending on the smelting capacity, the feed is blown into the cyclone at several inlets. The use of oxygen and material flow densities are controlled for optimum reaction kinetics inside the smelting cyclone. The feed melts immediately by the high temperature of 1800-2000 °C in the reaction area in the upper cyclone section. As a result of the intense vortex motion, the molten droplets are bonded in the slag that flows off. The first slag builds a protective layer on the inside surface of cyclone wall. Temperature equilibrium is established at the inner cyclone shell during continuous operation. By the effect of gravity, the molten slag steadily flows to the outlet opening and leaves the cyclone together with the water gas produced. The molten slag is separated from the gas in a settling chamber. Depending on the cooling properties, vitreous or crystalline slags are produced. Where slag quantities accumulate, a continuous slag granulation is applied.

First introduced in 1975 for extracting metals from sulfide concentrates, CONTOP smelting cyclone is now also used for processing metallurgical dusts. This will be described in Chapter 8.

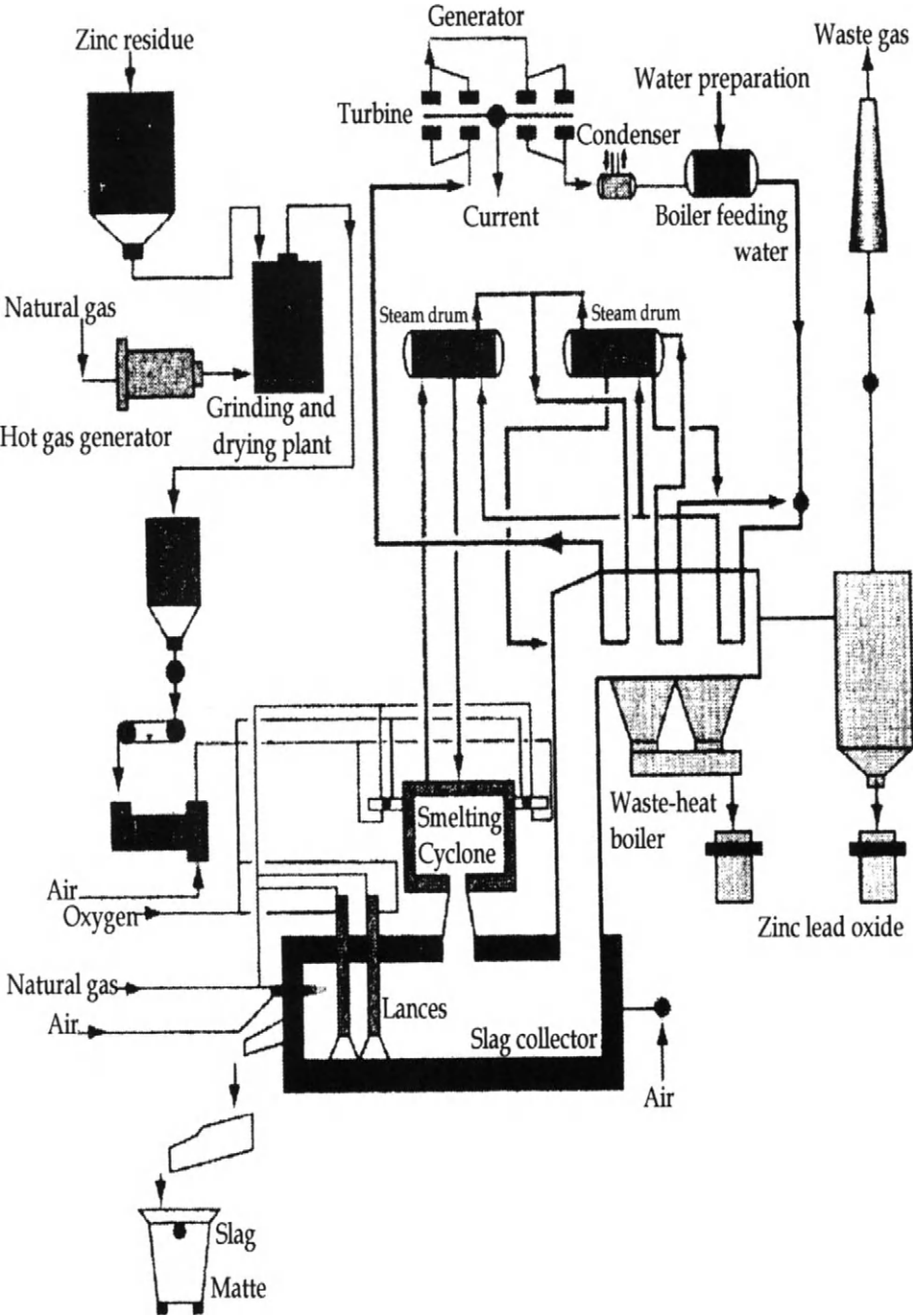


Figure 6.22. Process flow sheet of CONTOP[®] plant (Sauert *et al.*, 2000)

liquid slag, which helps to clean the metal bath. Metal and slag are periodically tapped from the furnace. The metal is cast from a refractory lined ladle. The slag is treated to obtain a sized material, which can be used as fill or ballast. The process water is treated to produce a filter cake, which is recycled in a separate processing plant.

The INMETCO process has been applied for metal recovery and by-products production from wastes of different kinds, including baghouse dust, spent acid solutions, pickling waste, nickel-cadmium batteries and superalloy wastes. (Hanewald *et al.*, 1991). Some of the applications will be described in Chapters 7 and 8..

6.4. Thermal Reactors

Various reactor designs have been described for thermal treatment of secondary materials with the objective of recovering and recycling metal values. Some of them are specially designed and used in recycling industry. A few prominent ones will be described.

6.4.1. TORBED^R Reactor (Dodson *et al.*, 1998)

In this thermal reactor, a compact shallow packed bed of particles is suspended above an annular ring of stationary blades or vanes (to some extent, similar to a static set of turbine blades) through which a process gas stream is passed at high velocity; Figure 6.24.

The high velocity gas jets (generated in the restriction between the blades) exchange energy on impact with the particles on the underside or base layer of the bed providing both vertical lift and horizontal motion. Impingement of such high velocity enhances the heat and mass transfer to that base layer. The blades and bed are arranged in such a way that the bed mixes rapidly in a controlled manner thus continually bringing material into the base layer and thus to the process gas stream. The passage of gas through the fixed blades produces a toroidal movement of the particles. See Figure 6.24.

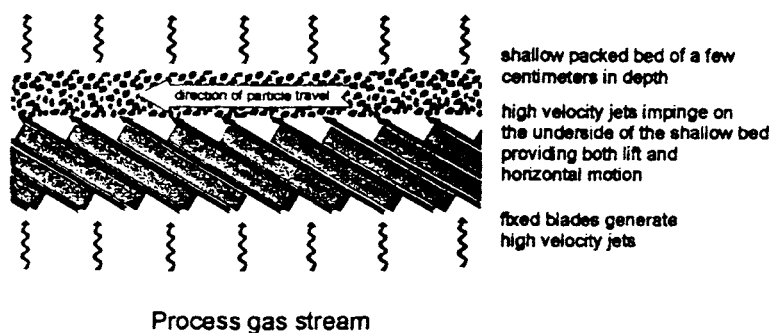
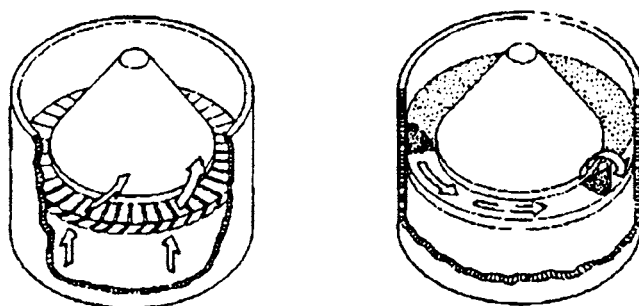


Figure 6.24. Compact TORBED^R Reactor - schematic diagram

The process gas mass flow through a Compact TORBED reactors can be set to suit the process; a smaller process gas mass flow can be used but at a higher velocity at exit from the blades to keep the bed in proper motion. They achieve higher specific throughputs (due to enhanced heat and mass transfer rates) without the inherent high pressure drop, long retention time and large solids inventory issues associated with fluidized beds. They are not limited to near spherical closely sized particles. They can

accept widely graded and irregularly shaped feed stocks including shredded, flaked and complex shaped extruded materials.



the passage of gas through the fixed blades produces a toroidal movement of the particles

Figure 6.25. Principles of operation of the TORBED^R Reactor

Compact reactors have a small solids hold-up, which is both an advantage and disadvantage. For processes taking place in milliseconds, seconds or at most a few minutes, these reactors can provide real time process control, allowing the process limits to be explored. The principal advantages are:

1. Heat and mass transfer rates higher per unit volume allowing smaller reactor size with rapid start-up and program change.
2. Faster processing of particles with more precision giving consistent product or process.
3. Low process gas stream pressure losses facilitating process gas circulation and operation with neutral, reducing or other special atmospheres at high temperatures.
4. Ability to process widely graded and irregularly shaped feed stocks.
5. Real time control that allows simplicity in operation and precise and simple automation.

Where a process retention time (for example, where phase changes occur) is by necessity more than a few minutes, the small bed mass of TORBED reactors are unlikely to be economically viable and conventional rotary kilns will be more applicable. It is worth noting, however, that perceived residence time requirements derived from other gas-solid contactors are often many times those needed in a TORBED reactor because of its enhanced heat and mass transfer characteristics.

The Compact reactors produce minimal particle degradation due to inter-particle motion and short retention times. Some applications require an inert resident bed in the reactor into which materials to be processed can be introduced. Liquids, slurries and sludges can be pumped directly into such a bed for evaporation, combustion or similar processes (where the bed remains virtually dry since if the bed becomes fully saturated with liquid, it will cease to operate and will slump).

6.4.2. Expanded TORBED Reactor

This modification retains an expanded diffuse bed of particles, which follow a toroidal circular pattern. Initially they are entrained in a high velocity central vortex (the process gas stream) whose cyclonic motion creates forces causing the particles to

separate radially outward. The particles are then transferred in an outer downward direction back to the base of the reactor to be re-entrained in the process gas stream. See Figure 6.26.

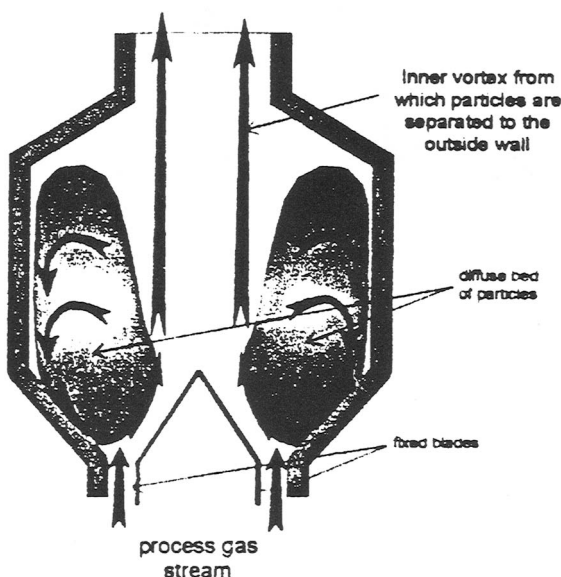


Figure 6.26. Expanded TORBED reactor

An expanded TORBED reactor provides fast and efficient gas/solid contacting and has the following advantages:

1. An equivalent particle retention time to a circulating fluidized beds (Section 6.2.13) is obtained in a smaller Expanded TORBED reactor since the horizontal component of the motion provides a longer contact path.
2. The cyclone effect within the Expanded TORBED reactor allows for the separation and direct recirculation of particles in the expanded toroidal bed without the need for internal or external cyclones for separation and subsequent re-injection.
3. The Expanded TORBED reactor can readily be "fuel injected" (see Section 6.3.3) to generate process gas temperatures in excess of 1600 °C.
4. High gas flow rates with low pressure drop are possible.
5. Selective capture of differing particle sizes (which may have different characteristics) is possible by extraction at different levels within the reactor.

6.4.3. General Characteristics

Both designs of TORBED reactors exhibit co-current (or modified cross-flow heat transfer as the off gases). Figure 6.27 shows a general comparison between a range of reactors and the TORBED reactors.

Particle residence time distribution curves usually approximate to fully stirred reactors except when there is a physical characteristic of the processed material that can be used to differentiate it and allow separation when processing is complete (e.g., change in density, vaporization or particle size reduction).

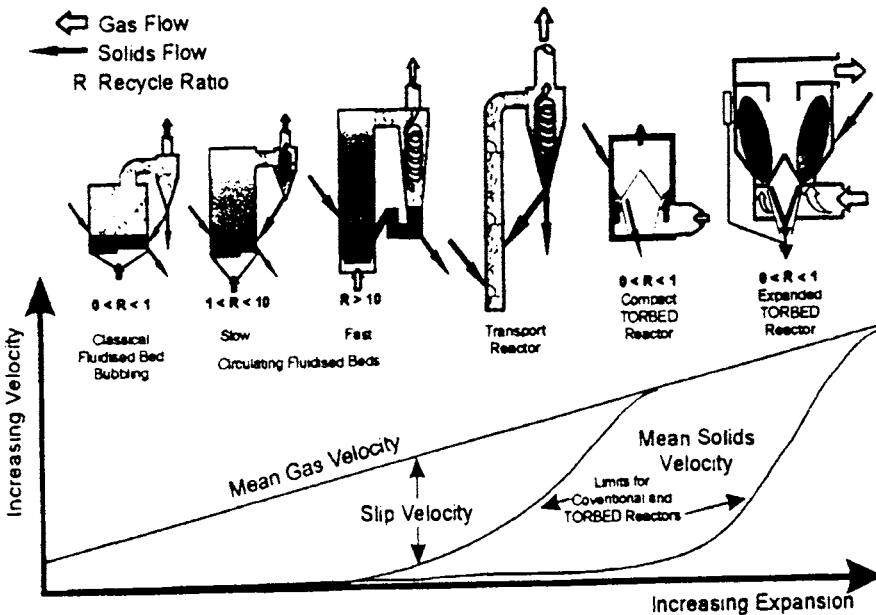


Figure 6.27. Illustrative comparison between a range of reactor types. (Dodson *et al.*, 1998)

Both reactor types can have gaseous fuel injected at blade level, which generates a combustion reaction directly within the bed of material in the reactor. Near stoichiometric combustion temperatures can thus be generated in the vicinity of the suspended solids.

TORBED reactors have been applied for fine powder processing, recovery of hydrocarbons from drilling wastes and the processing of electric arc furnace (EAF) dust. Some of the applications will be described in Chapters 5-8.

6.5. Plasma Processes

A plasma is produced at high temperature and consists of a partially ionized gas containing molecules, atoms, ions, electrons and free radicals. An ac or dc current of tens of thousands of amperes is passed through a gas space between two electrodes such as in an arc welding and in carbon-arc searchlights. A hole is drilled in the lower electrode of the arc and gas is forced around the upper electrode and through this hole. As the gas passes through the arc, it acquires the arc temperature before leaving the torch, which forms a plasma at high temperature. The process is represented in Figure 6.28.

Plasma flame can also be generated by induction heating as thermal plasma is a good conductor. The flame is started by a carbon rod and heating is done electrically with a radio frequency induction coil. The carbon rod is first placed in the center of the induction coil and heated by induction. Once the main charge is established, the rod is removed. The stream of gas carries the ionized gas away from the induction coil in the form of a plasma flame. Absence of electrodes in this process is advantageous to introduce solid substances along the axis of the plasma where chemical reaction may occur.

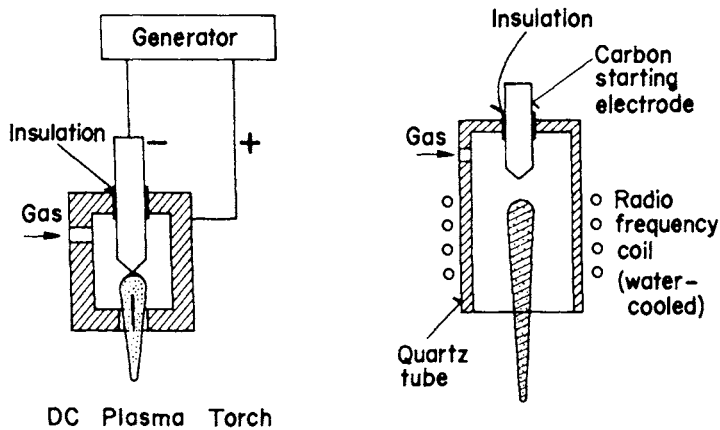


Figure 6.28. Generation of plasma (Habashi, 1969)

As compared with conventional heating devices plasma produces very high temperature. Since it is produced in the form of a jet, its innermost part is extremely hot, while the peripheral parts are at normal temperatures. There is, therefore, no contact between the hot gases and the container. A refractory is therefore needed, which eliminates problems of possible contamination. In general, electric heating produces no combustible gases in the furnace, except some possible air leak through the openings in the reactor or in some cases generated from the charge itself. This is a great advantage over carbonaceous fuels. Because of the small volume of gas, heat and dust recovery from the exit gases are less complicated. High temperature, up to 2,000 °C can be readily reached in an electric furnace as compared to a maximum of 1,500 °C attainable by burning a carbonaceous fuel. Higher temperature results in high rates of reaction. These advantages should, however, be weighed against the cost of electricity as compared to that of carbonaceous fuel. Choice between electric heating and carbon fuel heating is made depending upon the abundance or limitation of electric power generation in the region.

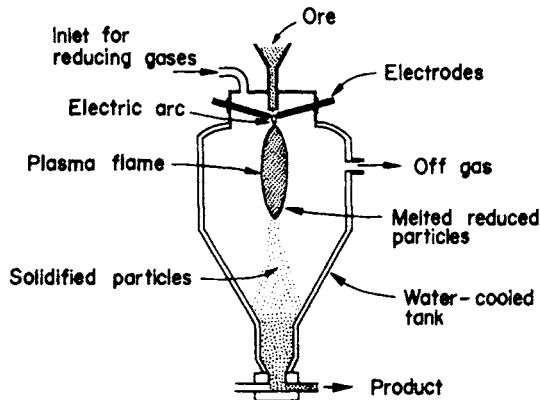


Figure 6.29. A plasma furnace for processing low grade secondary material (Habashi, 1969)

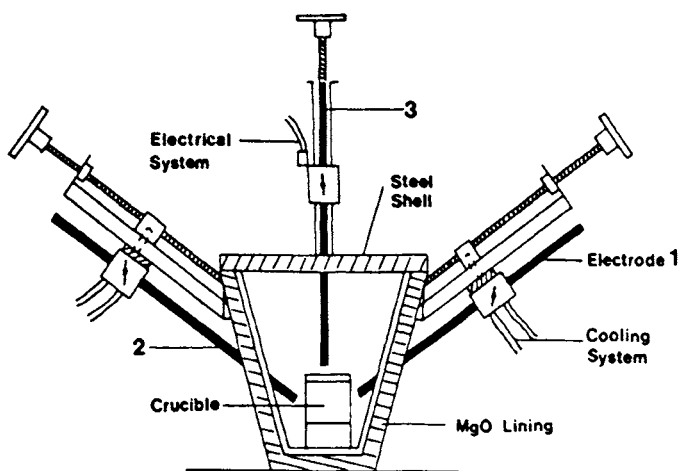


Figure 6.30. Schematic diagram of a plasma arc reactor (Habashi, 1969)

In a plasma furnace, the powdered material to be processed is charged from the top. On passing through the plasma flame chemical reactions as well as melting occur. The product is collected in a water-cooled tank at the bottom.

The use of plasma in the processing of metal slimes for metal recovery will be described in Chapter 8.

6.6. Size Enlargement Technologies. Pelletization

One of the common problems associated with particulate solids in recycling is the fineness of the material. Handling and transportation of such materials is difficult and may cause secondary pollution. Also, because of their large surface area, such materials easily oxidize and lower the metal yield. The problems can be largely overcome by size enlargement or densification of the feed material.

Three size enlargement technologies used in recycling industry are:

- tumble or growth agglomeration;
- agglomeration by the application of heat, called sintering;
- pressure agglomeration.

Heat treatment is done in rotary kiln. The fines are heated near the temperature of fusion. The reactions taking place and partial melting and recrystallization form solid bridges between the particles and increase the mechanical strength. In another technique, the powder is mixed with a small amount of charcoal and the surface ignited by gas burners. As the mixture moves along a traveling grate, air is pulled through the mixture to cause the burning zone to move through the bed by igniting the fuel in the deep zones. The product is known as "sinter".

One of the most commonly used methods for agglomeration is called balling. The powder is mixed with water, about 9-11 % of the weight of the powder and some desired additives to increase the strength and is then made to tumble at room temperature in a rotating disk or a drum. Agglomerates are formed in 1-4 minutes.

Agglomeration is a surface chemical phenomenon, which depends upon the surface tension of water and capillary action between the particles. When particles covered with a

thin layer of water contact each other, the liquid layer coalesces to form weak binds at the points of contact. (Figure 6.31) The rolling action in the balling apparatus reduces the internal pores causing the particles to be mechanically interlocked (Figure 6.32) The three principal factors contributing to the formation of balls are water content, characteristics of the powder and characteristics of the balling apparatus. Just enough water to bind the particles should be used as high water content would cause a plastic mass. Finer particles have greater points of contact. Balls produced in a rotating disk are more regular in shape than those produced in a drum.

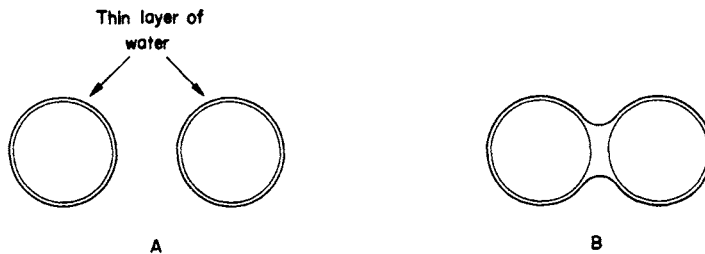


Figure 6.31. Formation of bond between two particles covered by a thin layer of water. A-before contact; B-after contact

Balls thus produced are called “green pellets”. They require gentle handling and are not strong enough in chemical reaction in a furnace. Mechanical strength can be increased by heat treatment, which causes physical changes resulting in their hardening. Binders, chemicals like bentonite, clay, lime are added to the powder (about 0.5 % of the feed) before balling to improve the mechanical properties of the pellets. Colloidal nature of clay and its binding action impart greater strength. Such additions are however, undesirable when purity is a major concern. Heating is conducted in autoclaves at about 200 °C and 1600 kPa. Hydrothermal reactions taking place result in the formation of gels, which bind the particles within a pellet.

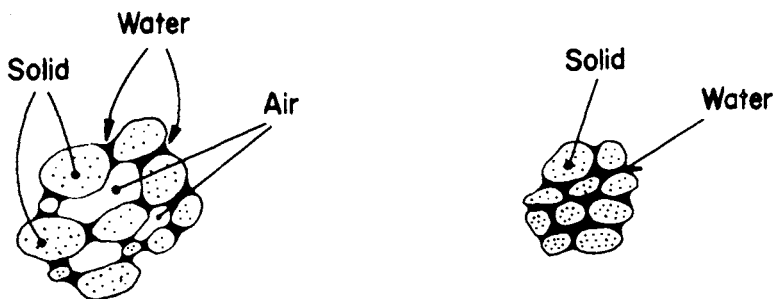


Figure 6.32. Elimination of pores during rolling

In pressure agglomeration the feed is made up of small particles and a binder to make it a little plastic. The moist, often sticky mass is extruded through holes in different shaped screens and dies, Figure 6.33. For mineral and metal processing wastes, mostly the screw (Figure 6.33, b.1) or the ram (Figure 6.34, 1) is used to extrude. Flat die pellet

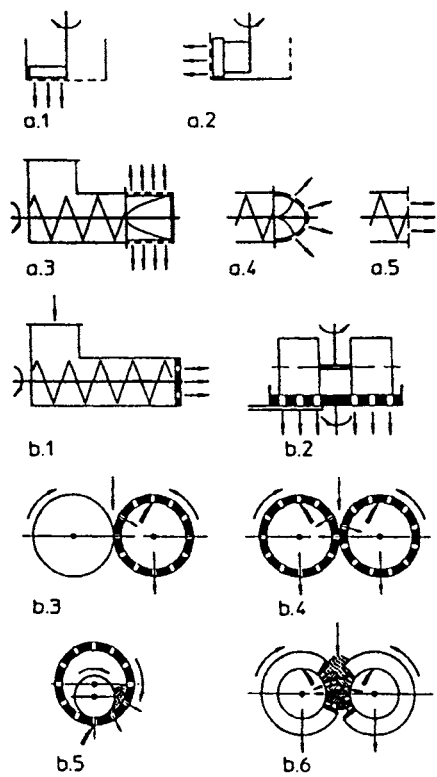


Figure 6.33. Schematic representation of equipment for low a) and medium (b) pressure agglomeration (Pietsch, 2002)

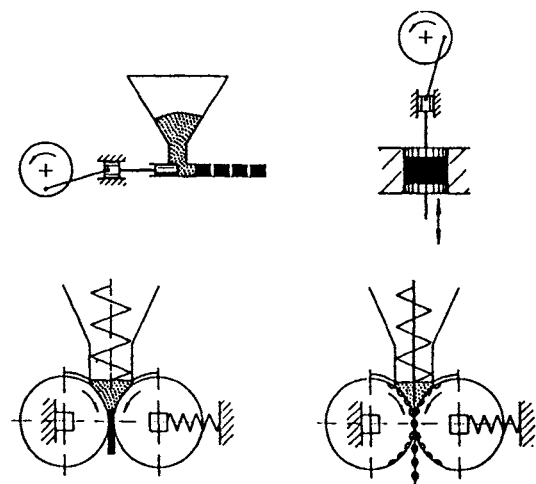


Figure 6.34. Schematic representation equipment for high pressure agglomeration (Pietsch, 2002)

presses (Figure 6.35) exerting medium to high pressure are suitable for some applications (Pietsch, 2002). High pressure agglomeration is the most versatile technology for the size enlargement.

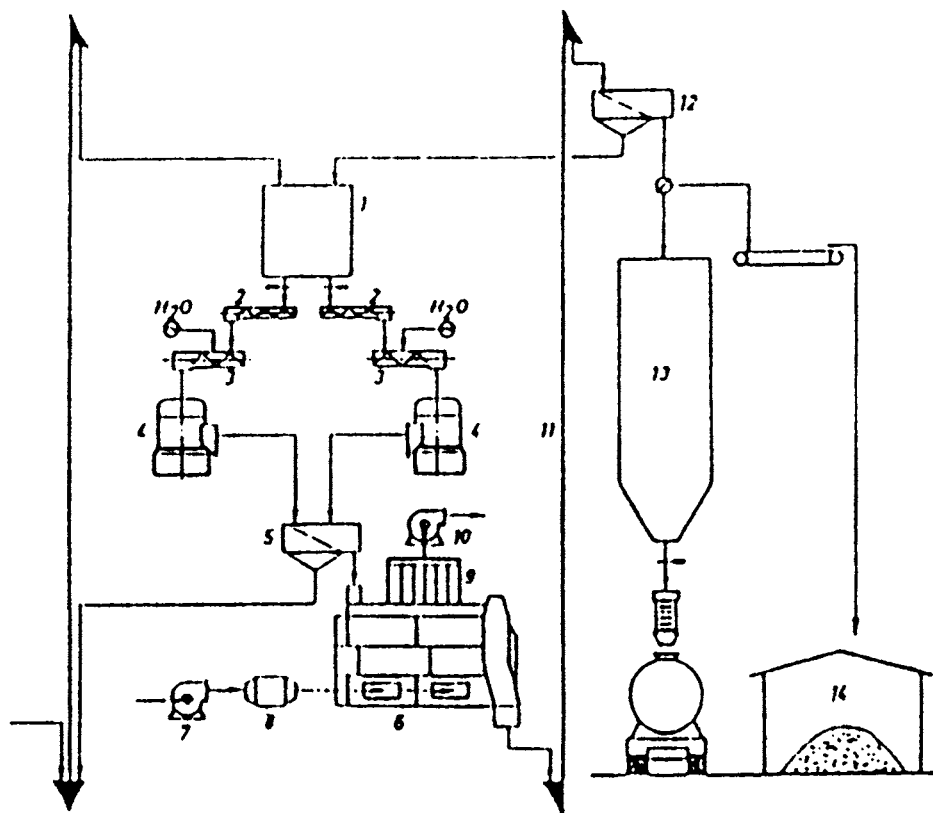


Figure 6.35. Pelleting of wet gypsum by medium pressure agglomeration (Pietsch, 2002)

Another technique to produce briquets or compact granules is called roll pressing. The particulate material is squeezed between two rolls rotating in opposite directions. The material to be processed enters the roll pressing system through a feed throat and is pushed by a feed screw or gravity force. In the feed zone defined by two angles αF and αE (Figure 6.36) peripheral speed of rolls is higher than the velocity of the material to be compacted. At the position of the rolls defined by the angle of entry αE slip between particulate material and roll surface vanishes and compaction process begins

Roller pressing has been used for compacting steel plant wastes and catalyst based on aluminum tailings. (Dec, 1996). The technique is conceptually simple sand produces strong agglomerates without any additives. A similar process has been proposed for briquetting anthracite (a high grade variety coal) fines to facilitate their recycling (Guzman and Price, 1996).

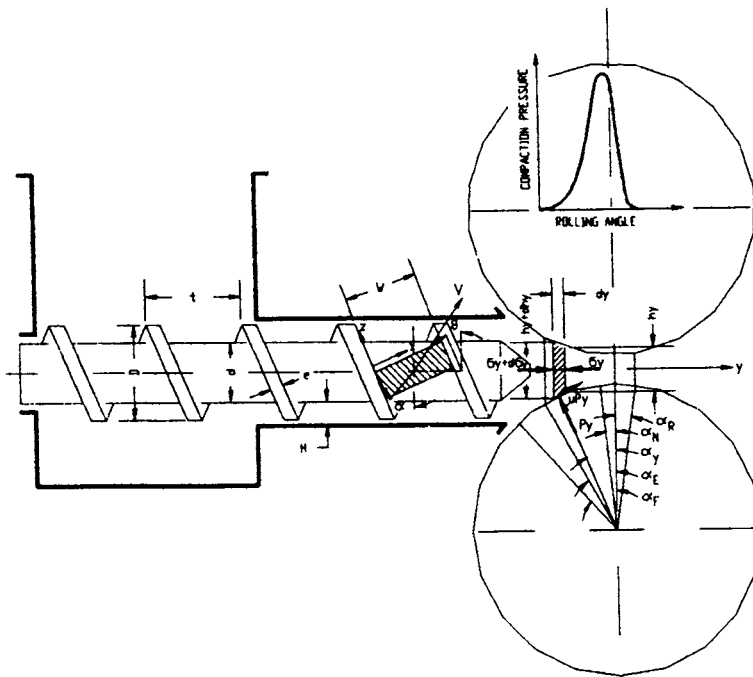


Figure 6.36. Diagrammatic cross-section of typical roll press (Dec, 1996).

In an alternative process, known as cold agglomeration, additives like lime or Portland cement are incorporated in the material before balling. The balls are then dried and allowed to cure at room temperature until the desired strength is reached. This process consumes less energy and no chemical change occurs in the material to be palletized. It has been used in the processing and utilization of ore tailings as mine backfill. It will be described in Chapter 9.

Selected Readings

- Habashi, F. *Principles of Extractive Metallurgy*, vol. 3, *Pyrometallurgy*, Gordon & Breach, London.
- Holman, J. P., 1997. *Heat Transfer*, McGraw-Hill, London.

Chapter 7

METAL RECYCLING

Recycling of metals from secondary sources is a growing industry. There are a large number of secondary sources, collectively called “scrap”, which is defined in the dictionary as “discarded metal in the form of machinery, auto parts, etc., suitable only for reprocessing”. As the primary sources of metal, natural ores are steadily getting depleted, there is an obvious recognition that the total supply of any metal on Earth is finite. It is evident, the metals have to be recycled from “scrap” to maintain a steady supply to meet the demands of industry and wherever else metals are used. In this context, the word “discarded” should be eliminated from the dictionary definition. This is even truer in the case of metals, which do not occur in abundant concentration and their extraction from the scarce primary resources is often expensive, which, in most but not all case may be justified by the price of the metals produced. This is the case for precious metals like gold and platinum group metals (platinum, palladium, rhodium). In such cases, precious metal content as low as 0.001% to 0.03% can justify reprocessing of the scrap to recover the metals in it. As an example, scrap containing only 0.003% rhodium has a value of \$2,500 per ton, even if all other metal values of the scrap are ignored (Hoffmann, 1992a).

Metals are a renewable resource. Most metals are used in industry in a fairly massive elemental form, which greatly facilitates recycling. The properties of metals that lead to their use such as high strength, durability, high density, electrical and thermal conductivity and magnetism also facilitate their recovery and separation from non-metallic and plastic contaminants as well as separation of metals from each other. Some metals require only melting, which makes them suitable for direct re-use in foundries, while other metals can be refined by volatilization (Sudbury, 1997).

Even with the scrap of relatively abundantly occurring metals (for example, iron), reclamation of metal from secondary sources is an established industry, motivated by both economic as well as environmental factors, as discussed in Chapter 1. Developments of new technologies for the processing of scrap have given added impulse for recycling. The present Chapter will discuss the principal processes of recycling metals from metallurgical scrap, that is, scrap generated in industries using metals as auto parts, machinery, and other engineering materials. Metal recovery from process wastes, where metal occur as their compounds will be discussed in the following Chapters, 8, 9, 10.

7.1. Iron and Steel

Steel dominates in tonnage, relatively cheap per ton, but is still by far the largest in gross value. It is used mainly in the construction, machinery and automobile industry. These therefore are the dominant locations to look for recycle materials.

Iron and steel scrap is a valuable feedstock in making new steel products. The huge

quantities of iron and steel produced over a long period, dating back to 19th century, has generated a secondary industry of processing the scrap. Ferrous scrap is sorted and processed into various grades for remelting in steel making furnaces. In the U.S., the use of old scrap as a percentage of total scrap consumed has been steadily rising. It is now estimated to be over 50%.

Three types of scraps from iron and steel industry are called “home”, “new” and “old”. Technological advances have significantly reduced the generation of home scrap. New or prompt scrap is generated in manufacturers’ plants and includes such items as stampings, turnings, and clippings. Old or obsolete scrap is iron or steel from post-consumer products such as automobiles, appliances, buildings, and bridges.

A major requirement in recycling scrap is to maintain the quality of steel products by minimizing contamination with other metals. Potential tramp metal contamination may come from the recycling of automobiles and municipal scrap. Detinned scraps command premium price.

The types of ferrous metals to be recycled can be classified into two main grades: ferrous scrap and ferrous waste and intermediary products. The form of the ferrous scrap to be recycled has to be considered in selecting appropriate technology, which is capable of recycling the material.

The common grades of iron and steel scrap include: heavy metal steel, plate and structured steel, hydraulic silicon bundles, short shoveling steel turnings, machine shop turnings, mixed turnings and borings, cast iron borings, mixed cast, shredded scrap, steel turnings (alloyed and alloy free) and foundry steel. The common types of iron and steel intermediary products include steel making slag, spent pickle liquor, flue dust, waste sludge, filter cake and mill scale.

7.1.1. Recovery and Recycling Technologies

A review of the principal techniques and processes employed for recovery and recycling in iron and steel industry will be first presented. That will be followed by some specific examples of recycling in industry.

7.1.1.1. Blast Furnace (BF)

The feedstock is primarily iron ore, but could include pellets, sinter, mill scale, and cast iron or steel scrap. The material is charged into the top of the blast furnace together with limestone and coke. The passage of the hot blast air through the charge leads to the production of carbon monoxide, which reduces the ore to produce carbon dioxide and metallic iron. The heat generated by the coke supplies the heat necessary for the reaction to proceed and also the heat necessary to melt the iron as it is formed. Most of the impurities concentrate in the molten slag. The molten iron is tapped into large refractory lined iron ladles, which convey it to the basic oxygen furnaces to produce steel. Some iron is cast as pig-iron and used as feedstock for foundries.

7.1.1.2. Basic Oxygen Furnace (BOF)

Basic oxygen furnace is essentially a top blown converter (described in Chapter 6) in which heat is internally generated by the oxidation of impurities within the charge. The heat balance is therefore determined by the relative rate of oxidation of metals, the temperature of molten iron (from the blast furnace) and the scrap. The scrap, which makes 20 to 30% of the charge, is added at the beginning of the cycle. The addition of

oxygen to the charge of the scrap and molten iron leads to the formation of iron oxide and carbon monoxide, which causes a vigorous exothermic action. Slag forming fluxes, mostly lime and fluorspar, are added to form a slag. When the carbon content of the molten metal is reduced to the desired level, the steel is tapped into a ladle and cast continuously.

7.1.1.3. Electric Arc Furnace (EAF)

The furnace receives energy from a three-phase transformer. Cylindrical solid graphite electrodes, suspended from above the shell and extending down through the ports in the roof are used to carry the current and strike an arc with the metal. Lime is used as flux material and oxygen injected into the bath late in the melt to refine the steel. Alloying elements are added to the pouring ladle or continuous casting tandish. Casting may be continuous or batch.

Some of the advantages of the EAF are lower cost than integrated arrangements, capability to produce a wide variety of alloy and stainless steels, making use of the low cost of scrap and pre-reduced pellets, production of steel without coke and without a source of hot metal or independently of a blast furnace

7.1.1.4. Sorting and Preparation Techniques.

Refining is carried out in the basic steel making process. Slag, fluxes, and scrap charges are adjusted to control the composition of the final melt, but if a certain element reports to the steel instead of going into the slag or furnace atmosphere, little can be done to control its direction. Some control is possible using ladle metallurgy techniques, which will be described under stainless steels. As the quantity of steel produced from scrap increase, relative to steel produced from virgin ore, it becomes necessary to monitor the levels of certain contaminants in the scrap circulating load, especially copper, tin and lead.

The steel making process can tolerate some contaminants including aluminum, zinc, and magnesium metals and paint, oils and greases. Contaminants such as tin, lead, and copper metals are not tolerated. The sources and impacts of common contaminants and their effect on the quality of steel are discussed in the following section.

Table 7.1. Contaminants in Steel Making.

Elements predominantly recovered into the steel	Elements partially recovered in the steel	Elements almost entirely eliminated
Antimony	Carbon	Aluminum
Arsenic	Chromium	Calcium
Cobalt	Hydrogen	Magnesium
Copper	Lead	Silicon
Molybdenum	Manganese	Titanium
Nickel	Nitrogen	Zinc
Tin	Phosphorus	Zirconium
Tungsten	Vanadium	
	Sulfur	

Copper is sometimes added as an agent to infer corrosion resistance; but it is a troublesome residual metal found in the scrap steel. Methods of transferring copper from the steel phase to the slag phase have not been entirely successful.

Tin affects the impact properties of steel, which is apparent in the presence of copper. This problem also arises from tin-bearing scrap such as food containers and auto bearings. Tin in steel behaves the same way as copper. The elements collect at the grain boundaries, and cause surface scabs during working. This can affect the surface quality in critical applications such as automotive sheet.

Aluminum generally enters the slag in steel-making. Aluminum is harmless to steel and is added intentionally as a de-oxidant.

Lead in small amounts improves the machinability of steel. It generally passes into the flue dust along with the zinc during the steel-making process.

Nickel increases the hardenability of steel. It occurs in the recycling of the scrap, which has not been segregated. Nickel and chromium can be utilized in alloy-steel-making as long as the scrap is properly segregated. Improper segregation can have a negative effect on the quality of carbon steel.

Phosphorus is undesirable, but is generally removed during BOF and EAF operations. Phosphorus and sulfur can be transferred, to some extent, from the metal to the slag by the addition of lime. However, that increases the cost of steel-making by increasing energy consumption and slag output.

Sulfur increases the likelihood of hot tearing and hot cracking. Its removal is facilitated by the use of highly basic slags, particularly under the reducing conditions found in an EAF.

Zinc is largely volatilized in the steel-making process and is converted to oxide, which occurs in flue dust. The concentrations of zinc in EAF flue dust is particularly high because the 100% scrap feed usually contains some zinc-bearing scrap in the form of galvanized sheet and brass fittings.

Other metals. Alloy scrap is sometimes used as an inexpensive source of chromium, manganese and molybdenum to increase the hardenability of steel. However, other elements such as arsenic and antimony are extremely deleterious. Chromium can be oxidized and reports to the slag more than some of the other elements.

Oil and grease, common contaminants in scrap, can increase the sulfur burden, to a small extent, to the furnace.

Rust. Most grades of ferrous scrap rust to some extent and may be contaminated by dirt during transportation, handling, and stockpiling. Rust can increase the energy requirements and reduce the yield of steel. Water is retained by scrap under humid conditions. Water can cause eruptions in the charge, reducing yield and increasing energy requirements.

Miscellaneous contaminants. Purchased scrap can be contaminated with glass, textiles, rubber and plastic. Non-metallic contaminants decrease yield from the scrap and remove heat from the charge unless they are combustible like, for example, rubber. Plastics can be a source of dangerous fumes. Acidic oxides increase the lime requirement and therefore the energy requirements from calcining reactions.

The numerous sources and forms of ferrous scrap require the use of numerous techniques to remove the contaminants and/or recover other valuable materials such as non-ferrous metals prior to entering the steel-making process. The following are the main separation/segregation and preparation techniques, which have been investigated and

applied in various recycle processes.

1. Manual sorting and preparation.
2. Size reduction processes.
3. Sweat furnace.
4. Shredding.
5. Magnetic separation.
6. Eddy current separation.
7. Electromagnetic separation.
8. Heavy metals separation.
9. Baling and compaction.
10. Incineration.
11. Color, magnetic, spark, chemical, spectroscopy and density testing.

7.1.1.5. Manual Sorting and Preparation.

Large items such as ships, automobiles, appliances, railroad cars and structural steel must be cut to allow them to be charged into a furnace. This can be done by shears, hand-held torches, crushers or shredders. Manual sorting requires the removal of components from the scrap by hand. It is most suitable when miscellaneous attachments have to be removed from the scrap; for example, radiators from scrap cars, plastic end tanks from radiators. The separation of metallics from non-metallics is also often accomplished manually.

7.1.1.6. Size Reduction Processes.

Reduction of the size of large scrap material to enable consolidation, shipment and subsequent feeding into furnaces is done using suitable equipments such as shears, flatteners, and torch-cutting and turning crushers.

7.1.1.7. Sweat Furnace

The sweat furnace is used by many metal scrap recyclers for the purpose of separating aluminum, zinc and/or lead from iron in composite parts. It can also be used to remove contaminants like dirt, rubber, plastics and other combustibles from aluminum, zinc and lead-bearing scrap. In addition, the furnace can be used to compact loose and bulky non-ferrous scrap for transportation to a secondary smelter.

The sweat furnace has an inclined hearth and is most commonly heated by natural gas. The temperature in the furnace is maintained at 730 °C to let the molten aluminum, zinc, or lead drip through the inclined hearth into the bottom of the furnace while ferrous and other higher melting point metals and non-combustibles remain on the hearth.

One problem with sweat furnace is that the aluminum, zinc or lead alloys produced may contain iron, and lower melting alloys as well as other types of contamination. Sophisticated temperature and emission control devices will have to be integrated

7.1.1.8. Shredding

By shredding with massive hammer mills, automobile hulls, appliances, and other large goods are reduced to fist-sized pieces. Three streams of material are produced: ferrous metals (iron and steel), a light fraction residue and a heavy fraction residue. The two residue fractions, either singularly or collectively referred to as automotive shredder residue (ASR). The process is schematically represented in Figure 7.1.

The low density or light materials, which are collected during the shredding process by cyclone air separation are called “shredder fluff”.

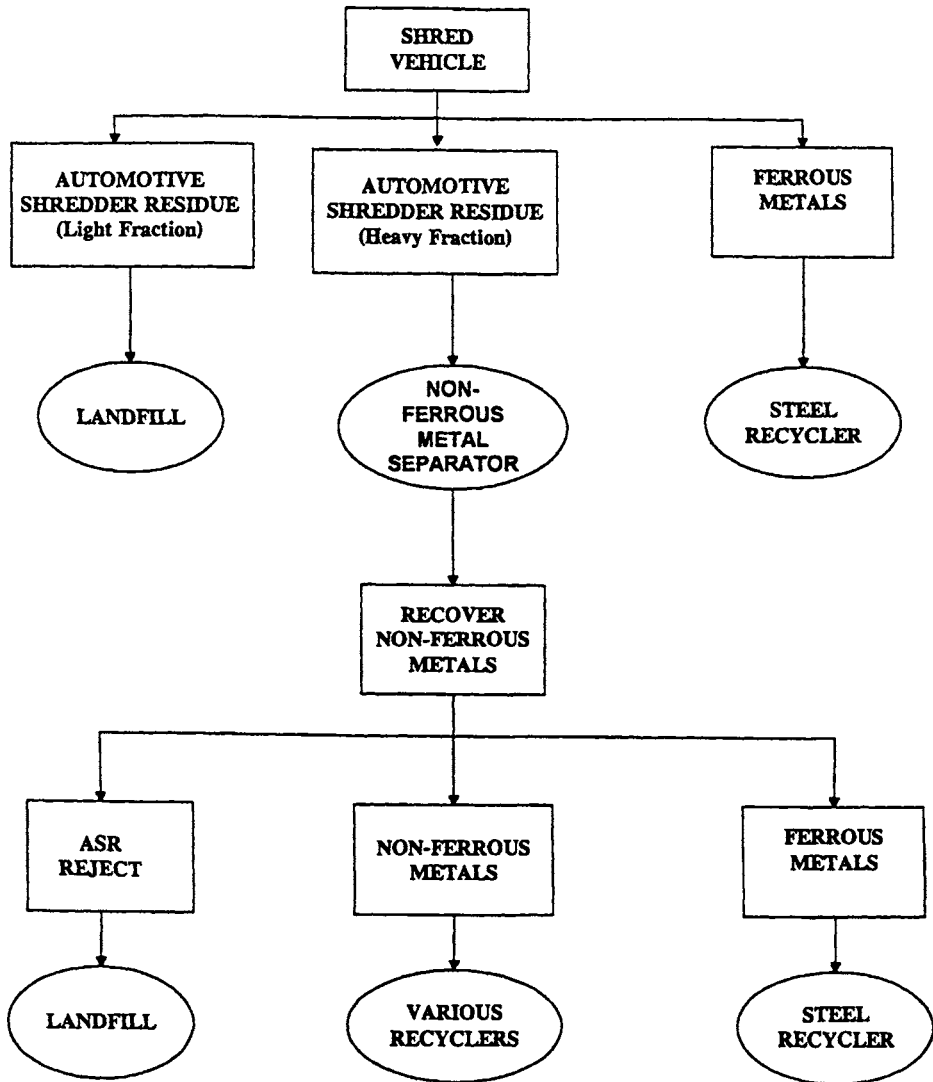


Figure 7.1. Metal shredding (CANMET, 1993)

The ferrous metals (iron and steel) are recovered by the shredder operator through magnetic separation and sold to steel mills. The ASR heavy fraction contains primarily aluminum, stainless steel, copper, zinc, and lead. The non-ferrous and ferrous metals are recovered from the ASR heavy fraction, either by the shredder operators or by non-ferrous metal separators who purchase the ASR from the shredding industry. Metallic fractions from the ASR heavy fraction are recovered primarily by heavy media and eddy current separation techniques.

7.1.1.9. Magnetic Separation

When large quantities of ferrous scrap are to be separated from other materials magnetic separation is the obvious choice. The two types of magnets are permanent magnets and electromagnets. The latter can be turned on and off to pick-up and drop items. Magnetic separators can be of the belt type or drum type. In the drum a permanent magnet is often located inside a rotating shell. Material passes under the drum on a belt. A belt separator is similar except that the magnet is located between pulleys around which a continuous belt travels. Magnetic separation has some limitations. It cannot separate iron and steel from nickel and magnetic stainless steels. Also, composite parts containing iron will be collected which could contaminate the melt. Hand sorting may be used in conjunction with magnetic separation to avoid these occurrences. (See Chapter 3 for discussion of magnetic separation techniques).

7.1.1.10. Eddy Current Separation

Eddy current separators are used to separate non-ferrous metals from waste and automobile shredder residue. The process generally follows the primary magnetic separation process. The process exploits the electrical conductivity of non-magnetic metals. This is achieved by passing a magnetic current through the feed stream and using repulsive forces interacting between a magnetic field and the eddy currents in the metals.

The simplest device following this principle is the inclined ramp separator. This uses a series of magnets on a sloped plate covered with a non-magnetic sliding surface like stainless steel. When a feed of mixed material is fed down the ramp, non-metals slide straight down, while metals are deflected sideways by the interaction of the magnetic field and the induced eddy current. The two streams are then collected separately.

There are several variations of the eddy current separator. These include the rotating disc separator where the magnets are arranged around a axis. Another system uses a conveyor with a head pulley fitted with magnets. Both system relies on the varying trajectories of materials either affected or unaffected by the magnetic fields, to make the separation. (See Chapter 3 for discussion of eddy current technique).

7.1.1.11. Heavy Media Separator

Heavy media separation (HMS) utilizes a medium normally consisting of finely ground magnetite or ferrosilicon and water. By varying the relative proportion of the solids the relative density of the medium can be adjusted. The specific gravity of the medium is typically halfway between the densities of the two materials being separated. Once separated, the products are allowed to drain; the medium recovered is returned to the process.

HMS separations can be conducted in an open bath to achieve a separating force equal to the force of gravity. For smaller size particles, the force of medium viscosity tends to work against the separating force. For such cases cyclonic separators are employed which effect a separation at several times the force of gravity.

7.1.1.12. Incineration

Some scrap processors use incineration to remove combustible materials including oil, grease, wood, plastic and paper and volatile metals such as lead and zinc. Incineration is usually carried out in static furnaces. The emissions are monitored or treated and therefore, volatile organic carbons (VOCs) are released to the atmosphere unchecked.

Additionally, incineration consumes materials, which could otherwise be potentially recycled.

7.1.2. Dezincing Technologies

In the steel-making process, the zinc in the melt reports to the flue dust. In integrated steel plants, the concentrations of zinc oxide range from 1.5% to 4% in BOF flue dust. BF and BOF flue dust are usually land filled, but they can be recycled back into the melt to recover the iron oxide. Continuous recycling of the flue dusts is not done because the cumulative loading of the flue dust with zinc could result in disposal problems.

Since mini-mills and integrated mills use EAFs to produce steel from 100% scrap, any zinc-bearing scrap included in the charge will result in zinc oxide going to the flue dust. The zinc content (15-25%) in EAF flue dust is high enough to cause leachate problems but not high enough for economic recovery of zinc. By keeping zinc-bearing scrap out of the steel-making process, the dust would not require treatment and could be land filled.

The main source of zinc is from galvanized sheet scrap. With the anticipated increase in the use of galvanized steel, the zinc concentration in BOF and EAF flue dusts are likely to increase. Pretreating galvanized scrap to recover zinc saves primary energy, decreases zinc imports and adds value to the scrap.

Two main processes of dezincing technologies to recover zinc from galvanized panels are: thermal and thermo-mechanical; and chemical and electrolytically aided chemical leaching.

7.1.2.1. Thermal and Thermo-Mechanical Removal

Various methods are used for the removal of zinc by thermal methods. In the first method the galvanized parts are heated to a temperature greater than 900 °C to evaporate the zinc. In the second method the galvanized parts are heated to a temperature sufficient to embrittle the coating, which is then removed by abrasion. In a third process, the coating is heated and subsequently removed by shot blasting. It is known as Toyota Dezincing Process, after Toyota, which is operating a 5,000 ton/month plant at Toyokin, Japan. The process consists of taking shredded scrap at 800 °C (below the temperature of volatilization of zinc) for 90 minutes. This produces a brittle zinc/iron compound. It is removed by shot blasting for 5 minutes. The quality of the zinc produced is not known, but it is probably contaminated with iron. The zinc/iron scale, which is removed can be treated by one of the zinc flue dust technologies described in a latter section.

7.1.2.2. Chemical and Electrolytically Aided Removal of Chemicals.

There are three chemical techniques for stripping zinc. In the first, sulfuric acid is used to dissolve the zinc coating. The disadvantage is that it is difficult to separate the dissolved iron and zinc. In the second, the zinc coating is leached by ammonia. In the third, caustic soda is used to dissolve the zinc coating.

The caustic soda dezincing process is considered to be the most promising. It consists of two major steps. Zinc is first dissolved from the steel scrap in a caustic soda electrolyte by applying an electric current; then the sodium zincate solution is electrolyzed to recover zinc in powder form on the cathode. The process is designed to handle baled scrap, weighing about 1,100 kg with a density of 2,400 to 3,200 kg/m³. The bales are introduced into rectangular electrolytic cells filled with hot caustic electrolyte. Electric

current is applied and the zinc is anodically dissolved from the steel scrap while hydrogen is evolved and some zinc is deposited at the cathode. The process can be applied to all types of galvanized steel scrap, presently in loose or baled form.

Dissolution rate of zinc in caustic soda can be greatly enhanced by galvanic coupling between zinc and steel. This galvanic coupling is present in the form of one side zinc coated material and cut edges from the zinc coated scrap and it is facilitated by the shredding that scours off the surface (Groult *et al.*, 2000).

After electrolysis the material is passed through a multi-station, counter-current rinse cycle to remove entrained sodium zincate. The zinc-enriched electrolyte is then treated in the electrowinning section using conventional cells with nickel anodes and cathodes. Zinc is occasionally scraped off and falls to the bottom of the cells. The powder is washed with water to remove residuals and is passivated to minimize oxidation. Cells of alternative design to improve the electrodeposition efficiency have been described by specific operations (Jiricny *et al.*, 1998).

A caustic leach is used to dissolve impurities such as lead, iron, nickel, tin, antimony and cadmium. They co-deposit on the cathode with zinc. It can be controlled by a cementation process using zinc powder. This is effective at controlling most impurities except tin and antimony.

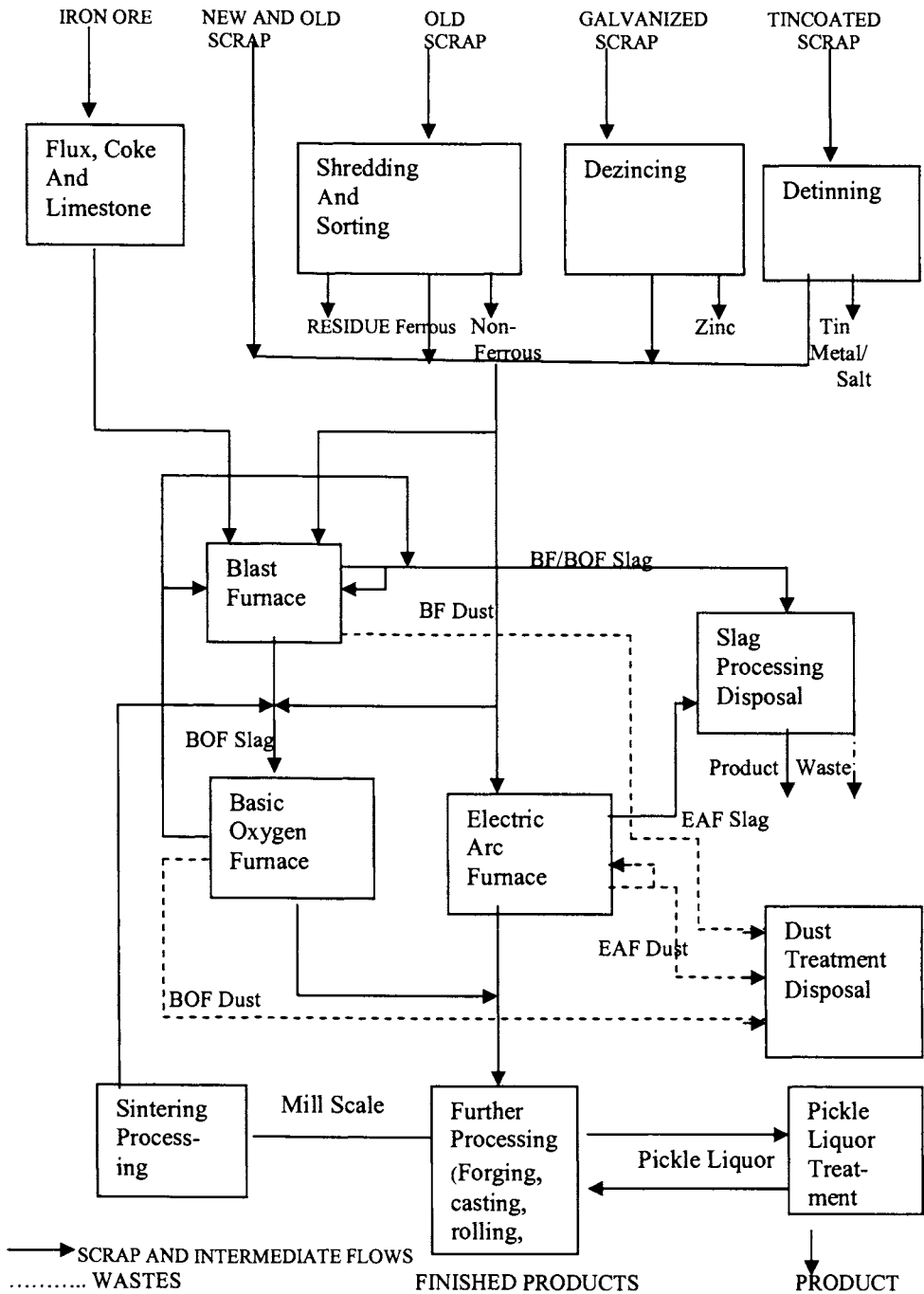
7.1.3. Detinning Technologies

Tin affects the impact properties of steel and is apparent only if the presence of copper. It behaves in the same way as copper. Both elements go to the grain boundaries and cause surface scabs during working. This can have an adverse effect on the surface quality of the steel products, which can be unacceptable in critical applications such as automotive sheet.

Typical tin plate consists of approximately 0.5% tin. The steel used in tinplate is of a high quality. The maximum acceptable level of tin content is 0.05 to 0.06 percent. Sorting, shredding, air separation and magnetic separation are used to prepare tinplate scrap for detinning. The two technologies of current commercial use are, electrolytic detinning and alkaline detinning.

The electrolytic detinning process consists of leaching in a hot alkaline solution. Metallic tin dissolves quickly, while the tin that has alloyed with the iron takes longer. The dissolution reaction is accelerated through simultaneous electrolysis. The scrap is suspended in baskets in a bath containing about 10 percent caustic soda, at a temperature of 80 °C. Steel cathodes surround the baskets. A spongy tin deposit is formed on the deposits. It is manually removed, compacted, melted and cast into ingots and sold to tin refiners. Production of one ton of tin deposit requires 10 to 12 kg sodium hydroxide, 9.9 m³ natural gas and consumption of 20 to 35 kWh power. The recovered tin has a purity in the range 95 to 97 percent, the main contaminants being lead and iron. The contaminants which can interfere with the process are aluminum, lacquer and organic wastes. The process can be applied to cans and industrial scrap. Most of the revenue is generated from the sale of the upgraded steel scrap rather than from the recovered tin.

In alkaline detinning an oxidizing solution is added to a sodium hydroxide solution to increase the rate of dissolution. This solution strips tin from tinplate in 4 hours under static conditions 1.5 hour when agitated. The free tin layer is removed quickly but the alloy layer takes longer. The tinplate is shredded prior to leaching and after detinning it is washed, bathed and sold to steel making operations. The solution containing sodium



stannate (Na_2SnO_3) is centrifuged or settled before being cascaded through electrolytic baths. A hard crystalline deposit forms on the cathodes, which is cleaned off and melted into ingots. The spent electrolyte is reused. The settled solids are sold to tin smelters as low grade tin ore. Overall tin recovery is 88 % and the tin cathode product is 99.5 %.

An alkaline detinning operation with capacity to process 20,000 tons of tinplate scrap annually is run by MRI, Hamilton, Ontario. Proler International in Houston, Texas, washes the tin scrap in caustic soda in a drum. Tin is precipitated from the wash solution as a stannous salt. Its plant treats 180,000 tons per year of tin cans.

A schematic illustrating recycling process in iron and steel industry is presented in Figure 7.2. It integrates the various steps described in the preceding sections. Note that the recycling from scrap is integrated with extraction of iron from primary iron ore, usually hematite. This is often the practice in iron and steel plants. However, recycling from scrap can be a separate process where it is better feasible.

7.1.4. Recovering Iron Powder from Scrap

Iron powder is a basic raw material for the manufacture of powder metallurgy components of automobiles, appliances, farm and garden equipments, tools and business machines. Other applications include welding electrodes, flame cutting and scarfing, electronic, magnetic and chemical industries. Such demands have given incentive for the recovery of iron powder from ferrous scrap. There are four methods to recover iron powder from scrap, which have been reviewed by Ramakrishnan (1983).

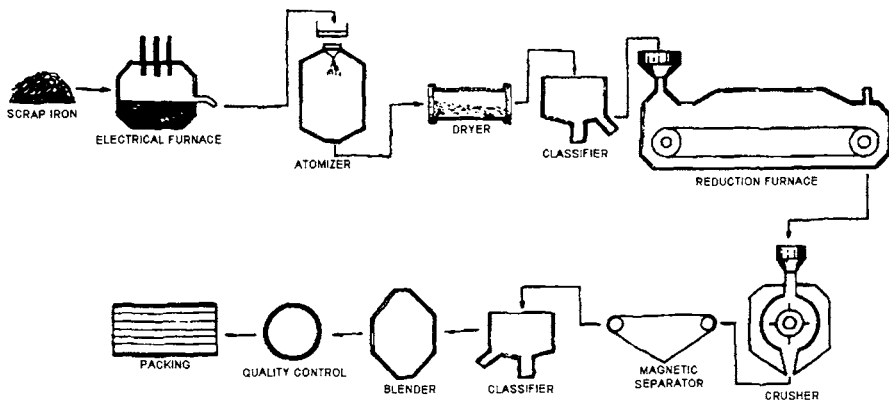


Figure 7.3. Flow sheet for the atomization of iron scrap to produce iron powder ((Ramakrishnan, 1983)

Atomization. In this process, a stream of molten metal produced from home, industrial or processed obsolete scrap, is broken up with high pressure air, water or gases, such as nitrogen or argon. A general flow sheet is shown in Figure 7.3. Iron powder is produced by direct high pressure water atomization of molten scrap. The powder is collected, dried and annealed. The non-magnetic materials, if any, are segregated in a magnetic separator. Atomization can also be used for producing high speed steel, stainless steel or special alloy steel powders. In these cases, it is preferable to use specially graded scrap and induction melting for producing the melt, which is subsequently atomized by nitrogen or argon to produce the powders. Considerable

savings in energy can be realized by making the melt from scrap (8.28 BTU per million ton) instead of the iron ore (23.12 BTU per million ton) (Ramakrishnan, 1983). (1 BTU = 1054.2 joules)

Chemical Methods. One of the most important chemical methods for the production of iron powder is direct reduction of the scrap (in the form of mill scale from iron and steel manufacturing processes) using gaseous or solid reducing agents. A typical flow sheet for the production of iron powder from mill scale is shown in Figure 7.4. The dried and ground mill scale is loaded in ceramic saggars using special charge heads, which are so designed that alternate sub-divisions can be filled with the mill scale and reducing agent, which is a mixture of dried and ground coke limestone. The loaded saggars are stacked and heated to about 1100 °C in a continuous tunnel kiln. The entire heating and cooling cycle takes a few days. The sponge iron is removed from the cooled saggars, crushed to powder, magnetically separated and subsequently reduced. The reduced powder is screened and blended depending upon the end use.

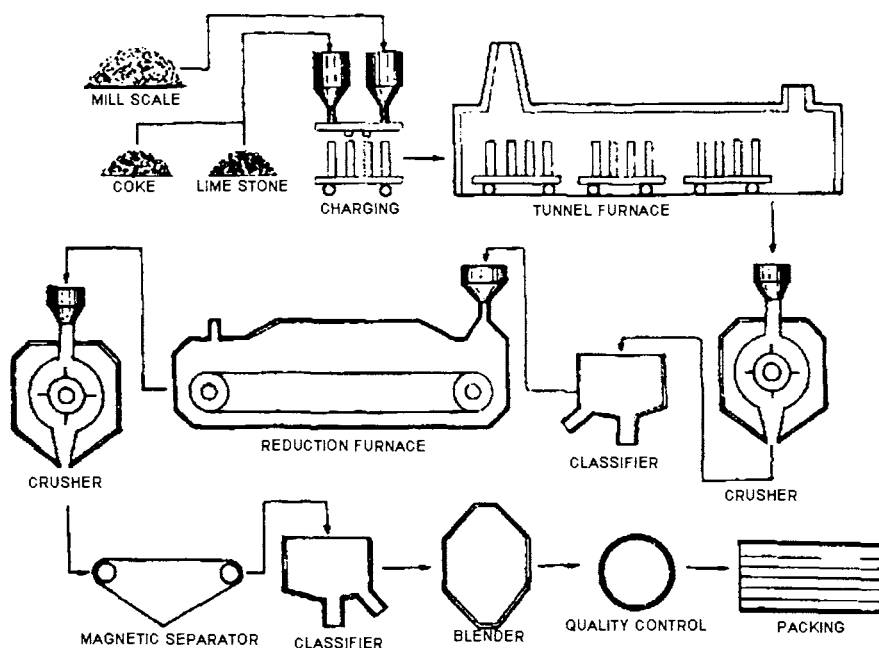


Figure 7.4. Flow sheet for reduction of mill scale to iron powder (Ramakrishnan, 1983)

Another chemical process has been developed to utilize low-grade scrap such as turnings, borings, tin cans and other types of ferrous scrap. The process consists of dissolving the scrap in hydrochloric acid, followed by evaporation and crystallization of the resultant solution to yield ferrous chloride crystals, which are dried, briquetted and converted to iron sponge by reduction in hot hydrogen. The hydrochloric acid produced from the reduction step is reused. Based on a 5-tons per day pilot plant, the production cost estimated makes the powder thus produced highly competitive with iron powders (Finlayson and Morrell, 1968).

Electrolytic Deposition. In this process, iron scrap is treated with hydrochloric or sulfuric acid to produce chloride or sulfate or a mixed chloride-sulfate electrolyte bath. Iron powder is produced by using a graphite or carbon anode or a stainless steel cathode. Generally, iron is deposited on the cathode as a brittle deposit, which is stripped, washed, dried, pulverized and annealed in a reducing atmosphere to soften the particles and to lower the oxygen content of the powder. The electrolytic process is expensive, but cost may be offset as it converts various forms of ferrous scrap into high quality iron powder.

Pulverization. These methods use cast iron turnings or machining swarf as the starting material. The machining chips are degreased, heavy pieces are removed by air separator, and the chips are hammer-milled to produce particles of less than 0.8 mm size. These chips are then impact-fractured by throwing them against a target surface by a high velocity stream. The powders are collected, classified and annealed (Vernia, 1973). In another method, the cutting fluid is separated from machining swarf and the cleaned and dried material is pulverized in a hammer mill at room temperature (Nakagawa and Sharma, 1977). Attempts have also been made to pulverize chips at cryogenic temperature (Daborn and Derry, 1988); but that can be considered only when value of the end products justifies the cost. See Chapter 3 for details on cryogenic comminution.

7.1.5. Intermediary Products and Waste Treatment

The source, characteristics and treatment practices associated with the various intermediary products and wastes generated by the steel-making industry are summarized in Table 7.2.

Table 7.2. Intermediary Products and Waste Treatment

Type	Process Source	Characteristics	Treatment/Reuse/Recycle
Spent Waste acid And pickle Liquor	Finishing	Non-metallic	Processed and recovered iron chlorides are used for phosphate removal. Neutralized with lime and land-filled.
	Pickling	Non-metallic, Hazardous waste	Neutralized with lime and land-filled. Processed and recycled for pickling or sewage treatment.
	Alkali cleaner	Non-metallic	Land-filled.
	Tin line	Non-metallic	Waste sludge is treated by an ion exchange process, chromic acid is recovered and recycled. Land-filled.
Spent Refractory	Melting	Non-metallic	Reused or processed and recycled. Land-filled or stockpiled.
Ingot hot Tops	Batch ingot Casting	Metallic	Metal is recovered magnetically and remaining material sold for use as roadbed aggregate.
Mill scale	Finishing	Metallic	Sintered and recycled.

Pickle liquor, or pickling sludge arises from the cleaning of steel using a hydrochloric

acid pickling process. The recovery processes are based on the recovery of chlorine from the ferrous and minor ferric chloride present in the spent liquor and from the residual hydrochloric acid. The spent pickle liquor is recycled by on-site acid regeneration systems.

Additional processes which are used to recover metals from surface finishing products, also applicable for treating pickle liquors are electrodialysis and ion exchange processes. They will be described under recycling of stainless steel.

7.1.6. Flue Dust, Slag and Sludge

These products, which are generated in many metallurgical processes will be discussed in Chapter 8.

7.2. Stainless Steel

Common grades of stainless steel scrap include stainless steel clips and solids containing alloying elements, nickel, chromium. These come from the manufacture of sinks, tanks, pipes, etc. Stainless steel turnings contain 16% chromium and 7% nickel.

7.2.1. Sorting and Preparation Technologies

Segregation and classification play important roles in the economics of steel production. The elements detrimental to carbon steel production, in particular, copper and tin are even more harmful in the applications of stainless steel, primarily because these alloys are used at higher temperatures and in more corrosive environments. The techniques used to sort and prepare stainless steel materials for recycling are described below.

Manual Sorting. This involves the removal of components from the scrap by hand. An example of where manual sorting and preparation are used is the removal of catalytic converters from scrap automobiles. Large items such as storage tanks and platforms must be cut to allow them to be charged into a furnace. This is done using torches, crushers, and shredders.

Magnetic Separation. This is used to separate the magnetic stainless steels and nickel from the non-magnetic stainless steels. It is, however, not generally used to separate stainless steel from iron and steel.

Baling and Compaction. Loose scrap and thin-walled low density scrap (tanks and tubing) are normally compacted by baling or briquetting. A baler is a heavy piece of equipment that uses up to three hydraulic rams to compress the scrap. In a briquetter, small scrap is compacted into pockets as it passes between two counter rotating drums. The use of bales and briquettes reduce transportation costs and facilitates the charging of the furnace.

Shredding. It is used to reduce the size of large stainless steel parts. Stainless steel found in automobiles is recovered from automotive shredder residue as described before.

Eddy Current Separation. Some non-ferrous metal separators utilize eddy current technology to recover the non-ferrous metals and stainless steels from shredder residue. Details are described before in Chapter 3.

Heavy Media Separation. It is used in some non-ferrous metal separators to recover the non-ferrous metals and stainless steels from shredder residue. Details are described in Chapter 3.

Sweat Furnace. This is used for the purpose of separating aluminum, zinc and lead

from stainless steels, which coexist in composite parts and to remove contaminants. It is described before (Section 7.2.1.7) and in Chapter 6..

7.2.2. General Description of Recovery Technologies

Stainless steel is produced in electric arc furnaces (EAFs). Charges to the EAF consist of various mixtures of scrap carbon steel, scrap stainless steel, and alloys (used to adjust the composition). Scrap carbon and stainless steels are charged to the furnace until the desired quantity of metal has been melted. The steel is decarburized by oxygen lancing, which also oxidizes a portion of the chromium going into the slag. The slag is reduced with ferrosilicon or ferrochromium-silicon master alloys, in order to recover the chromium and return it to the bath. The composition of the charge is adjusted by adding ferrochromium and ferronickel alloys. The melt is then cast into moulds, or directly processed into castings or other end use products.

While little refining is done during the melting of stainless steels, some adjustment of the steel's chemistry is carried out in the ladle. Ladle metallurgy is the treatment of liquid steel in the ladle. The principal objectives are, removal of sulfur, oxygen, hydrogen, and carbon; addition of ferroalloys with very high recoveries; and decrease or increase of liquid steel temperature to meet temperature specifications for continuous casting.

The finished steel from the furnace (basic oxygen or electric) is tapped into ladles. Most ladles hold all the steel produced in one furnace heat. Slag is allowed to float on the surface of the steel in the ladle to form a protective blanket. Excess slag flows from the ladle through a spout and is either collected in pots or allowed to run onto the floor, where it solidifies and is removed.

The following are some of the ladle-refining processes.

Ladle-without-cover – composition adjustment by sealed argon bubbling (CAS) process;
 - sealed argon bubbling process (SAB);
 - and argon-oxygen decarburization (AOD) process.

Ladle-with-cover -- Thyssen-Niederrhein (TN) process;
 -- Kimitsu Injection process (KIP); and
 -- Capped Argon Bubbling (CAB) process.

Vacuum Processes -- Stream degassing process;
 -- Rheinstahl Huttenwerke & Heraeus (RH) process;
 -- Vacuum-oxygen decarburization (VOD) process; and
 -- Dortmund-Hoerder (HD) process.

Brief descriptions of the various ladle refining techniques are as follows:

7.2.2.1. Ladle-Without-Cover

In these processes, argon gas is passed through liquid steel in a ladle to mix ferroalloys with the steel, homogenize the steel with respect to chemical composition and temperature, accelerate cooling, and remove oxide and sulfide inclusions. The use of argon in treating liquid steel in the ladle has greatly enhanced the flexibility of steel-making operations, significantly improving the surface and internal quality of the steel.

CAS Process. The Composition Adjustment by Sealed Argon Bubbling (CAS) process employs the enlarged chute or immersion tube, which is dipped into the liquid steel through which argon bubbles are emerging and pushing the slag away. The argon can also be injected into the liquid steel through a porous plug in the ladle bottom. Ferroalloys are added to the liquid steel in the ladle through the chute or immersion tube. This serves to decrease ferroalloy consumption as ferroalloys are added to the liquid steel under the protection of the argon gas that fills the immersion tube.

SAB Process. The Sealed Argon Bubbling (SAB) process is very similar to the CAS process, but a synthetic slag of lime, alumina and silica is placed on the liquid steel, inside the immersion tube, to produce clean steel.

AOD Process. In the Argon-Oxygen-Decarburization (AOD) process, the liquid steel is tapped from the furnace into a ladle and then pored into the AOD vessel. Either argon-oxygen gas mixture or pure argon is blown into the steel through tuyeres in or near the bottom of the vessel. The AOD process primarily removes carbon from stainless steel, and carbon and inclusions from carbon and alloy steels.

Scrap alloys consumed by the stainless steel industry include both in-house material and that purchased from dealers. The use of AOD ladle refining permits the use of 100 percent stainless steel scrap to be used. Superalloys can be placed into two categories: air-melted and vacuum-melted alloys. Air melting is cheaper and can accept recycled scrap. Vacuum melting is used to prevent the oxidation of alloying elements like aluminum, titanium and nickel which is a serious problem for these alloys.

7.2.2.2. Ladle-With-Cover

In these processes, argon is injected either through lances inserted into the steel or through porous plug in the ladle bottom. The injection lances are used in two processes designed to remove sulfur. In these processes (known as TN, Thyssen -Niederrhein and KIP, Kimitsu injection) it is very important to prevent the steel-making slag from accompanying the liquid steel as it is tapped into the ladle, as it contains iron oxide, which is detrimental to the removal of sulfur. In the TN process, either calcium silicide (CaSi) or magnesium is injected into the steel. In the KIP process, a mixture of 90% lime and 10% calcium fluoride is used. The ladle cover keeps air away, and should fit so closely that in the space above the steel is filled with argon, thus preventing oxidation. Both processes produce steel with low sulfur and oxygen contents.

CAB (Capped Argon Bubbling) Process. This is the best known ladle-with-cover process, which uses a porous plug for argon injection. Steel-making slag is kept out of the ladle and a synthetic slag (40% lime, 40% silica, 20% alumina) is added. The ladle is covered and argon bubbled through the porous plug and through the steel. Ferroalloys are added through a chute in the ladle cover. The process produces cleaner steel and requires less ferroalloy.

7.2.2.3. Vacuum Processes

In vacuum processes, liquid steel is treated by exposure to vacuum to decrease the hydrogen content to 2 ppm or less, which prevents hydrogen embrittlement in such steel products as rails and rotors for electrical generators. Vacuum also serves to remove carbon and add ferroalloys under nonoxidizing conditions.

Stream-Degassing Process. Stream degassing is accomplished by placing an empty ladle or mold in a tank. A ladle containing the molten steel to be degassed is set upon the

evacuated tank; the bottom of the ladle and the top of the tank are equipped with mating seals to exclude air. When the stopper rod of the tapping ladle is raised, molten steel flows through the nozzle, melts a metal diaphragm that seals the opening to the tank, and passes into the ladle (or mold) in the vacuum tank. As the stream of molten metal enters the evacuated space, it breaks up into tiny droplets exposing its surface to vacuum degassing. After the tank is purged, its internal pressure is raised to 101.3 kPa (1 atm) and the steel is removed and poured in the usual manner.

DH Process. In this process (Dortmund-Hoerder), a refractory-lined chamber, with one hollow leg or pipe extending from the bottom, is inserted into the liquid in a ladle. After the chamber is evacuated, liquid steel is moved up and down between the ladle and the chamber by raising or lowering. As the cycle is repeated 10-20 time, the liquid steel is exposed to vacuum each time it is drawn into the chamber.

7.2.3. Secondary Recovery of Superalloy Elements

The only commercial operation to recover superalloy elements from intermediary products and waste materials is INMETCO located at Ellwood City in Pennsylvania. The process consists of three basic steps: feed preparation, blending and pelletizing; partial reduction in rotary-hearth furnace; and smelting in an EAF and casting. (See Chapter 6 for description of INMETCO process).

The plant has the capacity to treat 50,000 tons per year of raw material to produce 20,000 tons per year of "pig-metal" (typically 8.5% nickel, 14.1% chromium and 69.5% iron). The processing costs are high and can be justified only when the alternative is disposing in hazardous waste landfills.

The materials treated at INMETCO include:

- Mill scale – resulting from the oxidation of stainless steel surfaces during processing operations.
- Grinding swarf – product of belt grinding of stainless steel sheet and strip.
- Nickel-cadmium batteries .
- Nickel-containing solutions – nitrate, sulfate, or chloride solutions of nickel from plating operations can be added during the pelletizing operation.
- Spent dolomitic brick – used as a slag additive.
- Spent chromium refractories and iron-chromium tailings in which the hexavalent chromium is converted to metallic chromium; magnesia is a slag additive.
- Dust collector bags from EAF baghouses.
- Superalloy wastes.
- Hexavalent chromium-containing rinse wastes.
- Plating liquids and cakes, containing nitric, hydrofluoric or hydrochloric acids. If sludge is produced at the steel mill by alkali precipitation, these are added into the pelletizing process.

The air emissions meet the state regulations. The water from a wet gas scrubbing system is treated to produce a cake containing lead, zinc and halogens. This is recycled to a secondary zinc producer. The slag is used as aggregate. No hazardous wastes are produced.

Application of the process to treat metallurgical dusts will be described in Chapter 8.

Hot Acidic Chloride Leaching/Hydrometallurgical Process. This process involves the following steps.

1. leaching – the metallic components of the alloy scrap are dissolved in a hot acidic chloride solution. The leach liquor typically contains 75 g/L nickel, 35 g/L chromium, 26 g/L iron, 14 g/L cobalt, 13 g/L molybdenum, 0.6 g/L manganese, 285 mg/L chloride and 1.5 g/L hydrogen ion;
2. adsorption of tungsten and silica by activated carbon;
3. molybdenum removal by solvent extraction using trioctylphosphane oxide (TOPO);
4. iron removal by solvent extraction using secondary amine;
5. cobalt removal by solvent extraction using tertiary amine;
6. chromium removal by precipitation;
7. nickel removal by precipitation.

For hydrometallurgical processing the scrap has to be degassed. Subsequent chloride dissolution of the scrap is used to recover a high grade calcium tungstate product from the leach residues. Iron, cobalt and manganese and nickel chlorides are subsequently recovered from the leach liquor by solvent extraction. Marketable cobalt chloride, manganese chloride and nickel chloride could be produced from the strip solutions.

Some of the applications of INMETCO in metal recycling from metallurgical dust will be described in Chapter 8.

7.3. Copper

Next to steel, copper is largest in tonnage and gross value. Used mainly in the electrical/electronics and plumbing industry. Recycle materials are used wire and pipe. Common grades of copper scrap include mixed brass and copper turnings, clips, electronic scrap, some containing precious metals, copper catalysts, copper wire and scrap obtained from discarded sheet copper, gutters, kettles, boilers, etc. Copper is also recovered from copper leach effluents, copper cement, drosses, slags, flue dust and acid plant blowdown slurry or sludge. They will be discussed in Chapters 8 and 9.

The recycling of copper scrap is accomplished either by “direct-use recycling” or by smelting and refining. Direct-use recycling involves the return of the scrap to the original source for reprocessing, for example, brass or tube mills. Brass and bronze scraps generally find their way back to ingot makers who turn the segregated feeds back into casting alloys for resale to foundries. Direct-use recycling eliminates the need for smelting or refining since the scrap is identifiable and will be prepared for reuse in the same application. It accounts for 41 percent of the total consumption in the U.S. and 37 percent in Japan (*CANMET*, 1993, p. 63)).

Copper scrap from the electronics, industrial, and communications industries is becoming more prominent and does not lend itself to direct use recycling. Scrap from these sources requires smelting and refining because of the higher concentrations of impurities (precious metals, plastics, and other metals). The collection, sorting and segregation of this scrap material is much more complex than for direct-use recycling.

Electronic scrap recycling is driven by the precious metal, mainly gold content. The gold content has, however, been declining over the past decade due to new technologies, which require less gold to achieve the same function. Some manufacturers have begun to substitute gold with palladium and other metals of lower cost. Dismantling of electronic components to remove copper bus bars, aluminum heat sinks, and steel cabinetry, results in a product that contains on average 25 percent copper to 0.007 percent (70 g/ton) gold.

In the last 20 years telephone companies have replaced electromechanical switching stations by digital stations. This modernization generates large volumes of low-grade

precious metal scrap, which is typically processed by copper smelters. The increasing use and ultimate availability of telecommunications systems for disposal will tend to offset the decreased precious metal content of electronic scrap.

Industrial copper scrap includes roofing, wire, cable, copper clad steel, automotive radiators, and automotive shredder residue (ASR). Copper-bearing residues and slags are by-products from numerous industrial processes. Concerns of industry about the liabilities associated with potential site contamination and the impact of more stringent environmental regulations, will continue to promote the recovery of copper by recycling of copper-bearing wastes.

7.3.1. Scrap, By-Products and Waste

The types of copper being recycled can be classified into two main grades: copper scrap and copper byproducts, and waste. The form of the copper scrap or waste to be recycled has a bearing on the technologies used and on the industry sector with capacity of recycling of material. Institute of Scrap Recycling Industries (ISRI) recognizes over 50 types of copper and copper alloy scrap. The major types are described in Table 7.3.

The collection, classification and reprocessing of copper-bearing scrap or secondary materials has developed to match the various steps involved in producing refined copper from primary sources, that is, using the basic steps listed below:

- sorting and preparation techniques to prepare scrap for further processing;
- melting in a furnace (shaft, etc.) to yield 70 to 90 percent copper (black copper),
- oxidation-refining in a converter to yield 96 to 98 percent copper;
- furnace refining to yield 98 to 99.5 percent copper and casting anodes; and
- electro-refining of anodes in a tank house to yield greater than 99.9 percent copper.

Often, supplementary processes (scrap preparation, scrap melter, scrap converter and scrap anode furnace) are used to prepare the scrap materials for acceptance into these unit operations. Generally, the secondary material grades match those of the primary process.

7.3.2. Sorting and Preparation Techniques

Scrap plumbing materials are usually fairly clean and require virtually no sorting. Copper found in electronic, automotive, and communication scrap, however, is accompanied by many other materials, which require separation. The following are some of the techniques for separating copper from other materials.

Manual Sorting. This involves the removal of components from the scrap (radiators, electronic components) by hand. The plastic or metal radiator end-tanks are typically cut off the radiator using a bandsaw. Some automobile and appliance dismantlers remove the wiring harnesses for sale to copper recyclers. Electronic components (computers, telephones, etc.) are disassembled to recover parts, which can be sold for reuse, and to recover materials for recycling. Printed circuit boards and other components containing copper and precious metals are sold to recyclers for further processing.

Shredding. Sometimes copper wiring is removed from scrap automobiles and appliances prior to shredding. The majority of the copper is, however, recovered from automotive shredder residue (ASR) as described before. Details will be described in Chapter 8.

Eddy Current Separation. Some automobile shredders employ eddy current technology to remove copper from ASR. Some non-ferrous metal separators utilize eddy current technology to recover the non-ferrous metals, including copper, from ASR.

Table 7.3. Main Categories of Copper Scrap and Copper Alloy Scrap Recognized by ISRI.

Type	Description
No.1 Copper Wire	Clean, untinned, uncoated, unalloyed copper wire and cable, not smaller than No.16 B&S wire gauge, free of burnt wire (brittle)
No.2 Copper Wire	Miscellaneous, unalloyed copper wire having a nominal 96% copper content (minimum 94%) as determined by electrolytic assay. Should be free of the following: excessively leaded, tinned, soldered copper wire; brass and bronze wire; excessive oil content, iron, and non-metallics; copper wire from burning, containing insulation; hair wire; burnt wire (brittle); and should be reasonably free of ash.
No.1 Heavy Copper	Clean, unalloyed, uncoated copper clippings, punchings, bus bars, commutator segments, and wire not less than 1/16 of an inch thick, free of burnt wire (brittle); but may include clean copper tubing.
No.2 Copper	Miscellaneous, unalloyed copper scrap having a nominal 96% copper content (minimum 94%) as determined by electrolytic assay. Should be free of the following: excessively leaded, tinned, soldered copper scrap; brasses and bronzes; excessive oil content, iron, and non-metallics; copper tubing with other than copper connections or with sediment; copper wire from burning, containing insulation; hair wire; burnt wire (brittle).
Light Copper	Miscellaneous, unalloyed copper scrap having a nominal 92% copper content (minimum 88%) as determined by electrolytic assay and shall consist of sheet copper, gutters, downspouts, kettles, boilers, and similar scrap. Should be free of burnt hair wire; copper clad; plating racks; grindings; copper wire from burning, containing insulation; radiators; fire extinguishers; refrigerator units; electrotype shells; screening; excessively leaded, tinned, soldered scrap; brasses and bronzes; excessive oil, iron, and non-metallics.
Refinery Brass	Minimum of 61.3% copper and maximum 5% iron and consists of brass and bronze solids and turnings and alloyed and contaminated copper scrap. Shall be free of insulated wire, grindings, electrotype shells and non-metallics.
Composition or Red Brass	Red brass scrap, valves, machinery bearings and other machinery parts, including miscellaneous castings made of copper, tin, zinc, and/or lead. Should be free of semi-red brass castings (78% to 81% copper); railroad car boxes and other similar high-lead alloys; cocks and faucets; closed water meters; gates; pot pieces; ingots and burned brass; aluminum, silicon and manganese bronzes; iron and non-metallics.
Yellow Brass Scrap	Brass castings, rolled brass, rod brass, tubing and miscellaneous yellow brasses, including plated brass. Must be free of manganese-bronze, aluminum bronze, unsweated radiators or radiator parts, iron, excessively dirty and corroded materials.
Machinery or Hard Brass Solids	Copper content not less than 75%, tin content not less than 6% and lead content not less than 6% or more than 11% and total impurities, exclusive of zinc, antimony and nickel no more than 0.75%. Antimony content not to exceed 0.50%. Free of lined and unlined standard red car boxes.
Yellow Brass Rod Turnings	Strictly rod turnings, free of aluminum, manganese, composition, Tobin and Muntz metal turnings; not to contain over 3% free iron, oil or other moisture; to be free of grindings and babbitts; to contain not more than 0.30% tin and not more than 0.15% alloyed iron.

Heavy Media Separation. Some automobile shredders employ heavy media separation technique to remove copper from ASR. Heavy media separation is also applied to recover the non-ferrous metals, including copper, from ASR. Details are found in Chapter 3.

Wire Chopping. A good source of high grade copper is wire and cable scrap. The common types of wire from which copper is recovered, include:

- building wire, utility wire, and power cable;
- communication cable of various kinds;
- auto harness wire and appliance wire; and
- special construction wires such as shipboard cable, mine cable, etc.

The basic processes involved in the chopping of wire are as follows:

- shearing
- shearing – to allow smooth feeding to the chopping equipment;
- primary size reduction – down to 19 to 32 mm size;
- magnetic separation of ferrous metals by an overhead magnet mounted over a - vibrating conveyor;
- secondary size reduction – down to a size smaller than that achieved by secondary size reduction.;
- sizing – a vibrating screen is used to produce three size fractions: coarse, fine and dust; and
- air separation – each size fraction is processed to recover clean metal, liberated metal with some insulation, which is recycled back to the separator, middlings with unliberated wire, which is sent for tertiary size reduction, and clean insulation.

Bag-houses and cyclones are used to collect the dust generated by the wire chopping process. Lead exposure and contamination of site cause potential problems that impact the wire chopping industry. Lead can be found in the form of solder, pigments, and stabilizers in the plastic insulation, protective sheathing, and electromagnetic interference (EMI) shielding.

The copper recovered from the chopping operation is typically fed to brass mills, tubing mills, and wire mills; with lesser amounts being consumed by refineries and specialty consumers. In the specialty markets, copper choppings or hydraulically briquetted material have supplemented, and in some instances replaced, virgin copper (for cathodes ingot or shot).

Cryogenics. This involves the freezing of components with liquid nitrogen or carbon dioxide to below its transition temperature, where it becomes brittle. The item is then impacted to shatter and separate the numerous constituent materials, after which, conventional recovery techniques are used to separate the metals. The technology can be applied to such items as fractional h.p. motors, starters, generators, transformers, circuit boards, electronic scrap, telephone switch gear, electrical meters, plastic encased electrical components, etc. Although cryogenics has been proven to be technically feasible, it is currently a very high cost process. (See Chapter 3 for description of Cryogenic comminution).

7.3.3. Copper Scrap Processing by Physical Separation Technique

Most old scrap occurs in some form of wiring, which makes it feasible to process it by physical separation techniques used in mineral processing (explained in Chapter 3).

The copper thus recovered is remelted and cast into rod or billet for further

processing' described in the following Section. The degree of refining required depends on the purity of the recovered copper stream.

7.3.4. Secondary Melting Technologies

For the recycling of copper, the melting furnaces generally accept the following lower grade copper bearing materials:

- residues,
- slimes (primary industry only),
- primary concentrates (primary industry only),
- electronic scrap,
- other low grade scrap,
- slag from the conversion or other refining and melting steps,
- flue dusts.

The charge is adjusted to a particular copper content to suit the process and is reduced usually in a shaft furnace, reverberatory furnace, top-blown-rotary-converter (TBRC) or in the Noranda reactor. Each one is described below. The charge to a secondary copper smelter is variable both in composition and physical nature. The types of copper-bearing materials processed include: blocks of blister containing more than 95 percent copper and weighing several tons; industrial by-products such as flue dust, slag, and black copper containing 70 to 90 percent copper; and bales of automobile radiators, household plumbing, electrical wiring.

Shaft Furnace. The low shaft, water jacketed shaft furnace is generally efficient because of its ability to transfer heat to the cold charge and its ability to melt virtually any solid material, regardless of composition. Shaft furnaces, however, tend to be somewhat labor intensive and not as environmentally clean as more modern furnaces. As selective melting is not possible, in addition to copper, virtually all metals (iron, zinc, lead, tin and the precious metals) are collected in the final product.

Reverberatory Furnace. These are used to process higher grades of copper scrap. They are reducing and somewhat less efficient in terms of metal recovery; iron and aluminum are not tolerated. Oxygen enrichment of the combustion burners results in generally high thermal efficiencies. The furnaces can be further equipped to perform limited refining by oxidation (fire-refining) followed by metal reduction to permit anode casting. Such operations are restricted to the melting of high-grade copper scrap only.

Top-Blown-Rotary Converter. TBRC has found application at two secondary smelters, one in the U.S. and one in Belgium. These furnaces combine in a single furnace the ability to melt, oxidize (convert), and reduce the charges. In theory, all operations from smelting to anode casting can be conducted in a single furnace. In practice, separate furnaces are used for each particular operation. It is also possible to recover metal or oxide concentrates of tin, lead, and zinc.

Noranda Reactor. The Noranda continuous reactor developed at the Noranda Technology Centre and the Horne Smelter (Quebec) combines flash smelting, (also called autogenous smelting; see chapter 6 for details) with simultaneous bath injection of oxygen-enriched air. It produces a copper sulfide matte with 70 percent copper content as well as precious metals found in the scrap material.

Figure 7.5 is a typical flowsheet for processing wire and cable (Sullivan, 1985). The Illustration in Figure 7.6 shows a "hierarchy" of vessels used to remelt copper scrap. The

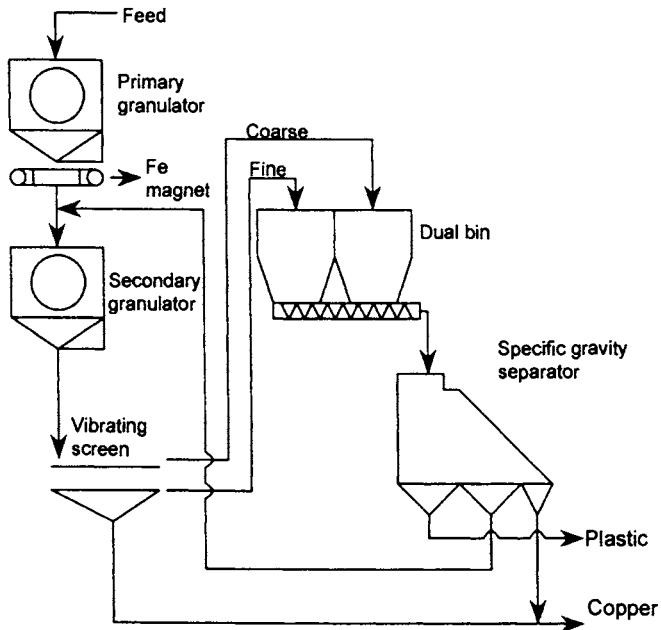


Figure 7.5. Schematic flow diagram for the processing of scrap wire (Sullivan, 1985)

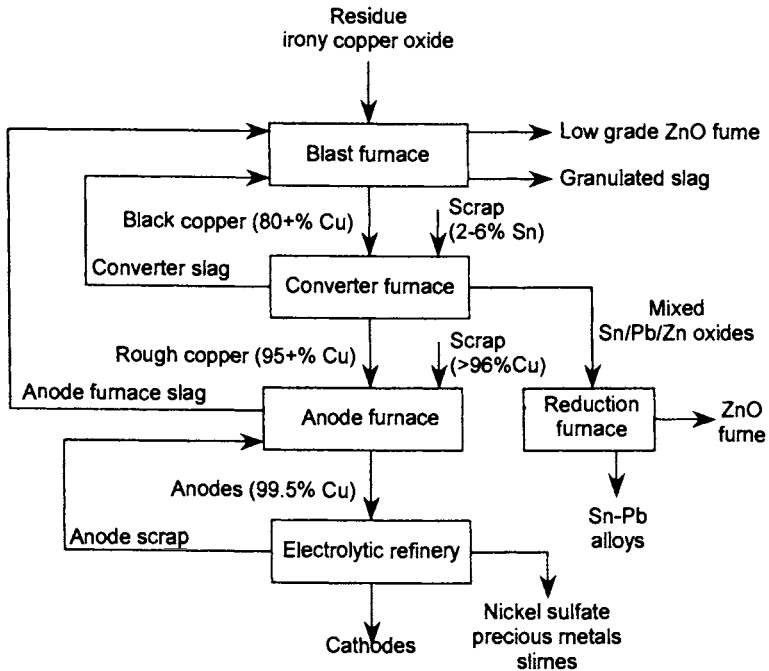


Figure 7.6. Flowsheet for copper scrap treatment (Nelmes, 1987)

blast furnace at the top is used to process the lowest grade scrap.; TBRCs are also used instead. This produces molten “black copper”, which is converted to blister-grade copper in a converting furnace. The “rough copper” is then fire-refined and electrorefined.

7.3.5. Copper Recovery by Smelting-Reduction Operation

The Ausmelt furnace described in Chapter 3 has been extensively used for recycling copper from secondary materials. Metal scrap is smelted at 1250 °C with fluxes and coal used as reducing agent. This produces black copper containing 80-90% Cu., a fume containing high levels of zinc and lead and an environmentally safe slag containing <1% copper. Furnace exhaust gases are generally ducted to an evaporative cooler before the dust is collected in a baghouse. The slag generated is tapped from the furnace and either discarded or converted to useful products like construction aggregates. (see Chapter 8).. The dust containing led, zinc and may be used as a secondary source of lead, zinc and tin; see Chapter 6). The black copper can be converted to >97% product. A flowsheet of continuous operation is schematically represented in Figure 7.7.

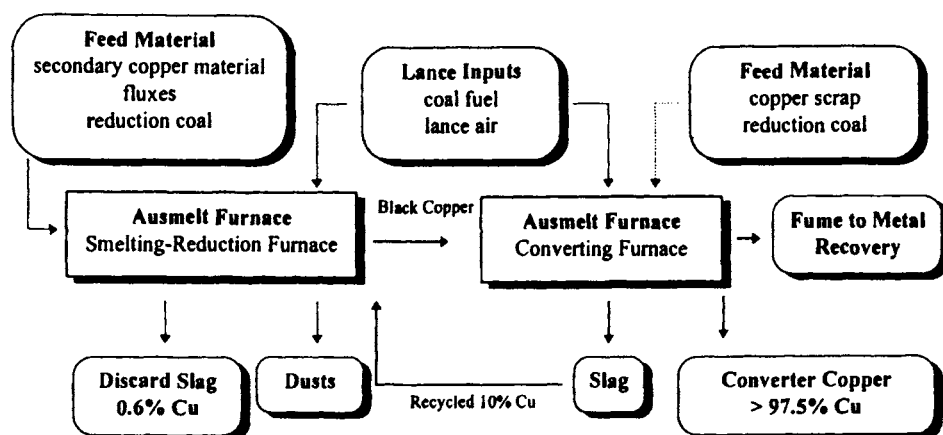


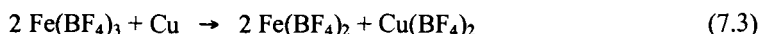
Figure. 7.7. Continuous production of converter copper from secondary copper material (Sofra *et al.*, 1997)

7.3.6. Electrochemical Method to Recover Copper from Alloy Scrap

In the conventional method of refining copper, used for many years, the copper scrap is melted in a converter or directly in an anode furnace, and cast into a massive anode. The anodes with a copper content of 93% are suspended in cells filled with sulfuric acid-based electrolyte, containing 130-200 g/L sulfuric acid and 15-50 g/L cupric ions. Cathodes consist of a thin sheet of copper, which is negatively charged. When a voltage is applied, copper passes into solution, while other elements, like precious metals or elements forming insoluble compounds such as lead, end up in an anode slime. The lead content in the anode is critical because if it exceeds 0.2-0.3% the anode surface gets passivated by lead sulfate. High purity copper is deposited on the cathode.

The pyrometallurgical processing of scrap for producing anode generates intermediate products like flue dust and metal-rich slag, which have to be melted down under reducing conditions. It is necessary to process those intermediate products by

additional steps. Efforts to eliminate the pyrometallurgical processing of scrap has led to the development of a new process for direct refining of small size copper scrap. It is called **Ecuprex** process (Olper and Maccagni, 1995). In this process, the copper scrap is solubilized outside the electrolysis cell by ferric fluoborate solution with free fluoboric acid. The reaction is represented by



During the leaching, lead and tin, which have lower potential than copper, go immediately into solution. The lead is precipitated as lead sulfate with calculated amount of sulfuric acid and the tin is oxidized to stannic hydroxide by ferric ions. The insoluble stannic hydroxide, $\text{Sn}(\text{OH})_4$, precipitates in the acidic solution. The copper bearing solution with lead sulfate and stannic hydroxide precipitated, leaves the leaching drum and is filtered in a filter press. The clean copper solution is fed to an electrowinning cell with two compartments, separated by a microporous polyethylene diaphragm, with an insoluble graphite anode and a permanent stainless steel cathode. Copper is deposited in the metallic form at the cathode, while ferrous ions are oxidized at the anode regenerating ferric fluoborate. The electrode reactions are,

At cathode, $\text{Cu}(\text{BF}_4)_2 + 2\text{e}^- \rightarrow \text{Cu} + 2 (\text{BF}_4)^-$

At the anode, $2 \text{Fe}(\text{BF}_4)_2 + 2\text{BF}_4^- \rightarrow 2 \text{e}^- + 2 \text{Fe}(\text{BF}_4)_3$

Overall reaction, $2 \text{Fe}(\text{BF}_4)_2 + \text{Cu}(\text{BF}_4)_2 \rightarrow \text{Cu} + 2 \text{Fe}(\text{BF}_4)_3 \quad (7.4)$

The hydrometallurgical process has important advantages of this process are: (1) by forming the cupric ion, the fluoboric acid favors the formation of low grain, compact, and hence purer deposits; (2) by strongly complexing the ferric ions at the anode, the fluoboric bath prevents migration through the diaphragm into the cathode compartment; if this occurs, the dissolution of deposited copper would cause a dramatic drop in the current yield. The high quality of the copper cathode (99.5%) and very low environmental contamination are other significant benefits.

7.3.7. Recycling Copper from Scrap by Cold Compression Technology and Electrorefining

In this process, the scrap is granulated to reduce down to 4 cm size and a knife mill having a cyclone for powder pulling down with a final wet vibrating screen to separate plastic from copper. The granulated scrap is then cold compressed by a hydraulic press having a load of 150 tons and quenched and tempered steel die. The product is made into a cylindrical shape anode with a diameter of 25 mm and a weight of 35 g (Lupi and Pilone, 2001). Electrorefining is done in a synthetic electrolyte containing 40 g/L Cu and 180 g/L sulfuric acid. A high grade copper sheet is used as cathode. The copper from the anode is electrochemically oxidized, dissolves in the electrolyte and deposits at the cathode. Lupi and Pilone (2001) have obtained high grade copper by electrodeposition. The method avoids any thermal operation, with potential economic and environmental benefits. The process requires readily available sulfuric acid in the electrolyte, much less expensive than the fluoboric acid used in the Ecuprex process described before. However, as the impurities from the copper scrap get accumulated in the electrolyte, a large quantity of it has to be bled off and purified. The process is still in development stage.

7.3.8. Recovery of Copper from Printed Circuit Board Scrap

Printed boards consist of laminated copper sheets and glass fiber sheets with external coating by solder (40% lead, 60% tin). In the manufacturing process, substantial quantities of borders and reject boards become scrap. The scrap is generated at many locations that range from small and large independent printed circuit board manufacturers to captive shops in large companies. Because of the solder coating, the scrap is classified as a hazardous waste as it is found to contain 5 mg/L of lead in the extract. Handling of such waste and shipment to hazardous waste land disposal facilities is often very expensive. Some generators have investigated the feasibility of recycling the printed circuit board scrap at a copper smelter, but this is not considered to be the most effective solution because shipment to, and use at, smelter may become subject to hazardous waste regulations and may be discontinued at any time. The removal of lead would allow the scrap to be reclassified as a non-hazardous waste, which may be disposed at local landfill sites at nominal cost. The scrap, however, contains as much as 45% copper; there is thus great incentive to recover copper as well as lead and tin for recycling as that would lead to a significant reduction of the industrial waste.

An electrodisolution method has been developed by Pozzo and coworkers (1991) to remove solder coatings from printed board scrap to facilitate the recovery of copper. Rotating trommel screen baskets, each 20 cm long, and made of stainless or mild steel are used as the anode and a semi-cylindrical shaped sheep of stainless steel as the cathode in the electrolyte cell. The anode is rotated with an electric motor at 40 rpm. The electrode setup and the electrolyte solution are placed inside a rectangular container made of polypropylene of capacity about 22 liters. Sodium hydroxide is found to be the right electrolyte as it dissolves both lead and tin rapidly. Eleven liters of 1 M solution is used. Samples of printed circuit board scrap with a bulk weight of 500 g are charged into the basket anode. With a cell voltage of 2 V both tin and lead dissolve rapidly and selectively from copper. An increasing rotation speed of the reactor basket improves the dissolution rate, while the percentage extraction of lead and tin remains nearly the same even when an increased amount of scrap is charged. Power consumption in the removal of lead averaged 97 MJ (27 kWh) per ton of the charge.

Printed board scrap could readily be delaminated by roasting at 325-350 °C for 15-30 min. During roasting, bromine appears to evolve, which necessitates the scrubbing of the exhaust gas. The delaminated copper and fiber sheets could be separated by gravity separation or by flotation. With the roasted and delaminated copper sheets, however, lead can be easily removed by electrolysis in 1 M sodium hydroxide solution, while tin is not removed even after 5 h electrolysis. Lead and tin-free delaminated copper scrap could, therefore, be produced by electrodisolution of the solder coating followed by delamination through roasting and by gravity separation or by flotation. The use of delaminated glass fiber may have potential use in construction industry, or it may be disposed off by an environmentally acceptable route.

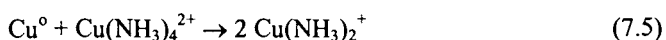
A process to convert printed circuit boards to a copper-nickel-tin alloy and a mixed oxide containing mainly lead and zinc and an environmentally acceptable slag with low metal content, which can be used in construction industry has been described by Bernardes and coworkers (1997). The feed material is heated in a crucible furnace, equipped with a top blowing lance and a waste gas post-incineration. The thermal treatment may be done in one heat or two different process steps by raising the temperature. The two stages are the incineration at 700 °C and the melting at 1250 °C.

The second step comprises heating up to the melting point, burning the semi-coke and volatilization of lead and zinc. The waste gases produced are cleaned in a scrubber.

Dissolution of copper from rejected printed wiring boards by bioleaching has been described by Nakazawa and coworkers (2002). This is done by using a strain of *Thiobacillus ferrooxidans* (see Chapter 5) isolated from an acid mine water at an abandoned mine and cultured in 9K medium of Silverman and Lundgren (1959); (see Chapter 5 for explanation). The rate of leaching and the yield of copper in solution is about 50% in 250 hrs., but both rate and yield are greatly enhanced in presence of ferric ions. With 600 mg/L ferric ions (as ferric sulfate) about 75% copper is leached in 150 hrs. The ferric ions oxidize copper metal to cupric ions and are then reoxidized in the presence of thiobacillus ferrooxidans. Thus, the ferric ions function as catalyst enhancing the rate of bioleaching.

7.3.9. Recovery of Copper from Electronic Scrap

Copper in the scrap is leached as cuprous ammonium complex. Leach solution is made of cupric sulfate, ammonia and ammonium sulfate. The cupric ammonium complex produced oxidizes the metallic copper in the scrap forming cuprous ammonium complex:



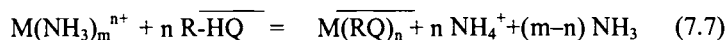
After solid-liquid separation, the solution is purified by a 2-step process comprising cementation and solvent extraction to selectively remove silver, zinc, nickel and cobalt. The purified solution goes to electrowinning where cuprous copper is oxidized the anode to the cupric state and copper is recovered at the cathode. The spent electrolyte from electrowinning is recycled back to the leaching circuit. The process is operated at an ambient temperature (25 °C) and under nitrogen atmosphere.

A hydrometallurgical process to recover copper and precious metals from electronic scrap has been developed by Koyama and coworkers (2003) and Alam and coworkers (2004). Flowsheet of the process is shown in Figure 7.8.

Iron and aluminum in the scrap remain insoluble as these metals do not form complexes with ammonia. However, some other metals including silver, zinc, nickel and cobalt form ammonia complexes and dissolve as impurities in the leach liquor. Silver is removed by cementation by copper, which is the ore electropositive element. Complete cementation is achieved in 30 minutes at a feed molar ratio of $\text{Cu}^0/\text{Ag}^+ > 6$. The cementation reaction is represented by



Other impurities, cobalt, nickel and zinc are removed using LIX 26 extractant, which is an oxine containing 7-tetrapropylene-8-hydroxyquinoline; see Chapter 4 for its chemistry. This is cationic exchange chelating extractant and extracts the metals probably by cationic exchange mechanism as represented in the equation,



where R-HQ denotes LIX 26 and bar represents organic phase.

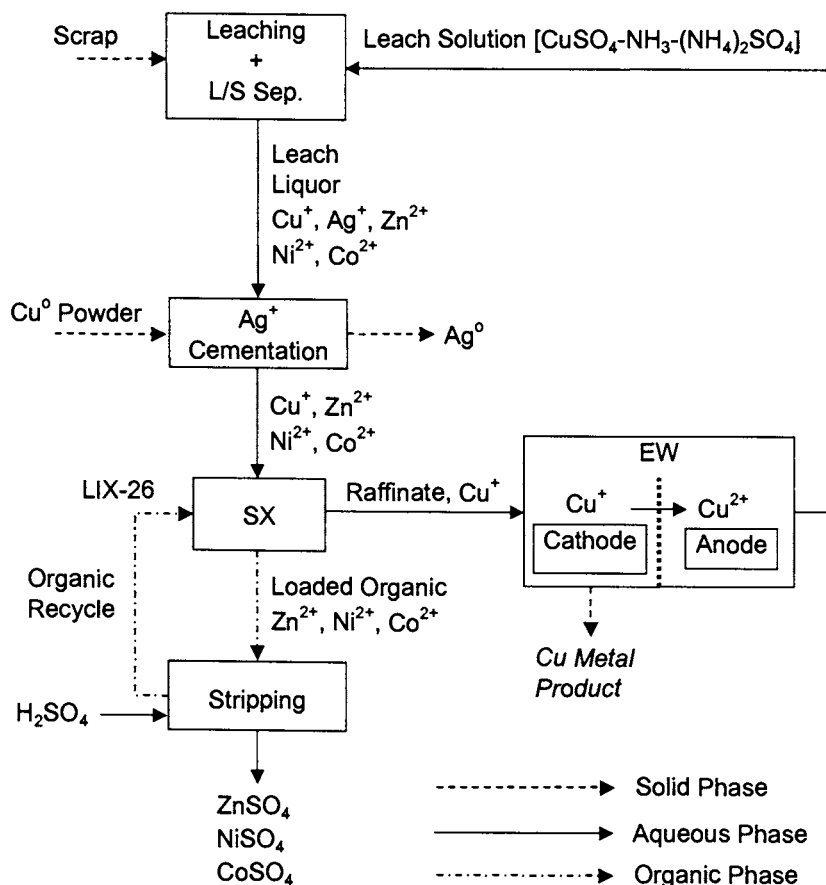


Figure 7.8. Hydrometallurgical process for the recovery of copper from electronic scrap (Alam *et al.*, 2004)

Following the removal of impurities copper metal is recovered by electrodeposition using copper plate as cathode and platinum anode.

Kinetics of leaching of copper and other base metals from electronic scrap containing gold and palladium has been described by Brandon and coworkers (2002). They found that the rate of leaching is governed by mass transport with respect to dissolved chlorine. The activity of chlorine for copper leaching is lowest; About 98% of copper, tin and lead are leached in 500 minutes, while 80-85% of the noble metals silver, palladium and gold in 60 minutes.

7.3.10. Recycling Copper Using Particle Shape

This is a novel technique specially applicable to recovery of copper from cables Huang *et al.*, 1995). As copper wire has elongated shape, it could be removed from the other materials by a particular type of sieving.

Under vigorously vibrating dry sieving, copper wire, with diameters less than the opening dimension of the sieve, would readily pass through the opening of the sieve. Little of the other material would pass. Thus a relatively clean separation of the copper wire could be made. For the wire to pass through the sieve opening, it is thrown into the air to make it rotate and land in a semi-vertical position with one of the wire ends in a sieve opening. The wire then works its way through the sieve. The screen is of the shaking vibratory type with an amplitude of vertical movement varying from 0.5 to 30 mm. The movement amplitude and intensity depend on the grain size.

This method has been used to separate a cable containing a few lead particles. It is illustrated in Figure 7.9. Copper wire is separated from lead materials by vigorously vibrating screening for 115 minutes. Most of the copper wire penetrates through the opening of the sieve (1.4 mm) and collects as undersize product. Lead materials are + 1.4 mm and separated on the screen. High grade (92.9%) copper wire is recovered, with percent recovery, 91.9.

If the difference of shape and size between copper and lead particles is small, direct shape separation using vibrating screening may not be effective. In such cases, the mixture of copper and lead particles is classified into narrow size classes, first by circulating screening (without vertical vibration). Each class is subjected to a lead grain flattening process using a ball mill. By this process, and by virtue of the different ductility of the two metals considered, a diversification of particle shape is obtained. The copper wires retain their original elongated shape, while the lead particles are significantly flattened until they become nearly laminar. Thus, the separation by vigorous vibrating screening is achieved, as described before. The process is schematically represented in Figure 7.10. The sample is classified into class sizes ranging from 2 to 0.5 mm, which increases the treatment efficiency. The + 2 mm fraction is a mixture of copper and lead, while the fraction below 0.5 mm is final lead product. The other classes are separated by vibrating screening for about 15 minutes yielding copper and lead products. The process still leaves large quantity of mixed materials not separated from each other. This mixture is flattened using a ball mill, which produces a mixture of flattened lead plates and copper granules. The lead plates are separated from the mixture by vibrating screen. The process could be repeated to achieve final separation depending on demand for the product and the cost. Although lead concentrate is of high grade, some non-lead particles may be locked with the lead.

One of the difficulties in shape separation using a stacked vibrating sieving machine is choking or clogging. U-shaped wire particles often spend a longer time to pass through the openings of the sieve. More often, they are caught by the sieve cloth or hang themselves to the grids. By reversing the sieve and briefly sieving, a small high grade copper concentrate may be produced while cleaning the sieves. Rotating screening is not a difficult design and the method can be adopted for industrial application. The difficulty will be to know, how long and how deep it would take to clean the screen cloth.

In another method, in addition to circulating screening, copper wire products can be further upgraded by shaking in a yank. Fine contaminant particles find their way down through the gaps between wires due to degradation. The process is schematically shown in Figure 7.11. It also includes steps to remove plastic components of the cable by heavy medium separation, which is usually an aqueous solution of calcium chloride, whose specific gravity could be regulated from 1.1 to 1.6.

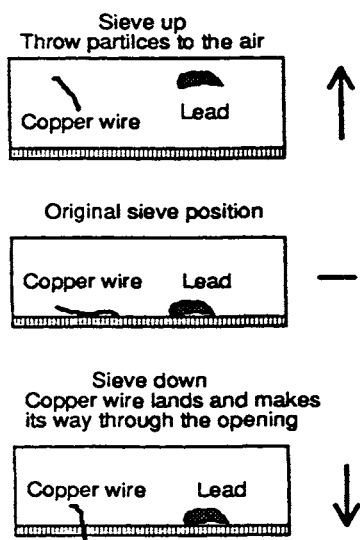


Figure 7.9. Separation of copper wire from a lead particle by vibrating screening (Huang *et al.*, 1995)

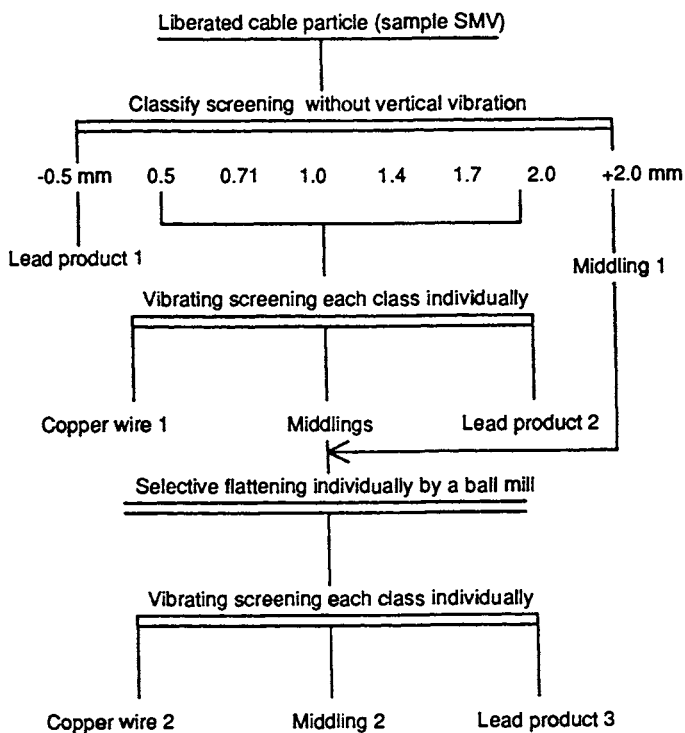


Figure 7.10. Flow sheet for treating copper and lead particles with similar shape and size

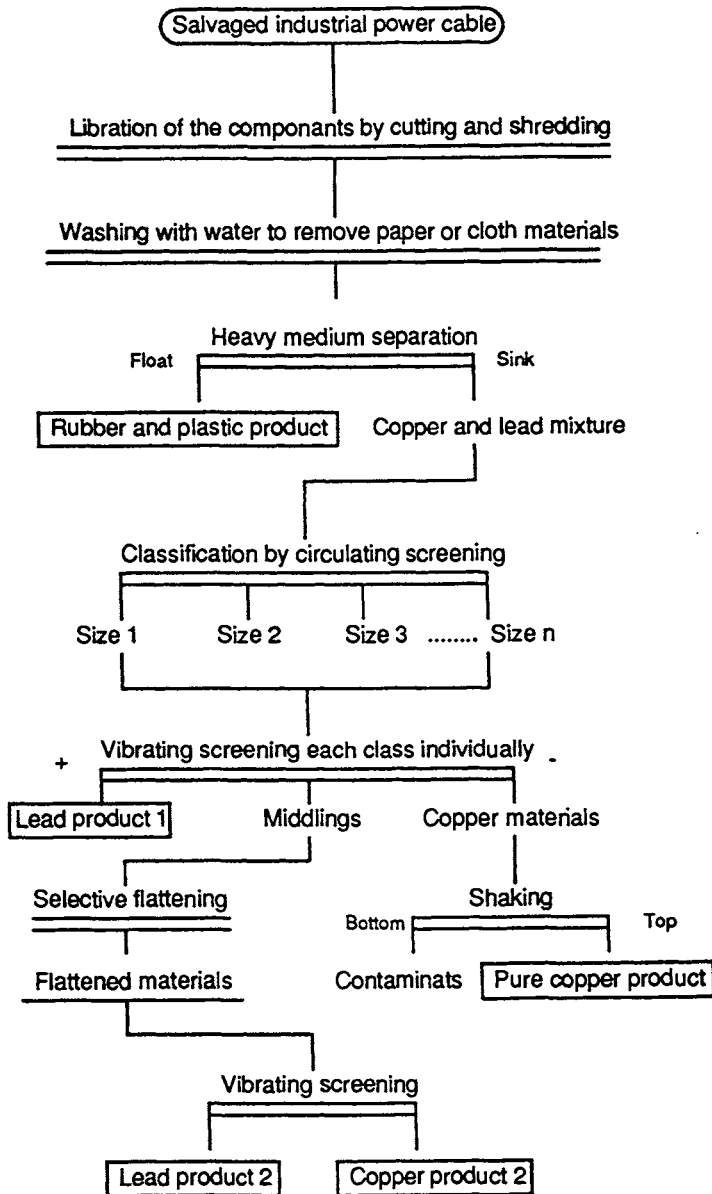


Figure 7.11. Separation process for recycling salvaged industrial cable (Huang *et al.*, 1995)

7.4. Lead

Lead is relatively small in tonnage and price is modest. Most lead is used for automobile batteries (~90%). Other traditional uses in the chemical industry, construction, soldering, anchors, and shot have all virtually disappeared. Lead-acid batteries constitute the largest market for lead, representing over 60% of the total lead

consumption. In the late 1980s approximately 30 percent of batteries were acquired through take-back programs; it has since gone to over 60 percent. Through legislative compulsory recycling, by prohibiting their disposal in landfills or by incineration, and by providing tax incentives to battery recyclers, by subsidizing the transportation costs of spent batteries, more than 90 percent of spent batteries are now being recycled in the western world. Because of lead's corrosion resistance, it is available for re-use after many decades. This has led to a significant increase in the share of global demand met by secondary sources. Currently, virtually all recyclers in the U.S. produce pure lead as well as the lead-calcium alloys, whereas recyclers outside the U.S. tend to produce the alloys only.

7.4.1. Scrap, Waste and By-Products

The types of lead being recycled can be classified into two main grades: lead scrap, lead by-products and waste. The form of the lead scrap and waste to be recycled influences the technology(ies) used and on the industry (primary or secondary) that has the capacity to recycle the material.

The common grades of lead scrap include:

- used lead acid batteries,
- soft lead scrap,
- mixed hard/soft lead scrap,
- lead-covered copper cable, and
- lead weights.

The common types of lead by-products, and waste include:

- lead contaminated soil,
- drosses,
- slags,
- flue dust, and
- acid plant blowdown slurry/sludge.

7.4.2. Sorting and Preparation Techniques

Manual Sorting. Automobile dismantlers remove lead-acid batteries from the vehicles prior to shredding. Some dismantlers segregate steel and aluminum wheels for recycling and are required to remove the lead weights to prevent contamination.; the lead weights are collected separately by lead recyclers.

Sweat Furnace. (see Section 7.2.1.7 and Chapter 6) The sweat furnace is used by the scrap metal industry for the purpose of separating lead as well as aluminum and zinc from iron and steel scrap. The sweat furnace can also be used to remove contaminants (dirt, rocks, rubber, plastics and other combustibles) from lead-bearing scrap. In addition, the furnace is used to compact loose and bulky scrap into solid "pigs" and/or "sows" for transportation to the secondary smelter. .

The lead remaining in a vehicle, after the battery and lead weights are removed, is recovered from automobile shred residue (ASR)

Eddy Current Separation. Some non-ferrous metal separators use heavy media separation technology to recover the non-ferrous metal, including lead, from ASR. Details of eddy current separation technique are described Chapter 3.

Heavy Media Separation. Some non-ferrous metal separators use heavy media separation (see Chapter 3) to recover the non-ferrous metals, including lead, from ASR.

7.4.3. Secondary Recovery Technologies.

One difference between the recycling of lead and that of other non-ferrous metals is that the battery breaking, past treatment, and refining steps have developed as a separate industry from primary lead smelting. The methods for recovery of lead from secondary sources, primarily lead-acid batteries, were initially derived from the technologies of primary lead smelting. Recent years, however, have seen the development of processing techniques specifically designed for lead battery treatment.

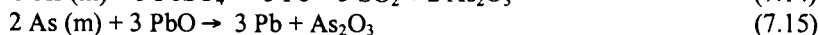
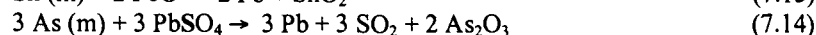
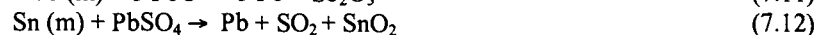
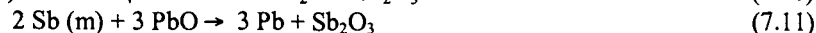
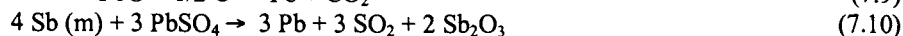
Five furnace types have found application in the lead recycling industry:

- blast (low-shaft, water jacketed);
- reverberatory (stationary);
- short rotary (also known as deep-bath rotary);
- rotary kiln (also known as long rotary); and
- ISASMELT.

Blast Furnace. This is the traditionally used furnace of primary lead smelting. It is well suited to treating a variety of secondary materials of variable composition and physical form. It is, however, somewhat more labour intensive than the other furnaces and its work-room and environmental emission contaminants are more difficult. Both Cominco and Brunswick Smelting in Canada test battery scrap in their blast furnaces.

Reverberatory Furnace. These are the preferred battery scrap smelting units in the U.S. The main objective is the reduction of the lead compounds to metallic lead bullion, and at the same time, oxidation of the alloying elements in the battery grids, posts, scraps, and connectors to produce a slag containing virtually all the alloying elements.

The following reactions take place in the reverberatory furnace (Prengaman, 1980)::



Note: 'm' in brackets denotes, the component in the molten state.

The slag produced by this type of furnace generally does not pass the TCLP (Toxicity Characteristic Leaching Procedure) leachate criteria. Therefore, the slag is often reprocessed using a blast or submerged arc electric furnace.

Rotary Furnace. Long (kiln) and short rotary furnaces are the preferred secondary lead smelting furnaces in Europe and Canada. Long furnaces permit continuous smelting whereas short furnaces are operated on a batch basis. The long furnace is fired at one end, with exhaust gases emitting from the other. The unique nature of the rotary kiln allows the treatment of a wide variety of lead-bearing materials, in addition to the lead acid batteries and still achieve 99.8 percent sulfur control to minimize sulfur dioxide emissions.

Short rotary furnaces are typically fired and exhausted from the same end. The ventilation is used to control the internal environment around the charge. This allows the

furnace to be charged while the burner is operating at low heat value settings.

ISASMELT Process is similar to Ausmelt described in Chapter 6 and in Section 7.3.5 of this Chapter. It employs two shaft-type furnaces; a single, vertically positioned lance enters each furnace through the top. Oxygen and fuel are carried into the bath where they mix and burn. Lead concentrates are charged to the furnace where the lead is oxidized to lead oxide and collected in a slag. This is transferred to the second furnace where it is reduced to produce lead bullion (crude metal), which is refined to market grade lead.

7.4.4. Refining Technologies

Two main refining processes for lead are pyro-refining and electro-refining.

Pyro-refining comprises three steps, drossing, softening and precious metal refining.

Drossing. The lead bullion, to which sulfur has been added, is slowly cooled to a temperature approaching the melting point of lead. The sulfur combines with copper to form cupric sulfide, which floats to the top where it is removed for further upgrading and eventual shipment to a copper smelter to recover copper.

Softening. This process is based on the preference for some metals to oxidize more readily than others. In this case, tin, arsenic and antimony oxidize more readily than lead when they are present. Softening may be conducted in a reverberatory furnace or kettle-type furnaces on a batch or semi-continuous basis. Air is injected into the molten bullion; tin, arsenic, antimony, and some lead are oxidized to form a litharge-based lead oxide slag. This is removed and further treated for by-product and lead recovery, and recycled back to the main circuit.

In an alternative method, called the Harris process, sodium hydroxide is contacted with the hard bullion to extract tin, arsenic, and antimony as sodium-containing compounds.

Bismuth is not removed in drossing or softening steps. It is recovered in a final refining operation, after silver and gold extraction, by the addition of calcium or magnesium to the molten lead.

Precious metal refining. The bullion from the softening step is transferred to a desilverizing kettle where metallic zinc is added in a step known as the Parkes process. The zinc combines with silver (and gold if present) to form an intermetallic compound, which separates as a dross on cooling. The dross is skimmed from the bullion, distilled in a retort to produce a gold-silver-lead alloy and zinc vapor is condensed, cast into ingots, and returned to the circuit for another cycle of precious metals extraction.

The gold-silver-lead alloy is charged to a cupellation furnace, most commonly of the small reverberatory type, and oxidized to convert the lead and other impurities to a litharge slag that is recycled upstream for re-treatment. The refined alloy, now containing only gold and silver, is cast into ingots and sent to a precious metals refinery.

Residual zinc in the lead bullion is removed by oxidation, as in the softening process, by vacuum distillation, or by the use of sodium slats, as in the Harris process. The final, fully refined lead product is cast into the shapes required.

In Electro-refining, the lead bullion, after drossing and softening, is cast into anodes and refined electrolytically. The electrolyte is a mixture of lead fluosilicate (PbSiF_6) and fluosilicic acid (H_2SiF_6). Pure lead is electrically plated out on cathodes, which are melted and cast in market shapes. Bismuth and the precious metals collect in the anode slime, which are treated in a cupellation furnace to extract bismuth in a litharge slag and produce a gold-silver metal for casting and refining.

7.4.5. Battery Breaking and Paste Recovery.

There are several battery breaking and paste recovery systems in operation. They are all variations based on two processes:

- mechanical breaking followed by a chemical recovery process; and
- mechanical breaking followed by an electrochemical recovery process.

7.4.5.1. Automated CX Breaker System.

The CX system crushes whole batteries, separates the various components, and desulfurizes the paste by sodium hydroxide or carbonate. The system uses mechanical screening and an up-flow hydrodynamic separator for separation of the battery components. The sodium sulfate brine produced is evaporated and crystallized to produce an anhydrous sodium sulfate suitable for use by detergent or glass manufacturers. The desulfurized paste is also suitable for leaching followed by electrorefining. Inputs to the process are whole undrained batteries, water, and sodium hydroxide solution. Outputs from the system are polypropylene, metallic lead, ebonite, PVC and other separator materials, and sodium sulfate solution. The steps involved in the process are:

battery breaking,
paste separation,
hydrodynamic separation,
desulfurization, and
sodium sulfate production.

Battery breaking. The batteries are crushed in a hammer mill and the wet screened to separate the paste from the other components. The separation of metallic (antimonial) lead from the oxide/sulfate lead paste is an advantage of this breaking and separation process.

Paste Preparation. Battery paste is typically comprised of lead sulfate (64%) lead oxide (40%) and other materials (4%). The paste from wet screening is collected as a slurry and the other components are fed to the hydrodynamic separator.

Hydrodynamic Separator. An up-flow column of water separates the metallic lead (which sinks) and the other components such as plastic and ebonite (which float). The floats are separated from the water by another screen. The separation of polypropylene from other plastics maximizes the value of the plastic for resale to recyclers.

Desulfurization. Sodium hydroxide or carbonate is mixed with the paste and waste acid from the to convert the insoluble lead sulfate to insoluble lead oxide. The soluble sodium sulfate is filtered out. The removal of sulfur from the paste results in lower power and fluxing requirements when compared with direct smelting of the paste. Desulfurization has the following advantages:

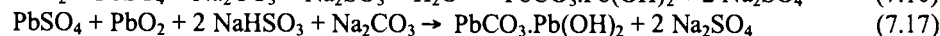
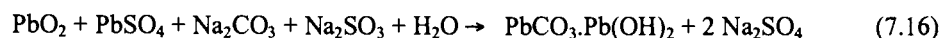
- sulfur dioxide emissions are reduced by 90 percent;
- treating of the acid removes sulfates from the wastewater, thereby allowing direct discharge to sewer; and
- slag production is reduced by up to 65 percent.

Recovery of Polypropylene. The shredded fraction from the separation of the castings of lead-acid battery scrap in the battery breaking are has been used as raw material to recover polypropylene, a plastic, which is widely used in various industrial material composites. Before transferring to the compounding plant, the collected polypropylene chips undergo intensive preparation steps. In a milling plant, they are washed to remove any paste and dust, shredded to a smaller and more homogenous fraction in a knife mill

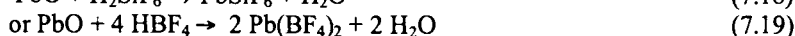
and dried to evaporate all remaining moisture. An example of a mill plant designed to permit integration of raw polypropylene chips from other operations into the process has been described by Martin and Siegmund (2000).

7.4.5.2. RSR Electrolytic Process (Prengaman, 1995)

This electro-refining process recovers lead as a high purity cathode from battery scrap. After battery breaking, the paste from the batteries is desulfurized using sodium carbonate which converts the lead sulfate to lead carbonate and produces a sodium sulfate solution. The lead dioxide in batteries is reduced to soluble form by one of the following methods: The dioxide may be reduced by the addition of sulfur dioxide to an alkali carbonate, which reacts with the lead dioxide to produce lead sulfate by the following reactions:



The sulfites are oxidized to sulfates and lead is precipitated as lead carbonate or basic lead carbonate. This is leached in hydrofluosilicic acid or fluoboric acid to solubilize the lead by the following reaction:



The solution thus obtained is the electrolyte to recover lead by electrolysis. The anode used in the electrowinning process consists of a graphite substrate covered with a tight-fitting sheet of a nonconducting inert mesh material over which a layer of lead dioxide is deposited until it completely covers the mesh. Such anodes are highly conductive and stable. Arsenic is added to the electrolyte in an amount approximately 5 ppm to prevent deposition of lead dioxide on the anode. The arsenic lowers the oxygen overvoltage and eliminates the deposition of lead dioxide. The cathodes are more than 99.99 percent pure and require no further refining. The process has the advantages associated with other hydrometallurgical/electrowinning processes in that it emits no sulfur dioxide or nitrous oxides, and produces no lead fume or hazardous slag. The sodium sulfate solution generated during desulfurization is treated in a wastewater treatment plant to remove traces of dissolved heavy metals. The leach residue is directed to an electric furnace for conversion to a non-hazardous slag.

The process comprises the following steps:

- battery breaking;
- paste preparation;
- desulfurization – this converts the insoluble lead sulfate to insoluble lead carbonate and soluble sodium sulfate which is separated by filtration;
- Lead dioxide decomposition – this involves a drying step which converts the lead dioxide and lead carbonate to lead oxide which is readily leachable;
- Leaching – the leach solution is fluosilicic acid which is a by-product of fertilizer manufacture; and
- Electrowinning. Engineering design to produce a full scale plant to electrowin lead has been described by Prengaman and McDonald (1990). The basic flowsheets are

represented in Figure 7.12 to 7.15.

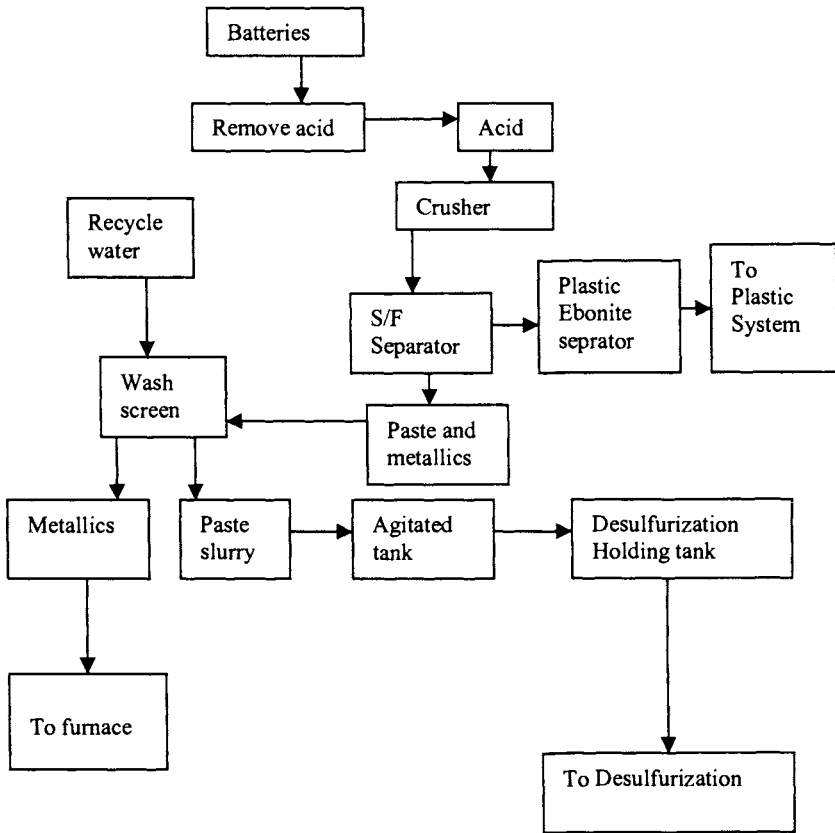
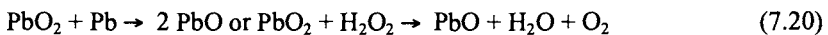


Figure 7.12. Battery wrecking and paste preparation (Pregaman and McDonald, 1990)

7.4.5.3. Engitec CX-CW Process

This technology, developed by Engitec Impianti, S.p.A., uses both electrowinning and electrorefining technologies. The desulfurized paste is leached by fluoboric acid and the lead is recovered from the solution by electrowinning with a proprietary activated copper/tantalum wire anode. The chemical reactions leading to solubilization of lead are the same as in the RSR process, except that lead dioxide is reduced by metallic lead present in the sludge) or by hydrogen peroxide, following the reaction:



In an electrorefining process, used to recover lead from the grids and poles, the lead scrap outside the electrolysis cells is solubilized by a ferric fluoborate solution with fluoboric acid (called CX-EW process, Olper 1995a). The extracted lead is deposited in the cathode compartment of a diaphragm cell. The following reactions take place:

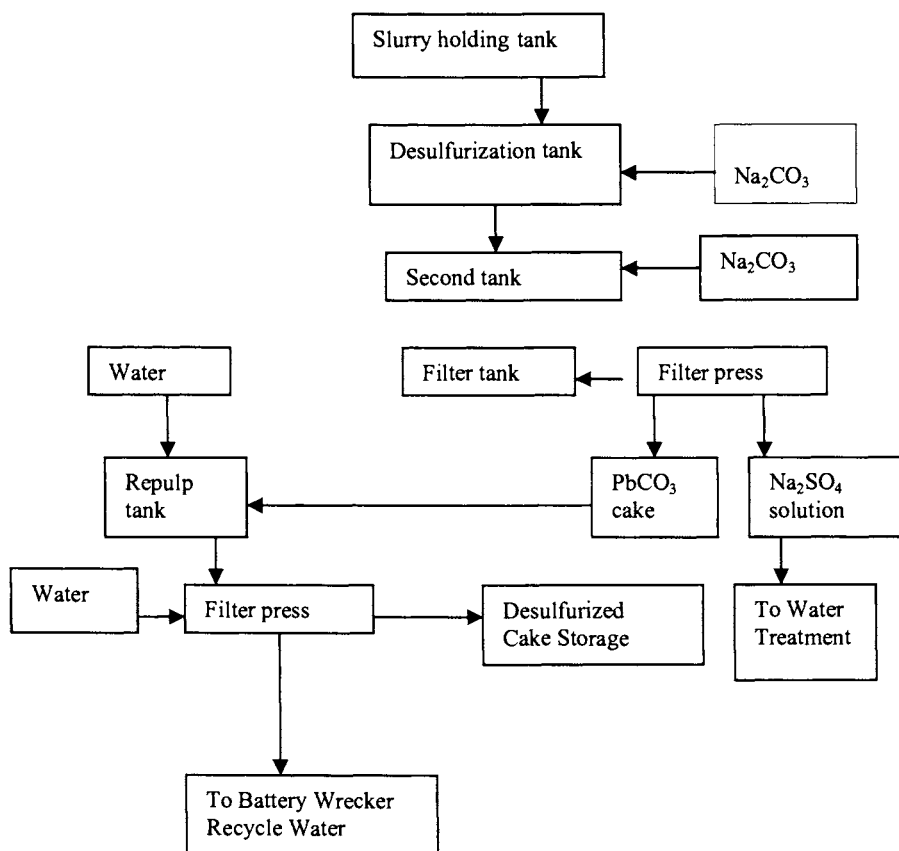
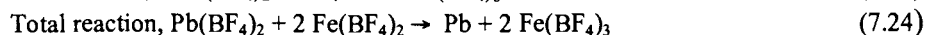
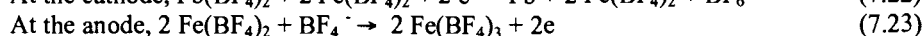
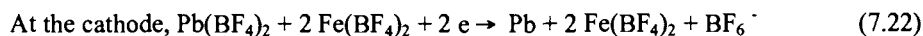
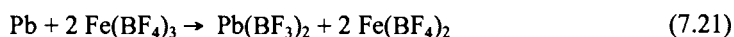


Figure 7.13. Desulfurization of the Paste (Prengaman and McDonald, 1990)

7.4.5.4. Soda Ash Smelting Process

A pollution free pyrometallurgical process to recover lead from battery residue has been described by Pickles and Toguri (1993). It is based on converting lead sulfate to carbonate by reacting with sodium carbonate (soda ash), decomposing the carbonate to the oxide and reducing the oxide to metallic lead by carbon. The process consists of four steps:

- Crushing and grinding of the battery residue. The residue is sieved to separate the metallic lead from active material (PbSO_4 , PbO and PbO_2).
- Mixing of the active material with alkali carbonates, (e.g., Na_2CO_3) to convert the lead sulfate to carbonate.

- Sintering of the pellets.
 - Smelting of the pellets to produce metallic lead and a sodium sulfate slag
- The sulfur is fixed as sodium sulfate in the slag, which minimizes sulfur dioxide emissions. The lead particulate emissions are reduced since the smelting temperature is low and pellets are employed. The sodium sulfate slag could be a marketable product.

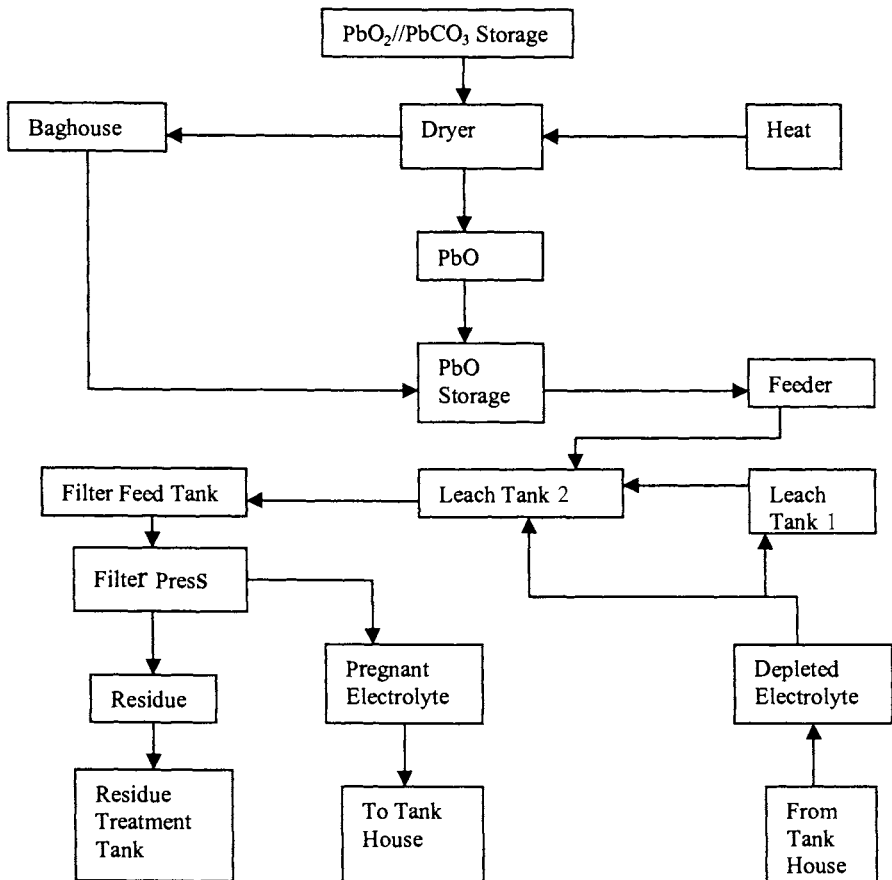


Figure 7.14. Decomposition of lead dioxide and leaching (Pregaman and McDonald, 1990)

About 25% of the lead could be recovered without carbon addition. This is due to the presence of some metallic lead in the residue and to the organics, which reduce a portion of the lead oxide. Maximum recovery, almost 90%, is obtained with stoichiometric amount of carbon. Higher carbon contents lead to decrease in metal recovery, probably due to increased production of matte at high charcoal contents. A smelting temperature of 900-1000 °C is considered to be the optimum to get maximum recovery and minimizing the sulfur dioxide generation. The amount of sodium carbonate required is slightly in excess of the stoichiometric requirement. With higher quantities the lead recovery decreases, attributed to increase in the oxygen potential of the system due to the carbon

dioxide in the sodium carbonate. In general, the amount of sulfur dioxide evolved in the soda ash smelting of the battery is less than 1% of the total sulfur in the original sample. The sodium sulfate solution is preheated and introduced into an evaporator/crystallizer from where a stream of crystal laden brine is removed and centrifuged. It is recovered as anhydrous “detergent-grade” chemical of greater than 99.5 percent purity.

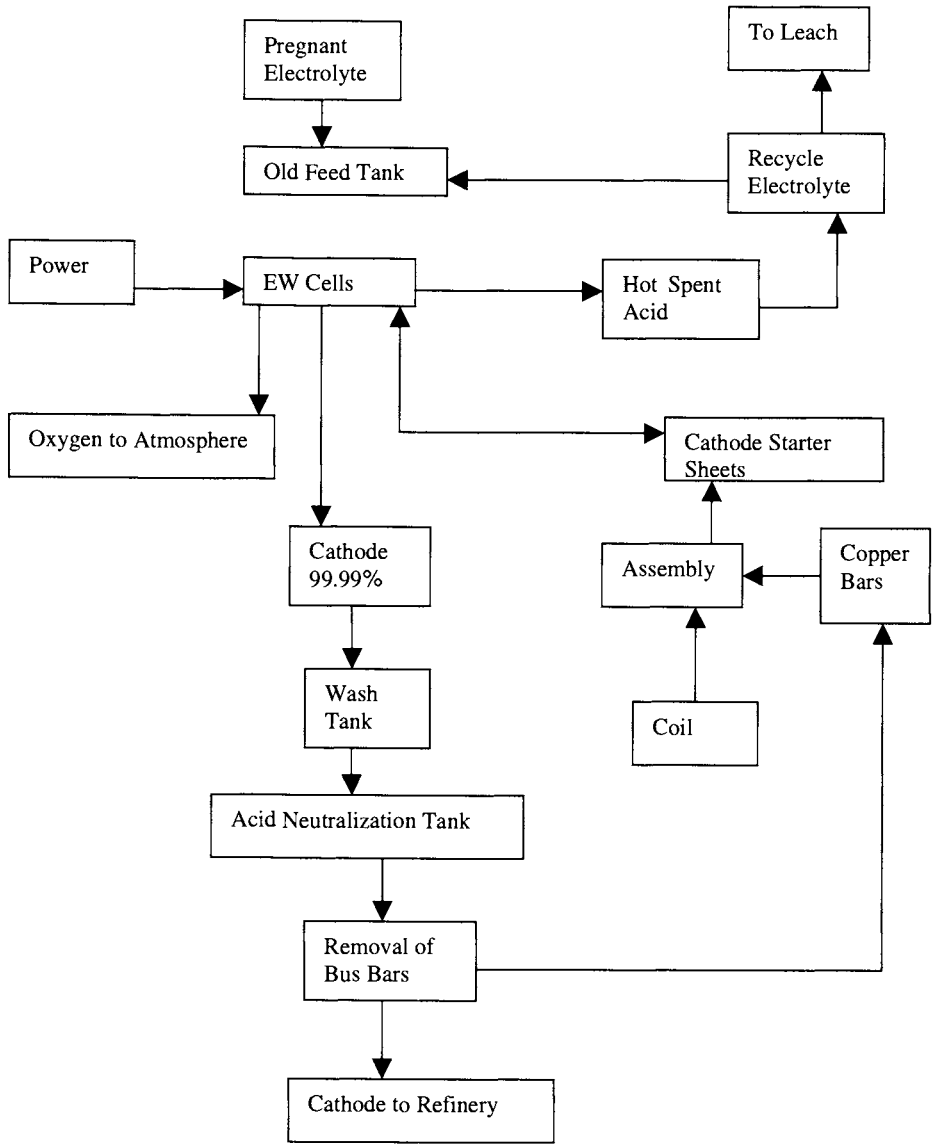


Figure 7.15. Electrowinning of lead (Prengaman and McDonald, 1990)

Some major lead recycling operations are listed in Table 7.4. Generally, most

operations follow technologies described in these sections. An illustration of an integrated plant, which recovers lead from used batteries and converts it into lead and lead alloy ingots and also recovers by-products, sodium sulfate and polypropylene, is shown in Figure 7.16. By-products processing will be described in chapter 9.

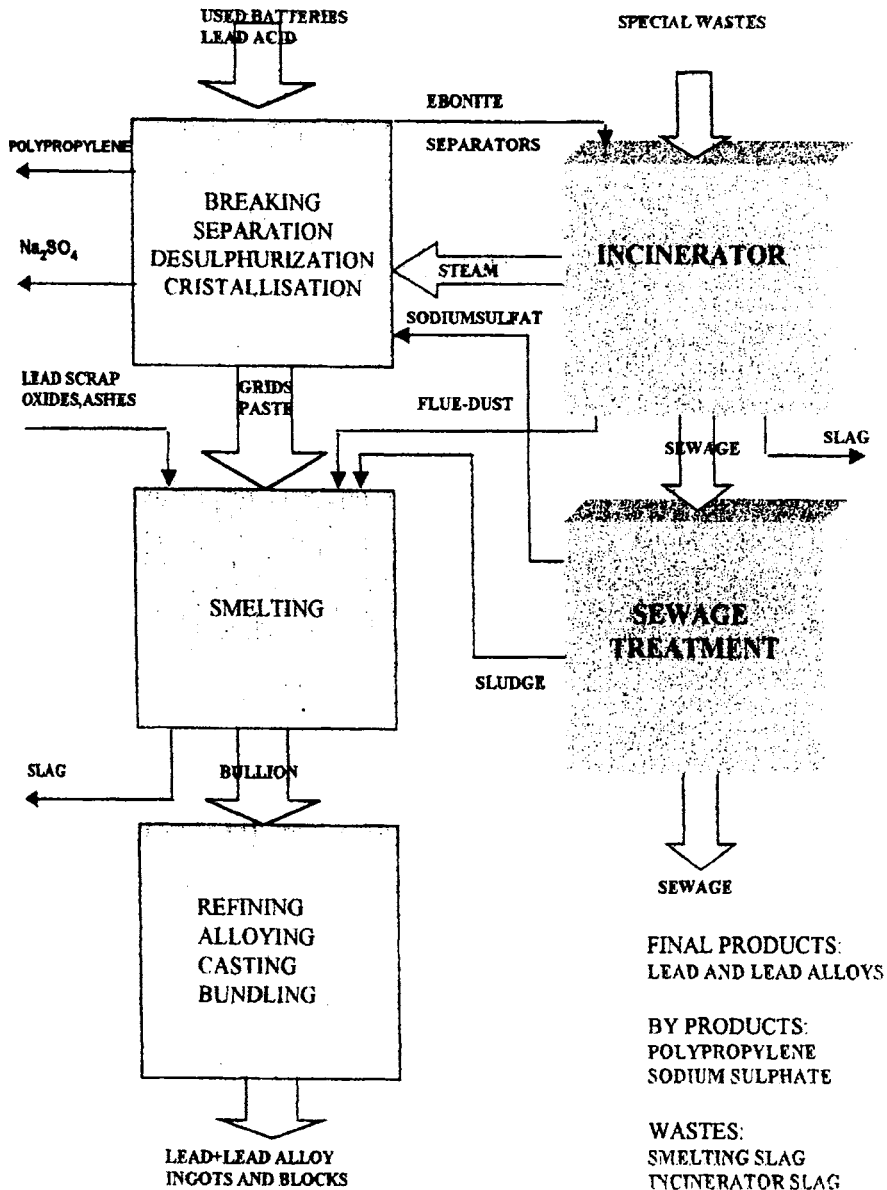


Figure 7.16. Combined flow sheet of Muldenhutzen Recycling operation (Behrendt, 2000)

Table 7.4. Major Lead Recycle Operations

Place	Production, tons per year
Braubach, Germany	45,000 refined lead
Britannia Lead, Northfleet, U.K.	40,000
Marcianise, Italy	40,000 refined lead
Metallum A.G., Pratteln, Switzerland	30,000
Tonolli, Mississauga, Ontario, Canada	50,000 refined lead
Doe Run, Missouri, U.S.A.	60,000 refined lead
Muldenhutzen, Germany (Behrendt, 2000)	45,000 lead and lead alloys; 4,000 tons sodium sulfate, 2,200 tons polypropylene
East Penn, Pennsylvania, U.S.A. (Leiby, 1993)	5,000,000 automotive units, 450,000 industrial units (batteries)

Flow sheet of Muldenhutzen operation is shown in Figure 7.16.

7.4.6. Waste and By-product Treatment

Wastewater treatment systems are used to clean the process water to levels suitable for direct discharge or for return to the smelter and refinery for reuse. In most cases, lime is used to precipitate the heavy metals. With particulate and sulfur removal circuits the emission of either dust or sulfur compounds is controlled. The emission of carbon dioxide is at present unavoidable. Other by-products and waste include slag, flue dust, acid plant blowdown sludge, and dross.

Lead Slag. All metals show varying tendencies to undergo oxidation. Since iron and zinc are more readily oxidized than lead and copper, they collect in the slag while the latter enter the bullion. However, zinc has a particularly high vapor pressure, so that if it is reduced from the oxide to the elemental form, it is easily extracted from the slag by an inert or reducing carrier gas.

The molten blast furnace slag is transferred to a second furnace where a reducing gas is blown and injected into the slag. Zinc oxide is reduced to metal, vaporized, and removed in the gas stream. Conditions above the slag bath or in the flue system are sufficiently oxidizing to cause the reoxidation of the zinc; collection is carried out with bag filters in the exhaust gas-cleaning system. This product is suitable feedstock for a hydrometallurgical zinc refinery.

Lead slag is classified as a hazardous waste because of the ability of acidic waters to leach lead, cadmium and mercury. At both operating and abandoned smelters, slags are a permanent part of the smelter plant site.

Flue Dust. Flue dusts are generally recycled to the smelting furnaces as they are produced; however, abandoned smelter sites may hold buried stocks of dust.

Acid Blowdown Sludge. This originates in the wet scrubbers which prepare roaster and smelting furnace exhaust gases for acid manufacture. The sludge may be considered hazardous waste because of its lead, cadmium, and mercury content. Extraction of the metals contained in the sludge is currently not economically justifiable.

Dross. A process developed in Australia (Imperial Smelting Furnace at the Sulphide Corporation, Pasminco) produces commercial lead oxide from the copper/lead dross. Lead component of the dross is leached by sodium hydroxide. The lead-rich liquor is then

purified by the addition of thiourea and magnesium sulfate. This is then carbonated to precipitate lead carbonate. This product is washed and calcined to produce a canary yellow litharge (lead oxide).

Metal recoveries from the wastes and byproduct treatment will be described in Chapters 8 and 9.

7.4.6.1. Volatile Organic Compounds

The refining process often generates waste gases containing volatile organic compounds (VOCs), dioxins and furans, all of which are serious health hazard if they are not isolated or destroyed. This requires the gases to be treated in a unit, which has to be integrated with the overall recycling operation. A system for that purpose, which is integrated with the refining of lead recovered from spent batteries has been described by Thalhammer (2000). The raw gas is forced through ceramic blocks where it is heated up to the oxidation temperature the VOCS, dioxins and furans are destroyed in the combustion chamber, generating water, carbon dioxide and heat. The hot purified gas heats up a second ceramic bed and is used to preheat the raw gas. The process is said to be clean; it does not produce any secondary waste such as contaminated water or polluted air. It also makes efficient use of heat generated in the process.

7.5. Zinc

Zinc tonnage is large but the price is low. Used mainly in sacrificial applications as galvanize coatings. Some zinc sheet is used as flashing in the construction industry. Zinc is the most cost effective means of protecting steel against corrosion. About two thirds of the zinc for galvanizing applications is used to produce galvanized sheet steel. Auto industry is a major market for galvanized steel. In a new car, on average, over 50% of the sheet steel is galvanized. Secondary sources from which zinc is recycled include zinc die-cast scrap, clippings, die-cast slabs and zinc dross.

Scrap metal is delivered to the secondary zinc processor as ingots, rejected castings, flashing, and other mixed metal scrap containing zinc. Scrap pre-treatment comprises Sorting, cleaning, crushing and screening, sweating, and leaching.

In the sorting operation., zinc scrap is manually separated according to zinc content and any subsequent processing requirements. Cleaning removes foreign materials to improve product quality and recovery efficiency. Crushing facilitates separation of zinc from the contaminants. Screening and air classification (see Chapter 3) concentrates the zinc metal for further processing.

A sweating furnace (see Chapter 6) slowly heats the scrap containing zinc and other metals to approximately 364 °C. At this temperature zinc melts but the remaining metals do not. Molten zinc collects at the bottom of the sweat furnace and is cooled. The remaining scrap metal is cooled and removed. It is processed by other secondary processing methods (described in the following sections).

Zinc is also recovered from flue dust, process effluents and acid mine drainage. They will be discussed in Chapters 8 and 9.

7.5.1. Current Recycling Methods

A large portion of the zinc consumed is lost by the very nature of its main use as a corrosion protection agent. The sources of secondary zinc are primarily galvanized sheet steel and die castings. Since brass and bronze scrap is typically recycled directly back

into brass and bronze alloys, the zinc constituent is rarely recovered. Figure 7.17 represents a schematic illustration of the zinc recycling process.

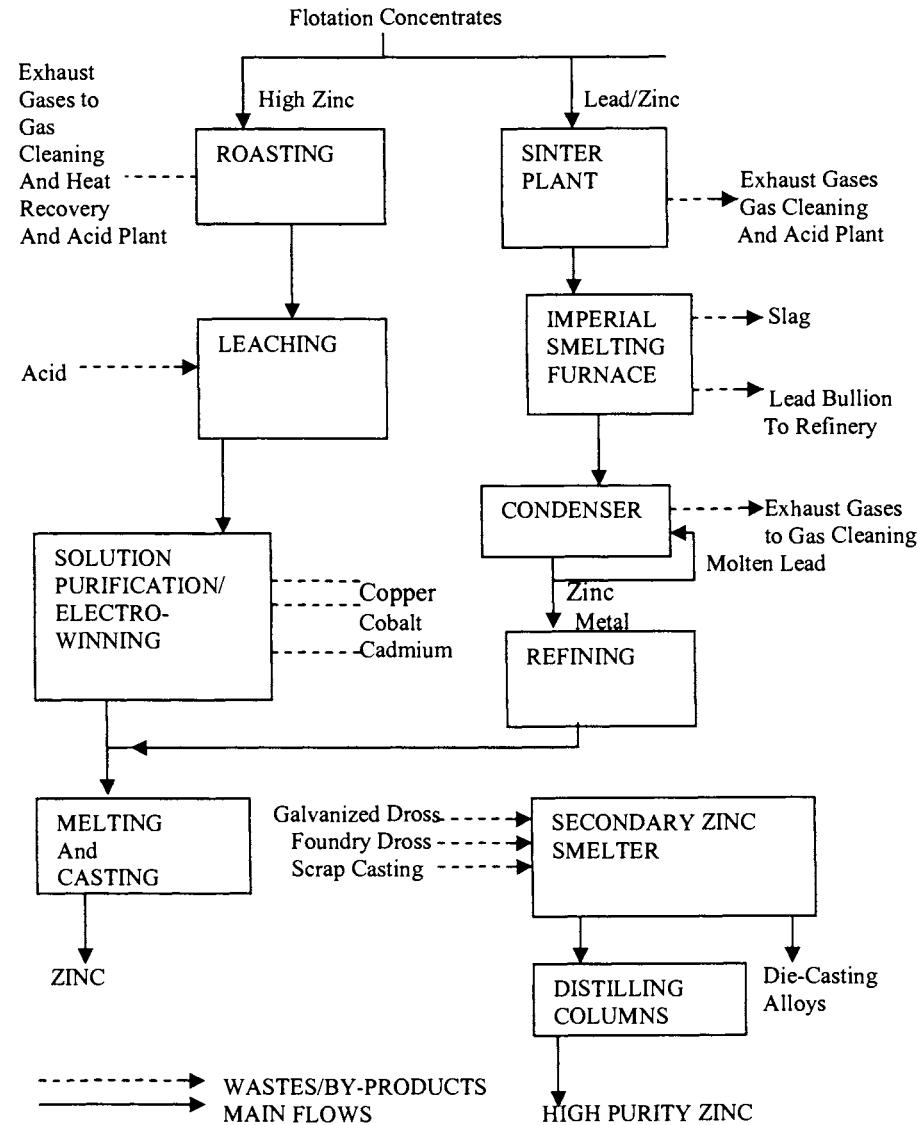


Figure 7.17. Schematic illustrating zinc recycling (CANMET, 1993)

The melting of zinc-bearing steel scrap (galvanized steel) in electric arc furnaces (EAFs) produces flue dust, which can contain up to 25% zinc as oxide. Their treatment has become necessary in view of their being classified as hazardous waste. The recycling of EAF dust has become an important secondary source of zinc. It will be described in Chapter 8.

Some organized automobile dismantlers routinely remove zinc die castings for shipment to master alloy producers or die-casting plants for remelting and casting. However, the majority of the die-cast zinc found in scrap automobiles is recovered from the automotive shredder residue (ASR). While the majority of scrap brass is recycled, some of it finds its way to the primary and secondary copper industries. In both primary matte or secondary converter, zinc would be oxidized to the slag and/or fumed into the gas stream. The recovery of zinc from the slag or flue dust may not be economically justified.

7.5.2. Recycling Technologies

The two basic processes for extracting zinc are based on smelting technology and hydrometallurgical recovery. Some automobile shredders employ eddy current technology or heavy media separation to remove zinc from ASR. (See Chapter 3 for description of eddy current and heavy media processes).

7.5.2.1. Zincex Process

This process combines a leaching procedure and a solvent extraction technique for solubilizing zinc from a wide range of secondary sources. It produces a zinc sulfate electrolyte suitable as a feed for zinc electrowinning. A waste stream containing soluble zinc, cadmium, and chloride is produced. It can be further treated to produce a cleaner effluent. Depending on the nature of the feedstock, generally non-hazardous leach residues are produced. The process is specially suitable for chloride-contaminated material and the following materials:

Zinc galvanizing bath ashes.

Ferrous metal processing flue dust.

Non-ferrous metal processing flue dust.

Die-casting scrap.

Zinc plant oversize skimmings.

Zinc plant chloride skimmings.

Waelz process oxide.

Most acid-soluble zinc compounds.

Further applications of this process in zinc recovery from metallurgical dust will be described in Chapter 8.

7.5.2.2. CATO Chloride Leaching/Solvent Extraction Process

In this process the materials are leached in chloride solutions and/or roasted with ammonium chloride. The zinc chloride is then extracted in tributyl phosphate in kerosene and stripped by an aqueous zinc chloride, ammonium chloride, and ammonia solution. Anhydrous zinc chloride is prepared by the thermal decomposition of the diamine salt followed by the recycling of ammonia. The zinc chloride is used as feed to produce high-grade zinc by electrolysis.

7.5.2.3. Pyrometallurgical Processes

Classical secondary zinc plants melt selected and prepared secondaries, followed by selective dressing and/or upgrading by vaporizing zinc. There is usually a preliminary physical concentration step, such as separating metallics from nonmetallics using an air-swept hammer mill, or a ball mill equipped with a trommel screen. Liquation furnaces

reject lead and iron from the metallics by taking advantage of the relatively low solubility of these impurities, at temperatures slightly above the melting point of zinc. Retorts are most often efficient when processing zinc metallics particularly those derived from galvanizer dross. Muffle furnaces are also efficient when processing zinc-rich metallics, especially diecast scrap. Sweat furnaces are used to preconcentrate retort and muffle furnace feedstocks.

Liquation: Crude zinc containing lead and iron in amounts exceeding grade of 0.05-1.4% Pb and 0.05% Fe, can be upgraded by liquation. The metal is held just above its melting point, preferably in an induction furnace. Solubility limitations and differing densities result in formation of three strata (Miller, 1970). The lighter zinc forms the top stratum; the lower the zinc temperature, the lower is its Pb and Fe content. Insoluble lead sinks to the bottom; the lower the temperature, the lower its Zn content. Excess iron concentrates at the zinc-lead interface as a musty Fe-Zn intermetallic compound (FeZn_3) assaying >90% zinc due to entrained metallic. If aluminum is also present, a FeAl_3 top dross forms (also > 90% Zn) that floats on the zinc. The liquation process can be carried out in a reverberatory furnace, in a kettle, or in a mold while melt is waiting for additional treatment. A typical liquated zinc contains 0.9% Pb and 0.02% Fe. The liquated metal can be further upgraded by column distillation to meet high grade standards (Broughton, 1997)

Scrap containing mixed metals and galvanizing residue are generally treated in sweat furnaces. The furnace is used to separate the lower melting point zinc from the other metals. In melting, the zinc inadvertently absorbs some contaminants. Master alloys can be produced from sweated zinc by dilution with virgin metal or re-alloyed to compositions meeting other specifications.

Zinc Retort: Feedstocks are milled and classified to recover metallics for retorting. Oxides and halides report to the fines fraction, e.g., minus 20 mesh. Zinc oxide can be retorted with a carbonaceous reductant, however, it is economically favorable to process the metallics to produce a specialty product, like zinc dust. AS salable dust, about 90% zinc is recovered.

Zinc vapor generated in the batch-operated retort may be converted to metal, dust or oxide. Metals can be condensed in a removable refractory-lined steel shell. Zinc dust is manufactured in a surface condenser constructed of uninsulated thin steel sheet. Dust production is of the order of 1 ton per m^3 of condenser volume; incorporating water cooling tubes decreases this volume to about 0.1 m^3 . Zinc oxide can be produced by burning in air the zinc vapor emanating from the retort. This is drawn into a hood, followed by a cyclone or settling chamber and then a baghouse.

Bottle retorts can economically generate a discard bottom residue containing as little as 5% Zn; but the production of solid waste can be avoided by leaving a higher level of zinc in the residue. This byproduct, in combination with zinc oxide fines, yields a 45-50% micronutrient fertilizer. Deposition of iron-rich scale on retort walls is minimized by blending galvanizer dross (up to 5%) with diecast scrap (up to 8% Al), preferably also containing copper. Iron is isolated as FeAl_3 intermetallic; copper probably weakens the SiC-intermetallic bond. Excessive addition of diecast scrap can result in aluminum foaming, as well as crusting over of the melt. The retort residue is poured and raked out while it is still hot. Energy consumption, when processing combinations of dross metallics and diecast scrap, is of the order of 16,380,000 kJ/mt zinc product.

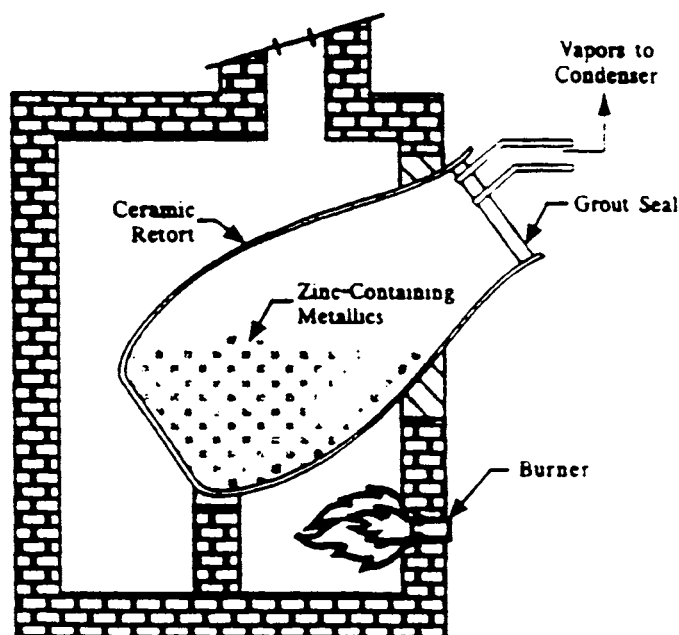


Figure 7.18. Bottle retort for zinc distillation (McElroy, 1980)

Retort furnaces produce high-purity zinc from the sweat furnace product by distillation. The impure alloy is melted and brought to a temperature above the boiling point of zinc (907°C), which is well below that of iron, copper, lead and aluminum. Zinc vapors leave the distillation units and are condensed to high purity metal. Repeated distillations can be used to produce even higher grade zinc products.

Muffle furnaces are used in some plants in the U.S. to upgrade dross and zinc metallics. A muffle furnace system is divided into two parts: one is for melting and the other for vaporizing. Zinc scrap is fed to the melting unit, usually a reverberatory furnace. Unmeltable are raked from the surface of the melt, and later screened for metal recovery. As the zinc melts, it flows under a partition curtain wall into the vaporizing unit. This underflow melt is low in iron content as the iron reacts with the aluminum component in diecast scrap to form FeAl_3 intermetallic, which floats. The skimmings typically assay 60-65% Zn and 2-3% Pb. They can be shipped for processing in electrothermic furnaces.

In a conventional muffle furnace, the vaporizing unit is fired in an upper chamber separated from the vaporizing metal below by an arch constructed of silicon carbide brick. Combustion gas from the upper chamber is exhausted into the melting unit. Zinc vaporized below is either condensed or burned to oxide as described before. Cadmium follows the zinc. Aluminum, copper and lead charged to the muffle furnace accumulates in the melt, typically about 36 tons. About once a week, up to 10 tons of this metal is tapped into a ladle. The resulting aluminum-rich alloy, called high-copper high-zinc slab, is sold to the secondary aluminum industry. It is used as a source of copper and zinc to prepare aluminum diecast alloys, primarily for the automotive industry. The chemical

composition of the slab varies in the range, 10-30% Cu, 15-50% Zn, and the balance primarily aluminum. Chromium should be below <0.1% and lead, <0.4% , but up to 1.5% is acceptable.

The Larvik Furnace is a modified muffle furnace, heated electrically rather than by gas firing (Lundervall, 1960) and is characterized by its very high material and thermal efficiency. Improved zinc recovery of higher purity can be obtained/. It is found particularly efficient for treating lower grade iron-rich residues containing zinc metallics. Graphite resistors provide heat in the first and second distillation sections; see Figure 7.19. Power consumption is 1500-2200 kwh/ton zinc produced, the actual consumption depending on the type of feedstock being processed. Energy efficiency in the Lavriks is almost twice that in a muffle furnace. However, electric power heating could cost so much more than natural gas heating. The superheated vapor travels countercurrent to the liquid zinc, cooling as it heats the melt to near its boiling point (907 °C). Vapors exit through a vertical column in which refluxing occurs. Lead condenses and runs down the column back into the furnace, where it settles to the bottom and is periodically tapped. With a suitably tall column, lead content of <100 ppm is achieved. Unmeltables, other than FeZn_3 , intermetallics that sink, are blocked by the curtain wall between the charging chamber "A" and the condensing chamber "B". these unmeltables are removed by skimming. Where the objective is to recover FeZn_3 , aluminum-containing feedstocks such as diecast scrap are not added to avoid formation of FeAl_3 top dross. High boiling point impurities flowing under the curtain become more concentrated as they flow toward the tap hole at the far end of the furnace. At this point a flux such as phosphorous pentoxide facilitates the tapping process by alloying accumulated iron waste with phosphorus, which lowers alloy melting point sufficiently for good tapping. The compartment "E" heats residual melt to about 1250 °C, thus fuming off most of the residual zinc, including that combined with iron. The discard iron alloy could contain about 2% zinc and up to 10% phosphorus.

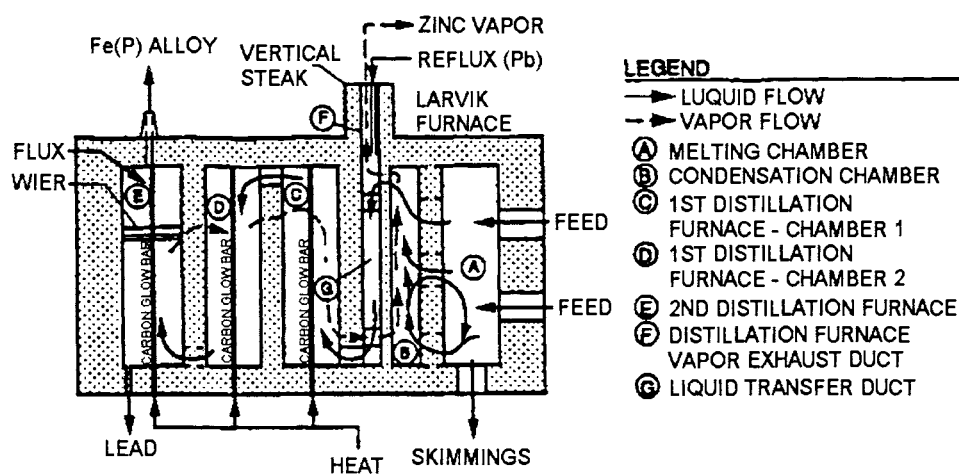


Figure 7.19. Larvik furnace for treatment of zinc secondaries

It is essential for thermal balance and efficiency that the heat required for melting and wall losses be supplied by condensation of zinc vapor from the second distillation

chamber E (Figure 7.19). Vapor from chamber C of the first distillation chamber freely communicates with the condensation chamber B. Melt entering the condensation chamber from the melting chamber is thus heated and enriched by this condensing vapor. Melt recirculates between the melting and condensing chambers by natural convection, or with assistance from a pump, to transfer heat to the incoming charge. A typical Larvik has capacity to treat up to 1800-28000 tons iron-rich dross per year depending on the content of the feedstocks processed.

The Sweat Furnace. A sweat furnace, reverberatory or rotary kiln, is used to process badly contaminated scrap. Selective melting (sweating) of scrap separates zinc from attachments of lead and metals with higher melting points than zinc, and from non-metals. Relatively clean scrap can be melted in an induction furnace, kettle, or crucible. For maximum efficiency, the material is continuously fed to an indirectly fired stainless-steel kiln lined with a ceramic coating. Zinc and aluminum-base alloys are sweated and reclaimed from other metals at a maximum feed rate of 900 kg/hr. The temperature profile along the length of the kiln is controlled to maximize metal separation efficiency. Energy consumption is about 756,000kJ/mt feed when sweating lead and zinc, and about 1,260,000 kJ/mt when sweating aluminum. Sweating sequentially separates lead, zinc, and aluminum (with melting points of 327°, 420°, and 660 °C, respectively) from metal attachments of higher melting point, and from nonmetallic residues.

7.5.3. Dezincing Technologies

The rapidly increasing use of galvanized steel has led to increased zinc loading for steel mills, and an additional gradual increase in zinc loading from recycle of old scrap. Removal of zinc from zinc coated scrap has developed to be an important recycling technology for metal recovery. Dezincing process should meet the following criteria (Houlachi *et al.*, 1995):

1. The process should achieve acceptable removal of zinc, lead, cadmium and other impurities from galvanized steel scrap to allow for recycling the steel scrap without causing operational and environmental problems to the steel industry.
2. The process should avoid generation of new environmentally hazardous wastes. Zinc should be recoverable in a form that can be either recycled or sold to the market with a high zinc credit.
3. The process should be economically attractive to the steel industry preferably having a cost lower or equal to the cost incurred currently in the steel industry from handling and treating galvanized steel scrap.

An electrochemical process for dezincing consists of a two step operation: first, the zinc is dissolved from the steel scrap in caustic soda electrolyte by applying current; in the second step the sodium zincate solution is electrolyzed to recover zinc in powder on the cathode; see Figure 7.20

The process is designed to process baled scrap. The bales of scrap, weighing about 1135 kg with a density of 2.4-3.2 g/cm³ are introduced into rectangular electrolytic cells filled with hot caustic electrolyte. The solution may be purified by cementation to remove the impurities, which affect the quality of the zinc. Electric current is applied and the zinc is anodically dissolved from the steel scrap while hydrogen is evolved and some zinc is deposited at the cathode. After electrolysis, the bales are passed through a multi-station, counter-current rinse cycle to remove entrained sodium zincate electrolyte. The zinc

enriched electrolyte is then treated in the zinc electrowinning section using conventional rectangular cells with nickel anodes and cathodes. The cathodes are scrapped periodically to let the zinc powder fall to the bottom of the electrolysis cell. Up to 70% of zinc contained in the large bales of galvanized steel scrap can be removed by this process (Houlachi *et al.*, 1995). By this process scrap with residual zinc below 0.1% has been dezincing (Dudek *et al.*, 1995).

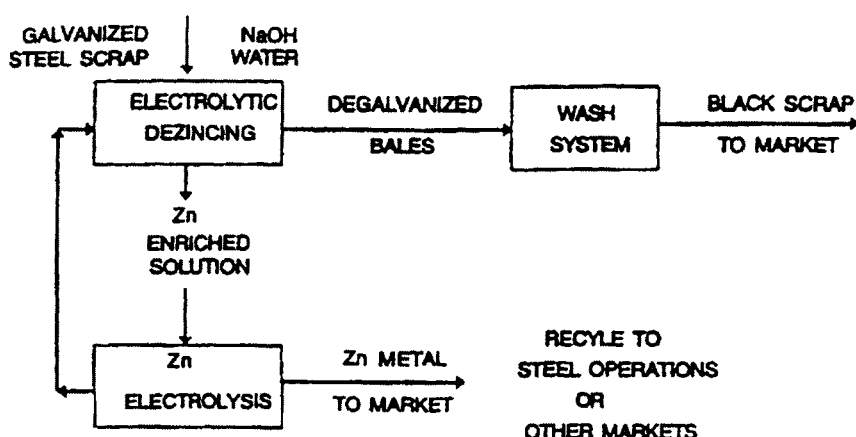


Figure 7.20. Caustic/electrolyte dezincing process (Houlachi *et al.*, 1995)

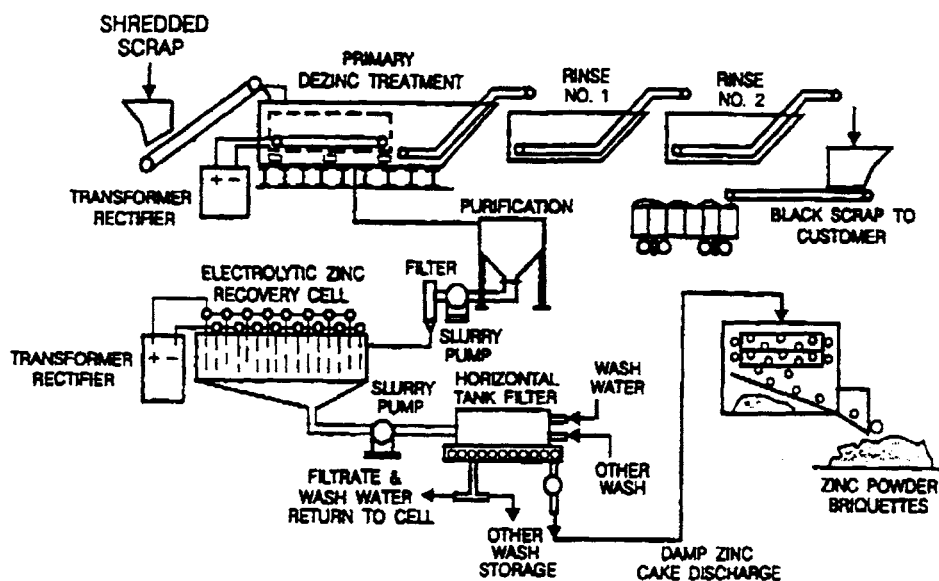


Figure 7.21. Pictorial flow chart of pilot plant for continuous degalvanizing of loose ferrous scrap (Dudek *et al.*, 1995)

Another electrochemical method for dezincing steel scrap and recovering zinc as metal or as zinc sulfate is based on selective electrodisolution of zinc from the scrap (Lupi *et al.*, 1998). Pure aluminum is used as cathode and the anode is made of galvanized steel. Zinc dissolution occurs at 0.1 V while the iron dissolution requires 0.6 V. The selective dissolution of zinc is achieved by controlling the applied voltage. Cell potential of 0.6 V at a current density of 250 A/m² in an electrolyte of composition 1 g/L Zn and 50 g/L sulfuric acid are chosen to be the optimum conditions for best selectivity and maximum zinc removal (Lupi *et al.*, 2002). About 0.5 kWh/kg are required to produce metallic zinc of high purity removing more than 98% zinc from the steel scrap.

7.6. Aluminum

Aluminum is widely used in a variety of consumer goods including containers and packaging, not only because it is one of the most abundantly occurring metals but also because of its special properties which include lightness and resistance to corrosion under most environmental conditions. It is easily fabricated into a great variety of complex shapes. The unique properties of aluminum has led to its use in transportation and construction industries, electrical parts, machinery and equipment.

The primary motivation for recycling aluminum is environmental concern. Total annual consumption of aluminum now exceeds 25 million tons (Gesing *et al.*, 2000). The supply comes from 20 million tons from primary metal reduction and 3-5 million tons from scrap. The pool of aluminum products in use by consumers is growing at a rate of ~20 million tons annually. All this metal will need recycling and will supply the scrap market. Without recycling millions of aluminum cans and packaging items thrown out every day will be a serious source of pollution.

7.6.1. Recycling Methods

The primary industry recycles predominantly municipal waste (containers and packaging) and industrial scrap (sheet, film and siding), which typically contain magnesium. The primary industry uses this scrap aluminum to supplement the production of aluminum from bauxite. Used beverage containers are a major secondary source of aluminum. The aluminum beverage can is one of the modern success stories in metals recycling, and the industry has developed the dedicated smelter, which handles nothing but this feedstock.

The second source is the transportation sector, which includes the automotive (Al-Si alloys in castings) and the aerospace (Al-Mg sheet) industries. Both produce large quantities of manufacturing scrap in addition to the scrap collected by the metal recycling industry. Recycling industry also uses scrap from electrical equipment, appliances, packaging, and the construction industry. Figure 7.22 shows a schematic representation of primary and secondary aluminum recovery.

A third sector has emerged to recycle dross, salt cake and red mud produced by the primary and secondary industries. Examples of this will be discussed in Chapters 9 and 10.

7.6.2. Scrap, Waste and By-products

The types of aluminum to be recycled can be classified into two main grades: aluminum scrap, and aluminum by-products, waste. The form of the aluminum scrap and waste to be recycled has a bearing on the technology used for recycling.

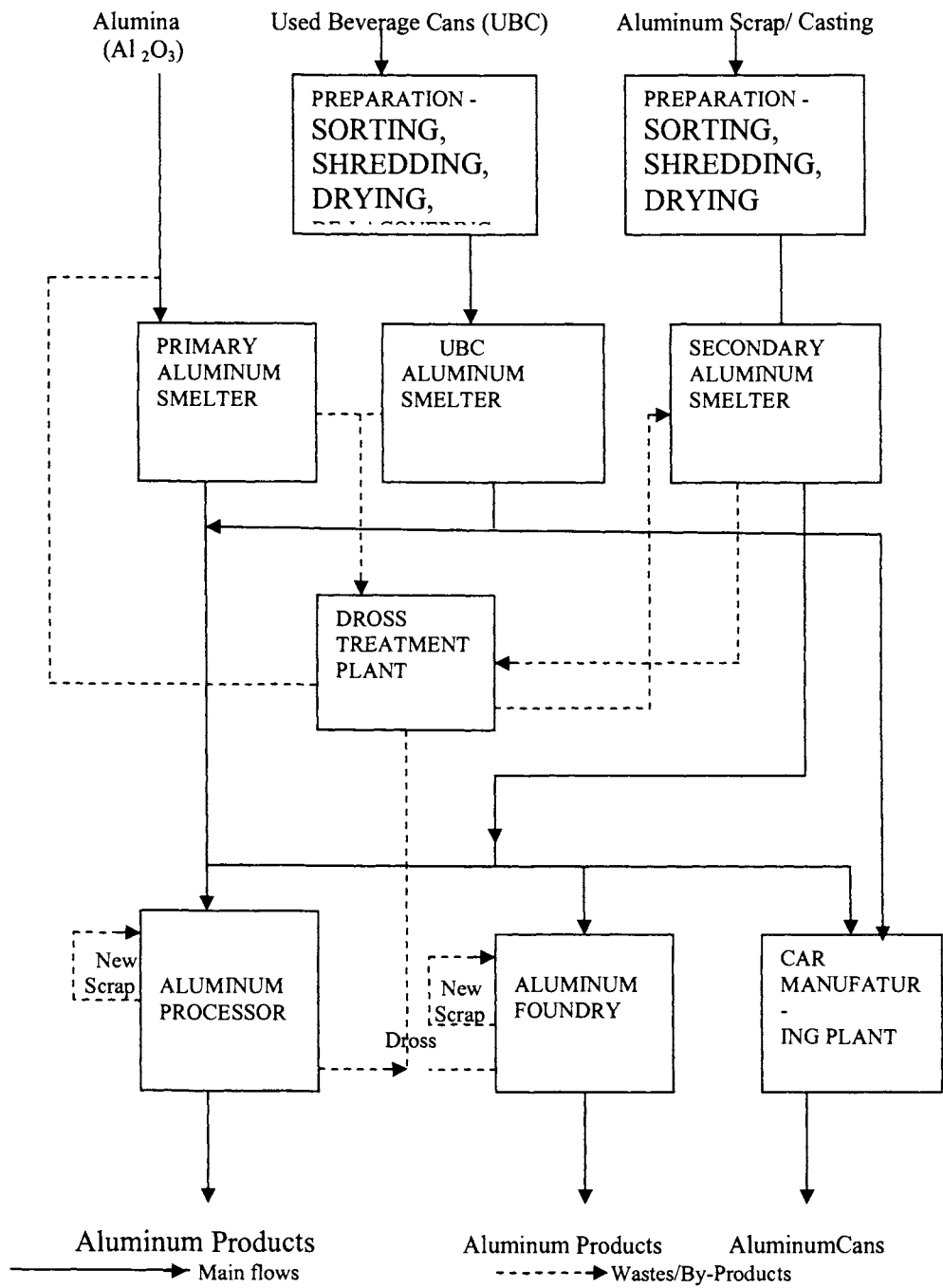


Figure 7.22. Schematic illustrating aluminum recycling (CANMET, 1993)

The common grades of aluminum scrap include:

- mixed cast alloys,
- aluminum brass condenser tubes,
- clean lithographic sheets,
- mixed low copper aluminum clippings and solids,
- clean mixed old alloy sheet,
- can stock, new or old,
- aluminum copper radiators,
- aluminum nodules,
- new wire and cable, pure or mixed,
- old wire and cable,
- pistons, borings, turnings and foil,
- sweated aluminum,
- new aluminum alloy clippings and solids, segregated or mixed,
- segregated new aluminum castings, forgings and extrusions,
- auto and airplane castings,
- insulated wire and fragmented scrap from automobile shredders.
- aluminum-lithium alloys..

7.6.3. Scrap Aluminum Sorting

New and segregated industrial scrap requires virtually no sorting, but other forms of aluminum require sorting and preparation. Many of the sorting techniques described before are also applied for scrap aluminum. The more common ones will be described.

Manual sorting involves the removal of components from the scrap by hand. The plastic or metal radiator end-tanks are typically cut off the radiator using a bandsaw. Electronic components (e.g., computers) are disassembled to recover those parts, which can be sold for re-use, and to recover materials for recycling. Heat sinks, face plates, and other components containing aluminum are sold to recyclers for further processing.

Magnetic Separation. Aluminum used beverage containers (UBCs) are separated from the look-alike steel UBCs by magnetic separation.

Baling and Compaction. Loose scrap and thin-walled low density scrap (i.e., UBCs) are normally compacted by baling or briquetting. A baler is a heavy piece of equipment that uses up to three hydraulic rams to compress the scrap. In a briquetter, small scrap is compacted into pockets as it passes between two counter rotating drums. The use of bales and briquettes reduces transportation costs and makes charging the furnace easier.

Shredding is used to reduce the size of large aluminum parts. Aluminum found in automobiles is recovered from automobile shredder residue (ASR). Shredders typically operate 2000-6000 HP hammer mills, which reduce a car hulk to pieces. This liberates individual materials and enables cost-efficient material separation for metal recovery. Dust, fluff, foam and some wire are removed by air suction. Shredders magnetically separate ferromagnetic iron and steel, which is sold to steel mills, and concentrate the remaining metals in the nonmagnetic metal shredder fraction (NMSF) for sale to the sink float plants. Some of the nonmetallic residue is also processed by sink-float plants to separate the organic portion for use as fuel in cement kilns.

Production of NMSF at the shredder is schematically represented in Figure 7.23. It comprises separations based on magnetism, density and electrical conductivity. Ferromagnetic particles are removed by magnet (usually drum) and nonmetallic fines

plus low density foams, paper and textiles are removed by air suction. Nonmagnetic electrically conducting particles are removed from the residue by eddy current separation. This leaves behind a nonmagnetic metal concentrate that may contain 30-95 % metallic particles by weight.

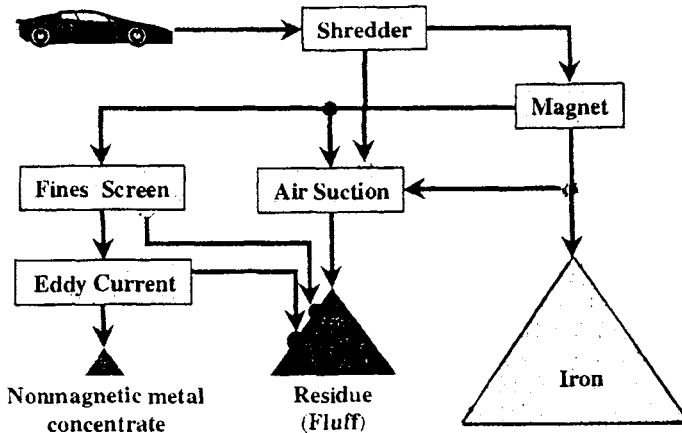


Figure 7.23. Shredder plant flow sheet (Gesing *et al.*, 2000).

Heavy Media Separation. NMSF is processed further by sink-float process. plants use water and water slurries as media for sink-float separation. It is performed in three steps: in water, in magnetite-water slurry and in ferrosilicon-water slurry, at respective specific gravities (SG) of 1, ~2.5 and ~3.5. In the first step, wood, paper, foam and textiles float; in the second, at an SG of 2.5, rubber, plastic, magnesium and hollow aluminum float; and in the third step, at an SG of 3.5, aluminum, rock and insulated wire float. The sink-float separation is not size dependent, but it is shape-dependent: dense, hollow, or boat-shaped particles float. It is not selective enough to separate by density differences of aluminum alloy.

Some automobile shredders employ heavy media separation to remove aluminum from the ASR.

Eddy Current Separation. As aluminum particles are present in both 2.5 SG and 3.5 SG media plant float fractions, metal particles are separated again from nonmetallics by eddy current separation (ECS), which yields mixed alloy aluminum product from the 3.5 SG float fraction and an aluminum-magnesium mix from the 2.5 SG float fraction. The separation throughput is not dependent on particle size, but it is shape-dependent as wire and foil particles are not efficient eddy current generators.

Some automobile shredders employ eddy current technology to remove aluminum from ASR. Some non-ferrous metal separators utilize eddy current technology to recover the non-ferrous metals, including aluminum, from ASR.

Color Sorting. Further separation can be accomplished through color sorting. In this procedure, the color of each particle is sensed and computer control is used to mechanically divert particles of a given color out of the process stream. As each particle is mechanically diverted the throughput of the sorter is particle-size dependent, but since the diversion force is not particle shape or size dependent, very high selectivity is achieved.

Electromagnetic separation has been used to separate UBCs from mixed waste.

Sweat Furnace is used for the purpose of separating aluminum from iron and steel that coexist in composite parts as, for example, in automotive pistons. The sweat furnace can also be used to remove contaminants like dirt, rocks, rubber, plastics and other combustibles from aluminum-bearing scrap. Additionally, the furnace can be used to compact loose and bulky scrap for transportation to the secondary smelter.

Wire Chopping Aluminum and copper are recovered from wire and cable scrap using wire chopping technology. The process is designed to separate the wire from the insulation materials. The process involves shearing, primary granulation, magnetic separation, secondary granulation, tertiary granulation, sizing, and air separation. See Section 7.4.2 for details.

The secondary aluminum industry utilizes shredding, drying and de-lacquering techniques to prepare the scrap for melting.

Shredders are used to reduce large parts and baled material to a size that can be fed into the furnace. Increasingly, cans are being shredded before melting to ensure that the fluids have a chance to drain before being subjected to temperatures that can cause steam explosions.

Drying, often using rotary kilns fitted with afterburners and baghouses, is used to remove contamination such as cutting oils, plastic and other organic material. Drying is essential for pollution control and to minimize oxidation during melting.

7.6.4. Decoating.

Before melting, UBCs have to be stripped of their lacquered labels, paint, the lacquer from inside the can and other combustibles. In most plants this is done by a rotary kiln or a conveyor type furnace. The lacquers are removed in a pyrolysis operation in which the coating is converted to vapors by heating and burning in a secondary combustion or incineration chamber and waste heat recovery. The clean scrap is then charged to the melting furnace.

Toxic fumes are often produced in the delacquering process originating from the toxic elements (mainly halides) of the lacquer; measures are necessary to eliminate potential health hazards. The fumes are fed into a combustion chamber where they are incinerated. The flue gas is passed into a filter system and stack. This is a dry absorption and cleaning system with lime, which binds the hydrogen chloride and fluoride, neutralizing them to produce calcium chloride and fluoride (Trosch, 1990).

A new thermal decoating system has recently been developed by Alcan, which processes aluminum scrap with a level of organic material up to 50% (Tremblay *et al.*, 1995). A fluidized bed consists of small particles in suspension in an upward gas flow, it assumes the properties of a boiling liquid. When it is immersed, a scrap material sinks to the bottom. The organics decompose by contact with the hot medium and the stream of air used to fluidize the bed. The temperature of the medium is chosen to ensure complete decomposition of organics and to ensure a safe margin to the melting point of the various alloys being processed. The medium transfers heat to the scrap in the heating mode and dissipates the heat released from the organics when heat is being generated. The scrap is transported through the fluidized bed by a rotary drum. After the process the scrap exits the drum through an outlet fitted with a series of internal flights to generate tumbling of the scrap to promote the separation of the materials. The particles of the medium fall through a perforated plate and are returned to the main bed zone. The components of a

decoater are schematically shown in Figure 7.24.

The fluidized bed decoater has been used to process a variety of scrap containing aluminum. Excellent metal recoveries ($> 97\%$) after decoating have been achieved in each case. The technique also ensures efficient control of gaseous emissions.

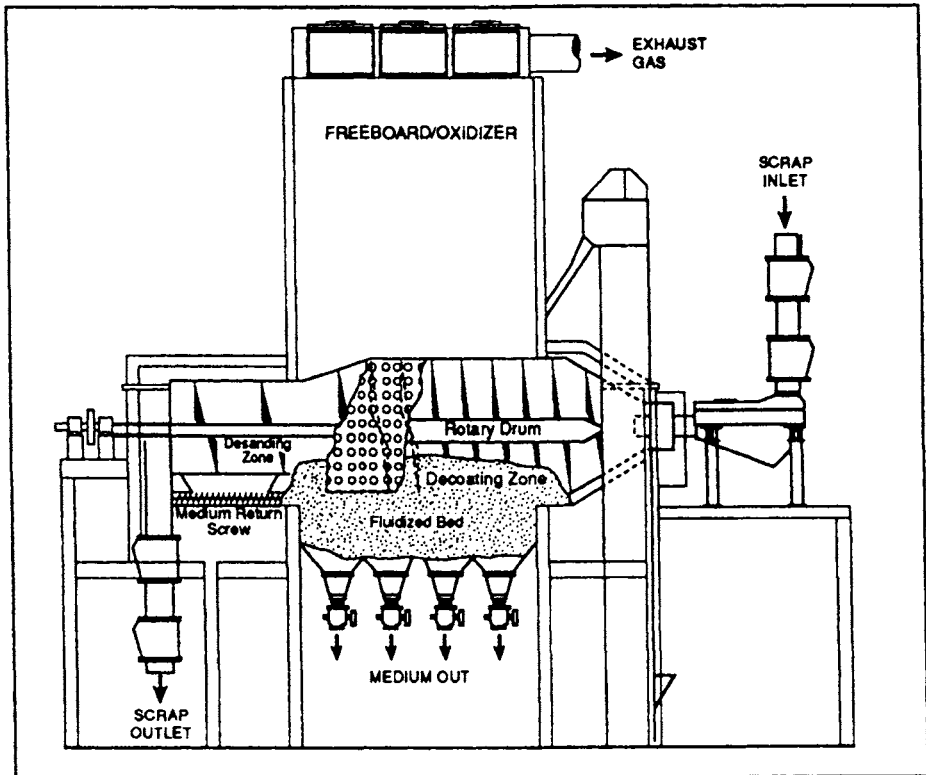


Figure 7.24. Components of fluidized bed decoater to process aluminum scrap (Tremblay *et al.*, 1995)

In *Alcan Belt* Decoater process (ABC), the shredded UBC is transported through the decoater on a wire mesh belt approximately 1.5 m wide by 15 m long. The decoater consists of five equal length zones. Hot process gas, supplied by an inlet fan, flows down the inlet hood through the wire mesh belt and out through the five collector ducts located under the belt; see Figure 7.25.

The process gas consists principally of air preheated in a shell and tube exchanger by indirect contact with the exhaust gas from the process after burner. The process fan pushes the air into the process to the hot plenum over the conveyor transporting the UBC shreds. The hot process fan gas pulls the gas from the plenum, through the layer of UBC shreds on the belt and the equipment and up to the hot gas fan, as seen in the process flow sheet. The exhaust gases are then treated in the emission control equipment to remove particulates, acid gases and nitrogen oxides.

Another device called "Vertical Floatation Melter" (VFM) for decoating and melting scrap aluminum has been described by De Saro and coworkers (2000). Its concept is

shown in Figure 7.26. Scrap is passed to the top of the cone where it falls towards the holding furnace. The products of combustion flow upwards, counter current and in direct contact with the scrap. A drag force is produced by the gases on the scrap impeding its descent. As the furnace is a truncated cone, the velocity increases as the scrap falls, thus increasing the drag force. For most scrap pieces, an equilibrium is reached in which the scrap weight equals the drag force and the scraps hung-up and do not fall. In the case of melting, as the scrap reaches a liquid state, it takes on a more aerodynamic drop shape, which reduces the drag force and allows it to fall into the holding furnace. The temperature of products of combustion is raised by a gas or oil fired burner in the end wall of the holding furnace.

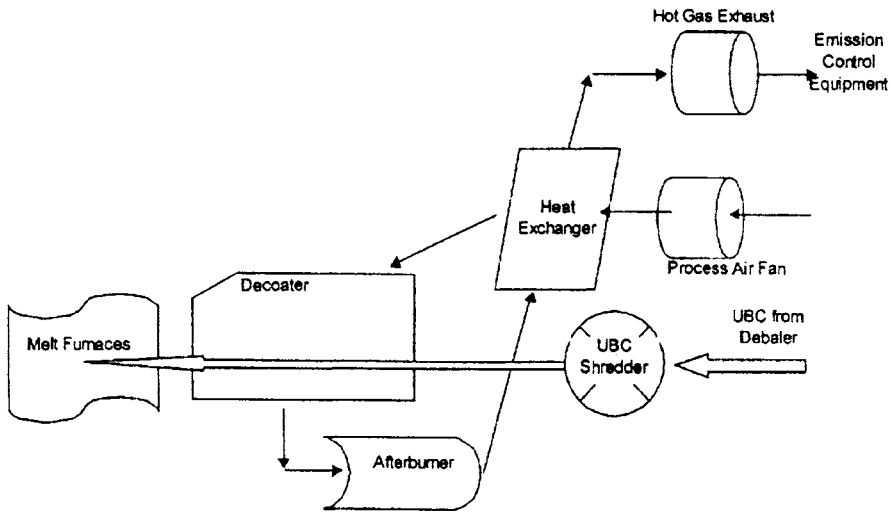


Figure 7.25. Flow sheet of Alcan belt decoater process (Stevens *et al.*, 2000)

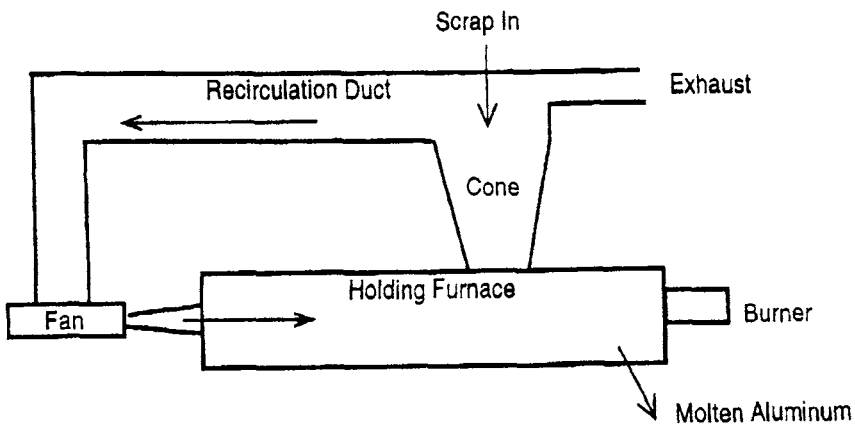


Figure 7.26. Schematic of "Vertical Floatation Melter" (De Saro *et al.*, 2000)

Scrap floatation is achieved when the weight of the solid pieces equals the drag force: $mg = \frac{1}{2} \rho V^2 C_d A$, where m = solid mass, g = gravitational constant, ρ = gas density, V = terminal velocity of the solid piece, C_d = drag coefficient of the solid piece, A = cross sectional or frontal area of the solid piece. It follows from this relationship that if the solid pieces spherical or rectangular, the sizes that can be floated are proportional to the square of the velocity. Particles of a wide size range can be floated.

The VFD decoats in a 2-step process. First, the high velocity gases strip or shear off the oils from the scrap. Second, the high temperature gases vaporize the remaining organics on the scrap. Once vaporized, the organics are rapidly carried out of the VFD cone by the high velocity gases and are combusted in a connected burner. After the combustion, a portion of the gases are recirculated back into the VFD, thus using the fuel content of the organics. The decoated scrap aluminum is fed into a conveyor belt and into the charge well of the furnace, where it is melted.

The recently developed innovation has been applied for a treating a wide range of aluminum scrap including UBCs and oily turnings. Many advantage have been claimed. They include rapid decoating, high fuel efficiency, no moving parts, simple to control and less expensive than a rotary kiln decoater. Metal yields of from 92 to 97% and energy use as low as 1975 J/g (850 Btu/lbm) have been achieved.

Several aluminum recyclers in the U.S. melt the UBCs directly in rotary furnaces without any pretreatment. Apparently, by this approach, the cost and ultimate recovery of aluminum is comparable to the pretreatment and melting process described before.

A method based on chemical treatment of the coating paints, called swell peeling has been described by Fujisawa and coworkers (2000). The specimens are dipped in the "peeling solution". The chemicals, consisting of a mix of halogenated acetic acid and formic acid and methylene chloride, swell the paint and the swollen paint is peeled from the surface. The role of methylene chloride is to cause swelling. The halogenated acids weaken the adhesive binding of the paint with the surface. Thus, when the swelling force generated by methylene chloride exceeds the adhesion force, peeling takes place. The investigators claim this method to be superior to the high temperature treatment methods described before, but they have not made a rational comparison to prove the point. In addition, any use of chemicals especially halogenated organics require appropriate ways to safely dispose off the products generated. The investigators have not described how the paint which is peeled off by the halogenated organics is handled and disposed off or if the organic compounds are recycled.

7.6.5. Recycling from Aluminum Turning Scrap

A practical concern in aluminum recycling is metal content of the scrap, which is often unknown. Due to the high reactivity of molten aluminum, metal yield of aluminum is a function of numerous parameters such as surface area to volume ratio (due to oxidized surface), shape of the scrap, type of alloy, contaminants and amount of required flux additives in the melting process. Metal recovery and yield may vary with the quality of the charged material. The metal recovery is defined as the percentage of metal gained from the metal content of the scrap; metal yield represents the percentage of metal gained from the total mass of the scrap. Often, the metal yield is lower than the metal recovery, due to the various contaminants and losses during melting. This aspect of metal recycling with reference to aluminum has been studied by Xiao and Reuter (2002) with aluminum turning scrap. Their findings are of importance in determining the operating conditions in

aluminum recycling. By a series of melting experiments at 800 °C they found that scrap distribution, contaminant, type and size of the scrap have significant effect on the melting behavior. The metal recovered from the tuning scrap ranges from 84 to 95% representing the metal content of the scrap if potential reactions of the salt flux with metal are disregarded. The presence of contaminants like oil and plastic pieces decrease the recovery (from ~ 95% to ~ 88%). The metal recovery increases with turning size.

7.6.6. Secondary Smelting and Refining

The secondary aluminum recycling industry has developed into two specialized sectors: one to reprocess only used cans, and the other to recycle all other forms of scrap, including beverage cans. The technologies for remelting the two forms of scrap are, however, the same. Reverberatory furnace and rotary furnace are mostly used for mixed aluminum recycling. Sweat furnace and electric induction furnace are employed in limited number of cases.

Reverberatory Furnaces are used primarily to melt scrap containing more than 70% metallic aluminum. The aluminum is charged into the combustion zone. The molten metal bath is covered with chloride-based salt fluxes to protect them from oxidation. This slag cover, containing absorbed aluminum oxide and entrained aluminum metal, is called "black dross". It is skimmed from the surface of the molten metal before casting and sent to treatment facility.

Rotary Furnace. In rotary furnaces, the burners heat the top refractory, which rotates under the charge. Due to lower stack losses, such furnaces are more efficient than reverberatory furnaces and are used primarily to melt scrap containing less than 70% aluminum. Dross and slag may also make up the feed to a rotary furnace. Considerable amounts of flux are required to promote the separation between metallic and non-metallic phases of the charge. Salt is the commonly used flux. As a result, the product formed, accumulation of aluminum metal, aluminum oxide, and fluxes is called "salt cake". The treatment of salt cake will be discussed in Chapter 9.

Sweat Furnaces are used primarily by the scrap industry to separate aluminum from iron in composite parts. Some small aluminum recyclers use the technology to produce casting alloys. Typically, sheet and clipping scrap are introduced to dilute the contaminants found in sweated aluminum. These smelters also supply local steel mills with de-oxidized material.

Electric Induction Furnace. Their use has been limited to foundries. The foundry's scrap is added directly to the charge; alternatively, the scrap is sent to secondary smelters for drying, alloy adjustment and smelting. Since inductive heat quickly penetrates the charge, losses due to oxidation are as low as 2% (compared to 10-20% in conventional gas-fired furnaces) and dross and slag generation are greatly reduced. Better temperature control in an inductively heated furnace prevents the oxide film on top of the bath from being disturbed, resulting in low air emissions.

Two methods are used to remove magnesium from aluminum (demagging). Since the majority of UBCs are recycled by the primary industry, dilution of the melt with virgin aluminum metal effectively reduces the magnesium concentration to meet the required specification. Alternatively, chlorine injection into the molten aluminum is used to remove magnesium. Chlorine gas is metered into the circulation pump's discharge pipe. By introducing chlorine gas into the turbulent flow of the molten metal at an angle to the aluminum pump discharge, small chlorine-filled gas bubbles are sheared off and mixed

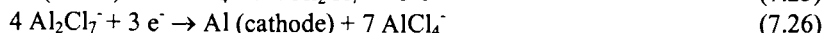
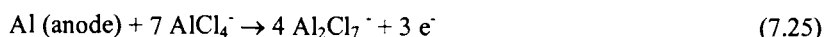
rapidly in the turbulent flow. The flow rate is increased until a thin vapor (of aluminum chloride) is seen above the surface of the molten aluminum, when the flow rate is decreased until no more vapor is seen. This procedure leads to almost stoichiometric consumption of chlorine resulting in minimum chlorine emission. The magnesium chloride produced is absorbed in the salt-based slag, which can be further treated by the methods to be described in Chapter 9.

Gases entrained in the molten aluminum are removed by a degassing process. Inert gases (preferably argon) are released below the molten surface to violently agitate the melt. The agitation causes the entrained gases to rise to the surface where they are absorbed in the floating flux. In some operations, degassing is combined with demagging. This combination process uses a 10% concentration of chlorine gas mixed with an inert gas. The combined high pressure gases are forced through a hand nozzle with a pattern of hole sizes across its face. The resulting high turbulent flow and the diluted chlorine content primarily degasses the melt.

The lead weights used in wheel-balancing are the primary source of lead contamination, experienced by recyclers who reprocess magnesium alloy wheels. Small quantities of lead tend to be fairly inert in the presence of aluminum. However, as lead cannot be easily removed, it is an impurity concern.

After smelting and refining, the molten aluminum is cast into ingots, which are the principle product of the secondary industry. In general, the die-casting alloys can use poorer grades of scrap due to higher specification limits on iron, manganese, copper, zinc and chromium. When corrosion resistance is required, such as for parts in outboard motors, copper limits are greatly reduced. In the permanent mould and sand-casting processes, iron levels are substantially reduced in order to improve ductility.

Electrolytic Process. Aluminum can be electrolytically deposited from aluminum chloride. This is applied to refine impure aluminum, which is made anode and the metal is deposited on cathode made of copper or pure aluminum. In a process described by Wu and coworkers (2000) the electrolysis is conducted at 105 °C in ionic liquids made of 1-butyl-3-methyl imidazolium chloride (C₄mimCl) and anhydrous aluminum chloride in the molar ratio 1.3-1.5. The following electrochemical reactions take place:



The process has current densities of 312-731 A/m², and corresponding voltage of 1-2 volts. A cathode current efficiency of 99% is obtained. Energy consumption for aluminum is about 3 kWh/kg-Al at a cell voltage and current density of 312 A/m². The process results in the removal of impurities like silicon, copper, zinc, iron, magnesium, nickel, manganese and lead. The refined aluminum is found to be 99.9% pure. The process has been applied to recover aluminum from aluminum alloy scrap and aluminum matrix silicon carbide (SiC) composite scrap (Kamavaram and Reddy, 2002). The process is specially advantageous in the matrix with silicon carbide as it eliminates the formation of aluminum carbide (by reaction with aluminum) because of the lower temperature at which the electrolysis is conducted. The ionic liquids are stable with very low vapor pressure and are re-used. The process is thus environmentally clean.

Fractional Crystallization Process. This process was originally developed at Alcoa to purify primary aluminum from smelters containing high levels of impurities like silicon,

iron and gallium, which come from alumina and to some extent from the materials used in the operation and the construction of the smelting cells. Impurities can also be introduced into molten aluminum during melting operations and from the use of scrap materials. The process, schematically shown in Figure 7.27 consists of two steps. In the first step, molten aluminum is treated in a holding furnace with boron to precipitate those impurities, which cannot be purified by fractional crystallization. The melt is then transferred to a crystallization furnace. The liquid metal is cooled from the surface by forced jets to form purified crystals, which descend under gravity and settle at the lower part of the process furnace. The liquid is increasingly concentrated with impurities as a result of which the purity of the crystals forming from it progressively diminishes. The crust formation on the furnace is prevented by a mechanical tamper. The cooling/tamping action is stopped just before solidification is fully completed. At the end of this stage, the furnace is made up of a semisolid mixture containing crystals and interstitial liquid between them. The purified crystals are recovered by tapping the interstitial liquid from the higher tap hole. The impure crystals are then remelted using a hot top and removed from the furnace until the desired purity aluminum product is achieved.

The degree of purification attainable depends upon the value of equilibrium distribution coefficient (k), which is the ratio of the solute concentration in the solid to that in the liquid. The lower is the distribution coefficient for an impurity the higher is the degree of its partitioning in the liquid, and thus the purer is the crystal in that impurity. For the eutectic impurities in aluminum, k has values ranging from a very low value of 0.03 for iron to around 0.95 for manganese. Only eutectic impurities can be removed, which include iron, silicon, copper and nickel. By contrast, manganese has distribution coefficient 0.93 and does not move well during crystal formation. Zinc and magnesium show intermediate behavior.

The alloy scrap is melted in an induction furnace and then transferred to the crystallizer (purification furnace). The melt is skimmed and the purification done as described before. At the end of the solidification process, the metal in the crystallizer turns into a mushy bed of crystals with impure liquid in the interstices. The purest crystals are those that form at the start of tamping and they lie at the bottom of the bed. The level of purity decreases gradually in the upper layers of the bed. Following the principle of distribution coefficient, silicon shows the largest movement from the upgrade into downgrade, followed by iron, gallium, zinc, copper, magnesium and manganese. At a yield level of 80%, the silicon content in the upgrade is reduced by nearly 50% with respect to the charge.

Another technique, also based on fractional crystallization principle, is called zone melting. In this technique, a specific redistribution of alloying elements can be attained in a bar by repeated melting and solidification. The principle is illustrated in Figure 7.28. A sample of the material is pulled in horizontal direction through a ring-shaped heater in a fixed position. A confined part of sample is melted by supplying required amount of heat. By moving the sample through the heater, this molten zone travels through the sample from head to end. Essentially, the material is recrystallized at a controlled rate of crystal growth, equaling the pulling rate of the sample. Crystal growth rates in zone melting tests are typically in the range, $G = 10^{-6}$ to 10^{-4} m/s.

The process is still in the experimental stage and further refinements may well be developed in future.

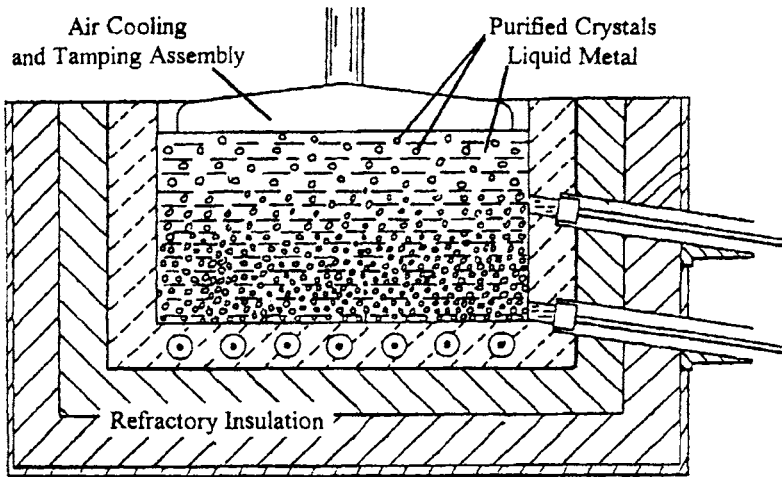


Figure 7.27. Schematic of the furnace for fractional crystallization process (Kahveci and Unal, 2000)

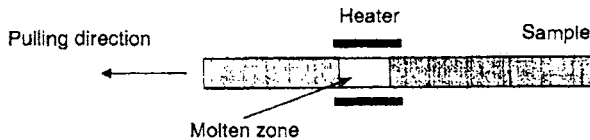


Figure 7.28. Principle of zone melting (Sillekens *et al.*, 2000)

7.6.7. Aluminum Wrought-Cast Separation

Aluminum alloy compositions may be broadly categorized as either wrought or cast, depending upon the alloying elements and their relative quantities. Wrought alloys typically contain low percentages of alloying elements, specifically silicon, which is usually less than 1%. Casting alloys may contain the same elements as wrought, but in greater amounts; and silicon content, generally in the range 1-12%, may exceed in some alloys. To increase the use of recycled metal in wrought secondary alloys, wrought particles have to be separated from cast particles. Common wrought alloys have low silicon and iron alloying element concentrations, while the common die casting alloys contain ~1% Fe and ~10% Si concentrations. Cast alloy contamination of the wrought alloy scrap forces the use of such scrap in secondary cast alloys only. There is a characteristic difference in particle shape and surface texture, which permits labor intensive hand sorting of wrought from cast shredded particles. Several techniques have been suggested for automating this separation.

Before subjecting it to further treatment, initial upgrading of the shredded scrap is done by screening. This results in a cast (undersize) fraction and a mixed cast-wrought (oversize) fraction. This screening could reduce considerably the volume of the material to be processed.

A process called hot crush technique has been developed to separate the cast and wrought fractions (Ambrose *et al.*, 1983; Brown *et al.*, 1985). In this process, the low eutectic temperature of Al-Si casting alloys is made use of. The cast and wrought mix

alloy is 'soaked' at 520-560 °C for 1-2 hour. Above the eutectic temperature, the cast alloy is embrittled by loss of ductility, and can be size-reduced by autogenous milling. The wrought particles are then separated by screening. This technique can be combined with decoating. However, it is not cost efficient for bare scrap as the scrap has to be heated near to melting temperature, and with excessive size reduction it will not be possible to sort cast alloys. Under the present market conditions, the die casting and foundry alloys require all available shred scrap, which makes further separation unnecessary.

7.6.8. Aluminum-Lithium Alloys.

This is a relatively new class of alloys introduced for application in aerospace industry. A typical alloy contains approximately 2% lithium, a reactive metal in atmosphere and toward refractories. As the alloys have been in industrial use for only about 10 years, recycling methods are in development stage. Of the various possible options, vacuum distillation has been recognized as the most cost effective and technically, the most viable one. The feed is enriched by a combination of heavy medium separation taking advantage of the 10% density difference of Al-Li compared with other alloys; and eddy current separation, which is based on differences in the ratio of conductivity to density.

Vacuum distillation can reclaim a lithium distillate of sufficiently high purity, which can be used as high-grade alloying material.

7.7. Nickel and Cobalt. .

Nickel is relatively small in tonnage, but unit price is relatively high and hence gross value is high. It is used primarily in the manufacture of stainless steel (> 60%) with superalloys for gas turbines an important second use. Nickel often is a component of high chromium alloy foundry products noted for heat and wear resistance. Stainless is used extensively in the food and chemical industry and these are thus the primary source of recycle stainless steel. Superalloys are recycled by the gas turbine industry manufacturing industry or its customers the aircraft and electrical generation industries.

Cobalt is smaller than nickel in tonnage but is one of the highest priced of the common base metals. Used in superalloys and as a catalyst (with nickel, molybdenum and vanadium) in the food, chemical and petro-chemical.

Nickel and cobalt are recycled from alloy scrap and a variety of metallurgical dusts. Common grades of nickel scrap are derived from nickel silver clippings, nickel silver sheet, plate, pipe, rod, tubes, wire, screen, etc. Both pyrometallurgical and hydrometallurgical techniques have been applied.

7.7.1. Recovery from Superalloy Scrap (SAS)

In a process developed by the U.S. Bureau of Mines, the mixed scrap is converted to a matte containing 4-7 percent sulfur by adding sulfur directly to the molten metal. The matte is then granulated and ground to a minus 35-mesh particle size and leached with a solution of hydrochloric acid plus chlorine. This treatment leaches essentially all nickel, cobalt, chromium, iron, aluminum and molybdenum into solution in about 3 hours of leaching time, leaving tungsten, tantalum, titanium, and niobium in the residue. The nickel and cobalt are recovered by a solvent extraction-electrowinning process. Figure 7.29 represents the flowsheet.

7.7.1.1. Electrodeposition Method

Based, on electrochemical principles, electrodeposition has been extensively used for metal refining, and has been extended to refine metals recovered from scrap. An electrorefining process to recover nickel, cobalt, chromium and other metals from mixed and contaminated superalloy scrap was developed by the U.S. Bureau of Mines. The process is based on controlled potential electrolysis (CPE) to selectively deposit a nickel-cobalt alloy and permits the recovery of chromium, tungsten and molybdenum as impure metal hydroxide residues; Figure 7.30.

The selectivity of elemental deposition is enhanced by CPE. It is based on the principle explained in Chapter 4 (Section 4.4) that different metals exhibit different reduction potentials; see Tables 4.8 and 4.10..

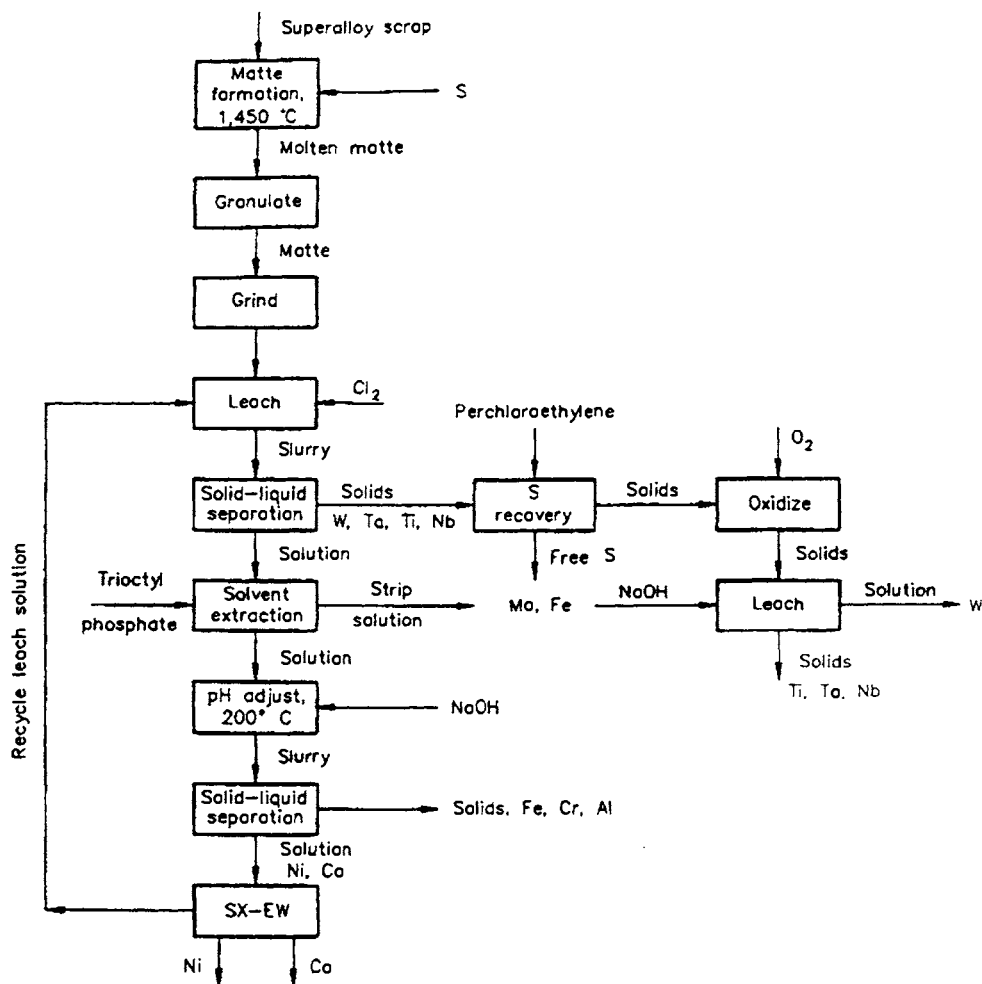


Figure 7.29. Flowsheet for separation and recovery of nickel and cobalt from superalloy scrap (Hundley and Davis, 1991)

A double membrane electrolytic cell (DMEC) has been designed to recover high purity cobalt and nickel by electrowinning (Redden and Steele, 1990). It consists of an anode compartment and a cathode compartment by two industrial anionic membranes. The separation between the two membranes forms a third compartment, referred to as membrane compartment. An impure SAS anode is electrolytically dissolved in the anode compartment, and the resulting anolyte is treated by hydrometallurgical techniques, (schematically described in Figure 7.31) to produce purified chloride electrolytes, which are then circulated to the cathode compartment of the DMEC where high purity metal is electrolytically deposited at the cathode. The Operation of DMEC is schematically shown in Figure 7.32. (More details of double membrane electrolytic cell will be described in Chapter 12).

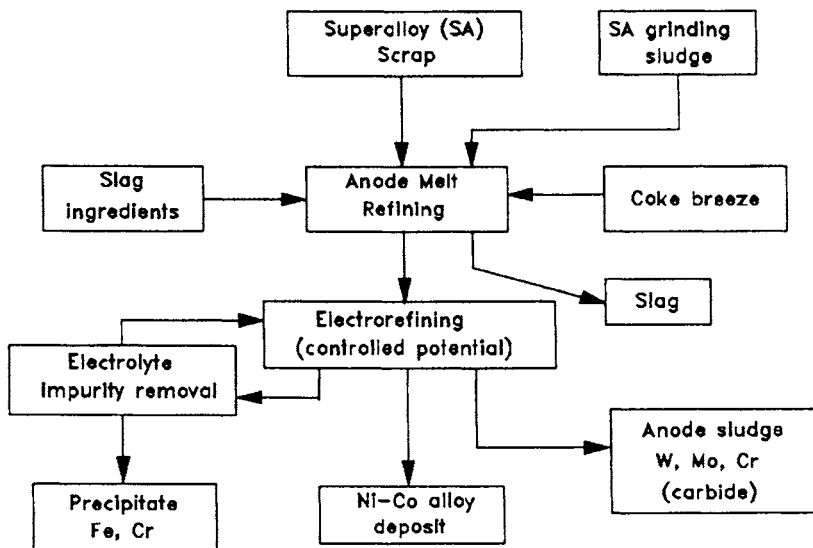


Figure 7.30. Flowchart for recycling superalloy scrap by electrochemical processing (Lutz *et al.*, 1990)

The function of the DMEC membranes is to separate the impure anolyte from the purified catholyte solutions while allowing chloride ions to pass from the catholyte to the anolyte. A stream of diluted, spent catholyte solution flows through the membrane compartment and the effluent is recycled to the anode compartment. The configuration nearly eliminates the transfer of anolyte impurities to the catholyte and makes it possible to produce very high grade metal products at the cathode. The membranes are anion selective. They are made of cross-linked polymers of vinyl monomers containing quaternary ammonium anion exchange groups.

Electrochemical method has also been applied for the recovery of nickel from a superalloy scrap containing many impurities. This requires a series of pretreatment steps to separate the impurity components (Zhiming *et al.*, 1987). Another application of this process is for the recovery of nickel from nickel-cadmium batteries from which other metal components (iron and cadmium) are separated by hydrometallurgical treatment. It is described in the flowsheet shown in Figure 7.33.

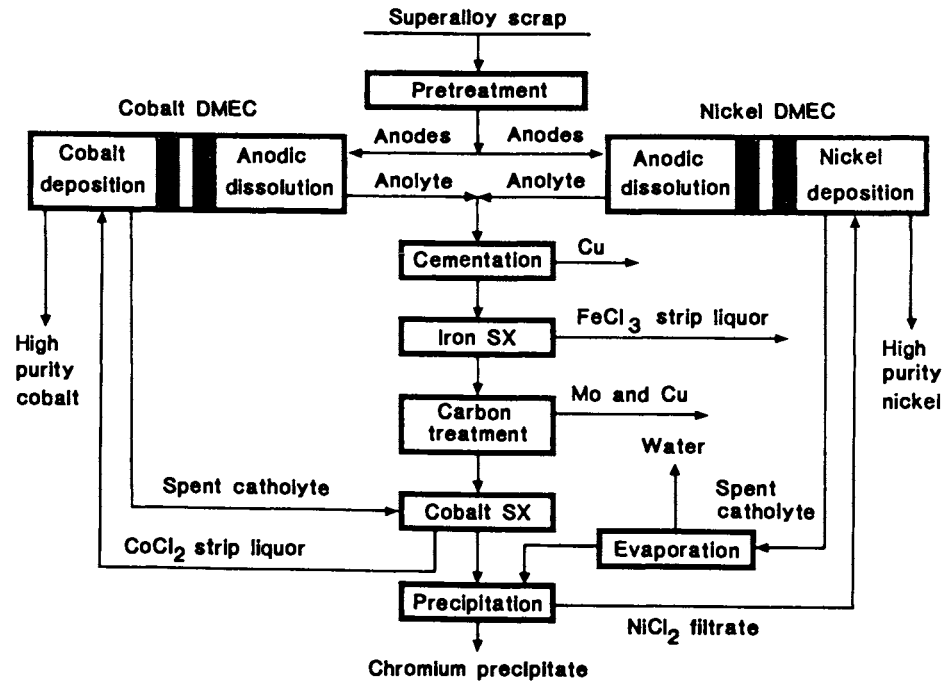


Figure 7.31. Generalized process flowsheet for electrowinning of cobalt and nickel (Redden and Steele, 1990)

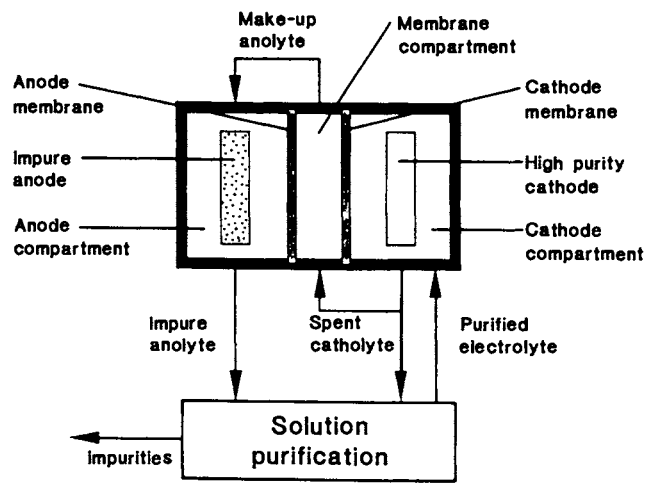


Figure 7.32. Schematic of DMEC operation (Redden and Steele, 1990).

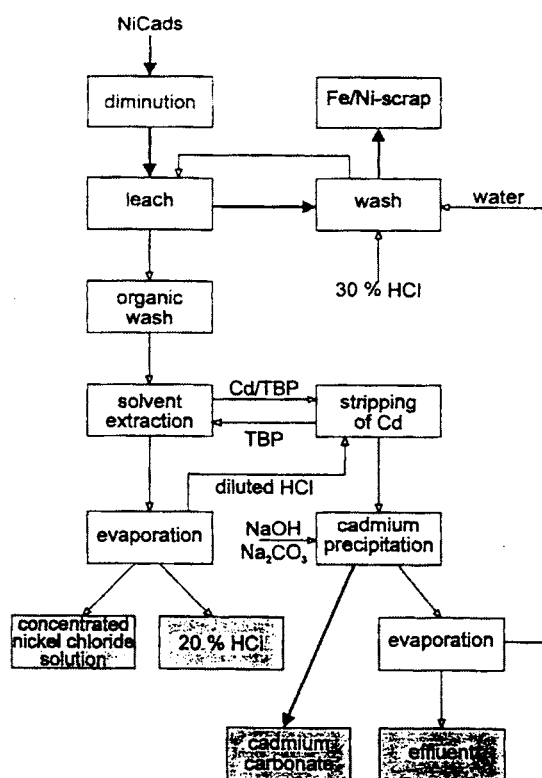


Figure 7.33. Block diagram of the hydrometallurgical process for the treatment of nickel-cadmium batteries (van Erkel *et al.*, 1994)

Metal recycling from batteries will be further described in Chapter 10.

7.7.1.2. Solvent Extraction Procedure

Separation and recovery of cobalt and nickel from other metals has been achieved by successive solvent extraction steps; see Figure 7.34. Each metal is preferentially extracted by a specific solvent. This is based on principles of solvent extraction explained in Chapter 4 (Section 4.3). Iron and cobalt (and molybdenum when it is present in the alloy) are solvent extracted and the nickel remaining in solution is precipitated at pH 8. In another process, the iron is precipitated as ferric hydroxide at pH ~3 (where nickel and cobalt remain in solution; see the hydroxide precipitation diagram in Chapter 4; Figure 4.1.) Cobalt is extracted by tertiary amine and nickel, which remains in solution, is precipitated at pH 8 as before.

7.7.1.3. Pyrometallurgical Process

In the pyrometallurgical process for secondary nickel-containing materials sulfidizing smelting is applied to produce nickel matte, separating the undesired components into slag. Copper is separated from cobalt and nickel by electrolysis (since the deposition

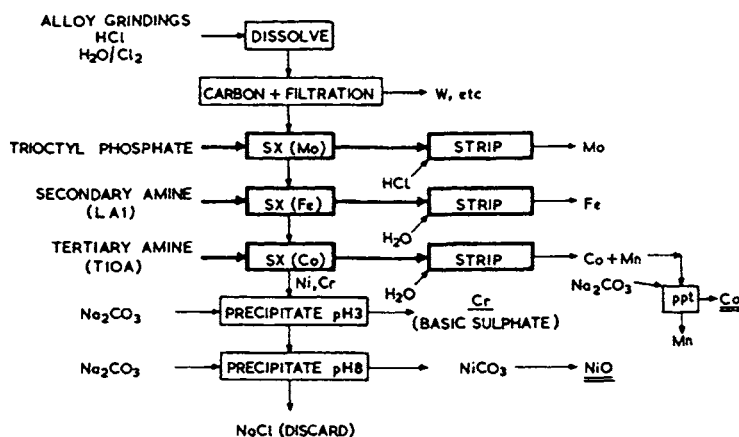


Figure 7.34. Nickel and cobalt recoveries from ally scrap by solvent extraction (Holman, and Neumeier, 1986)

potential for copper is lower than that for nickel and cobalt; see Chapter 4). Cobalt is then precipitated as oxide. The nickel in solution is either recovered by electrolysis or converted to nickel sulfate. The process is schematically shown in Figure 7.35.

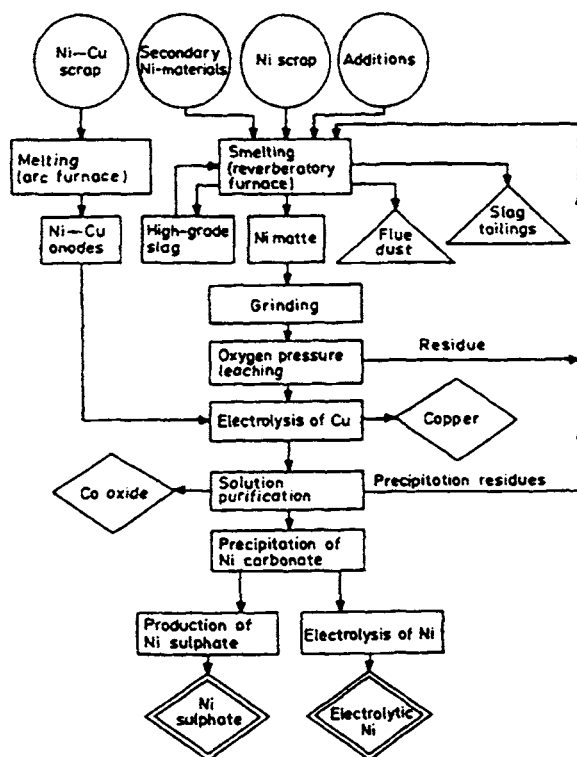


Figure 7.35. Recovery of nickel and cobalt by pyrometallurgical processing (Martens *et al.*, 1988).

7.7.2. Recovery of Cobalt and Nickel from Alnico Scrap

Alnico scrap generated during the manufacture of alnico permanent magnets typically contains 85% nickel and 11.7% cobalt. Recovery of these metals by leaching with cupric chloride, followed by solvent extraction has been demonstrated by Alex and coworkers (1995). With 0.4 M CuCl_2 at a temperature and in presence of oxygen flow, nickel and cobalt are selectively leached. The quantities leached increases with increasing leach temperature, reaching 75% Ni, 74% Co and only 1.2% Fe. Absence of oxygen flow, lowers the selectivity as up to 18% iron is also leached. In the presence of oxygen, iron is oxidized to Fe (III) state and forms insoluble goethite (FeO.OH). This minimizes the dissolution of iron by combination with cupric chloride. Nickel and cobalt are leached by cementation reaction with cupric chloride; (explained in Chapter 4). After the reaction, copper is formed as metal and copper hydroxychloride ($\text{Cu}_2(\text{OH})_3\text{Cl}$). After solid-liquid separation, cupric chloride is regenerated by leaching with 10% hydrochloric acid. Cobalt and nickel are recovered as their salts by solvent extraction. The extract also carries residual cupric chloride. A suggested flowsheet is shown in Figure 7.36.

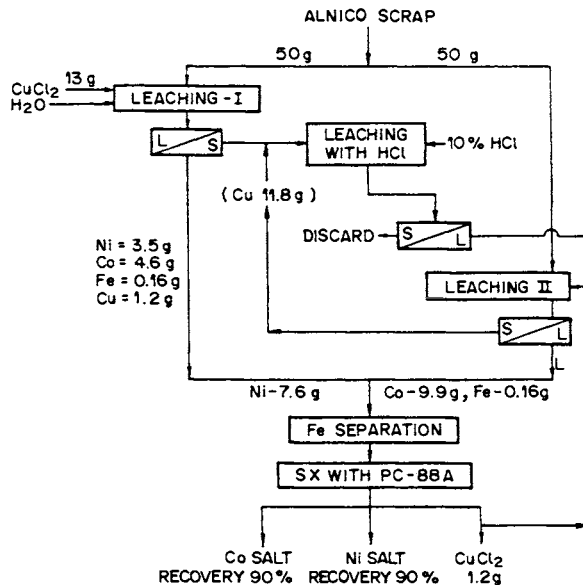


Figure 7.36. Suggested flowsheet for the processing of alnico scrap to recover cobalt and nickel (Alex *et al.*, 1995).

7.7.3. Separation and Recycling of Nickel by Metal Organic Vapor Deposition (Terekhov and O'Meara, 2000)

This method is specially applicable for the separation of nickel metal from metal scraps. It is based on forming nickel carbonyl (Ni(CO)_4), by reaction with carbon monoxide, the technique used for the purification of nickel for many years. The synthesis is done in a fluidized bed reactor, where the powder containing the metal reacts with carbon monoxide. The volatile metal carbonyl is separated by fractional distillation in presence of carbon monoxide as carrier gas. The carbonyl is then thermally decomposed and carbon monoxide is recycled. The method has been applied to recover nickel from

radioactive contaminants such as uranium and thorium (Terekhov and O'Meara, 2000).

7.7.4. Nickel Recovery from Superalloy Scrap by Electroslag Melting

A secondary remelting process called electro slag crucible melting (ESCM) has been applied, with modifications, for recycling valuable scrap of strategic metals and alloys, in particular, nickel (Prasad and Rao, 2000). Originally developed for the production of high quality ingots of specialty steels, in this process the metal to be refined is taken in the form of a consumable electrode in a refractory lined crucible. High quality liquid metal is produced, which can be cast into desired shapes.

In the procedure to treat a superalloy scrap, Prasad and Rao (2000) used a water cooled electrode made of steel, except the lower part, which was copper. The mild steel should be able to carry the required process current of about 4000 A. The electrode is cooled by water supplied through a coaxial mild steel tube. The cooling water enters through the inner tube, impinges on the bottom of the electrode and exits through an annular space. Stubs of the refractory metal molybdenum are fixed against the bottom of the electrode to prevent chilling of slag. The superalloy scrap is melted using a 350 kVA, AC electro slag refining furnace. The scrap is subjected to magnetic separation and preheated at 400 °C for about 4 hours before melting. A slag consisting of 70% calcium fluoride and 30% alumina is used. Titanium dioxide is added to the slag to minimize the loss of titanium in the metal during melting. The slag mixture is preheated at 800 °C for 4 hours. The electrode is lowered into the mould till above the bottom plate. The liquid slag is poured into the mould. As soon as the liquid slag fills the gap between the electrode and the bottom plate, the electrical circuit is completed, which starts the electro slag process. After the slag is sufficiently superheated, the scrap is charged into the slag. Towards the end of the process, the power is gradually reduced to impose a condition of hot topping. Schematic of the process is shown in Figure 7.37.

The ESR superalloy ingots produced are sound and free from defects. The process has potential for scaling up to produce larger diameter ingots as well as for recycling a wide range of superalloy scrap.

Recovery of nickel and cobalt from spent catalysts will be described in Section 7.16.

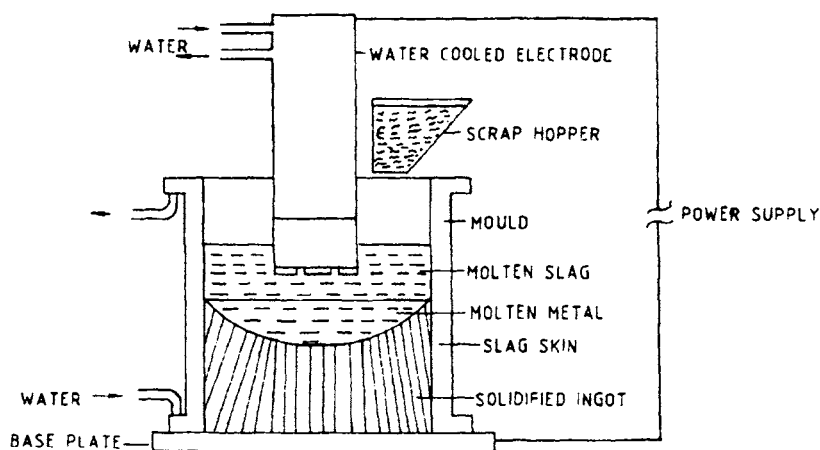


Figure 7.37. Schematic of Electroslag smelting set up (Prasad and Rao, 2000)

7.8. Precious Metals

Recycling of precious group metals, which include, silver, gold, and platinum group metals (PGMs) - platinum, palladium and rhodium is largely undertaken by separate specialist industries. Gold products comes from jewelers, silver from film and chemical industry catalysts and platinum group metals as residues from the base metal industry, analytical laboratories and increasingly from automobile catalysts. Recycling of precious group metals, present the greatest challenge for a number of reasons:

- (i) the very small percent content in which precious metals are found in waste and scrap materials;
- (ii) the mixed nature of precious metals in these products; a single metal is seldom present;
- (iii) the variety in the chemical and physical properties of the host materials ranging from metallic to non-metallic and from solids to solutions and everything in between;
- (iv) the high value of the precious metals combined with their dilute and mixed nature require that the weight and the assay of the constituents be determined. This may lead to additional costs and processing times.

To ensure constant and reliable sources of supply of precious metal-bearing material of known and consistent composition, recycling facilities tend to operate in closed loops with collectors, reproprocessors, and end-users. The following types of facilities have developed to recycle precious metal-bearing materials:

- (i) primary smelters and refiners specializing in electronic scrap , plating sludges, and many other types of precious metal-bearing scrap and waste materials because of its ability to extract the valuable metals in the presence of contaminants and other materials associated with theses materials;
- (ii) companies that use melting furnaces, recover silver and gold from metallic forms of scrap including jewellery, coins, tableware, stripped electronic scrap, and manufacturing scrap;
- (iii) companies that concentrate on reprocessing used photographic films to recover silver are often associated with major film manufacturing industries;
- (iv) companies that concentrate on recovering PGMs from industrial catalysts, usually in close association with major catalyst manufacturers and end-users;
- (v) dedicated secondary refiners recovering PGMs from automotive catalysts only.

The types of precious metals being recycled can be classified into two main grades: precious metal scrap and precious metal by-products and waste. The form of precious metal scrap and waste to be recycled has a bearing on the technologies used and on the industry sector (primary or secondary) that is capable of recycling the material. The common grades of precious metal scrap include jewellery, coins, tableware, electronic scrap and catalysts. The common type of precious metal by-products and waste include anode slimes, sludges, ashes, refractories, crucibles, photographic films, filters, resins and carbon.

7.8.1. Review of Recovery and Recycling Technologies

The two broad classes of technologies to recover precious metals from scrap and waste materials are pyrometallurgical extraction methods and hydrometallurgical extraction methods. Specialized processes have been developed to recycle industrial wastes including automobile catalysts, electronic scrap and photographic material.

7.8.1.1. Pyrometallurgical Extraction Methods

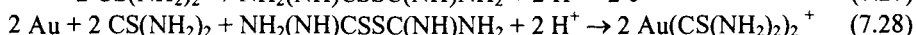
Precious metal-bearing scraps are mechanically reduced to forms suitable for handling, sampling and minimization of loss. The sized metal is then mixed with reductants and fluxes, and smelted in the presence of lead or copper, which act as collectors. The choice of the collector material is optional in many cases. Lead smelting may be conducted at a lower temperature, but lead-containing systems tend to show more aggressive attack towards furnace lining and crucibles. Iron is also a suitable collector for automotive catalysts, particularly for platinum and palladium. It is inexpensive and is readily dissolved by acids in the refining circuits, but it requires smelting temperatures a few hundred °C higher than those necessary for copper.

Various types of furnaces (see Chapter 6) with lead or copper collectors are used for secondary smelting operations. Plasma furnaces with iron collectors have been used for the recovery of platinum and palladium from automotive catalysts. Incinerators, as a pretreatment step for the destruction of plastics and other organic combustibles, may be used as an integral part of any smelting system requiring volume reduction and concentration.

7.8.1.2. Hydrometallurgical Processing Methods

Hydrometallurgical treatment techniques offer important advantages over smelting processes. They include, low pollution (wastewater is produced, but there is no pollution of air), decreased in-process inventories, shortened treatment cycles, and higher recoveries. One major deficiency, however, is their inability to achieve complete extraction. A significant fraction of precious metals may be left undissolved because of physical encapsulation within the host product. A new residue, of highly decreased value, is generated for treatment in a pyrometallurgical loop. Hydrometallurgical recovery of precious metals appears to be best suited for handling selected feeds such as, for example, individual types of catalysts of known and predictable compositions and characteristics..

Leaching of gold from computer circuit boards by thiourea has been investigated by Sheng and Etsell (1998). Thiourea is reduced to formamidine disulfide, which oxidizes gold. The following reactions occur:



The reactions are controlled by ORP (redox potential, as explained in Chapter 3). If the ORP of the solution is too high, formamidine disulfide reaction irreversibly oxidized to further products of oxidation. On the other hand, increasing thiourea concentration and ORP leaches more gold. Careful control of ORP is required to minimize loss of thiourea. Figure 7.38 summarizes, plotted based on the leaching results after 1 hour, the effect of both thiourea concentration and ORP on gold leaching. It shows that minimum thiourea concentration is necessary for gold leaching for a specific thiourea concentration.

Hydrometallurgical method has been used for the recovery of precious metals from catalysts. A process to recover palladium from petroleum catalysts by leaching in alkaline potassium cyanide solution has been described (Sibrell and Atkinson, 1995). The palladium is leached forming the metal cyanide complex. Palladium is recovered by the thermal decomposition of the complex at 250 °C. High temperature cyanide leaching of auto catalysts has been applied to recover a concentrate of precious group metals (PGM)

(Kuczynski *et al.*, 1995). Sodium cyanide (1% solution) selectively dissolves the PGMs. Three stages of autoclave leaching of a pellet catalyst with sodium cyanide at 160 °C for 1 hour dissolves on average 95% of the palladium, 96% of the platinum and 73% of the rhodium. Heating the leach solution to 275 °C for 4 hours destroys the cyanide almost completely (0.2 mg/L residual concentration) and produces a powder metallic PGM concentrate analyzing > 50% PGM.

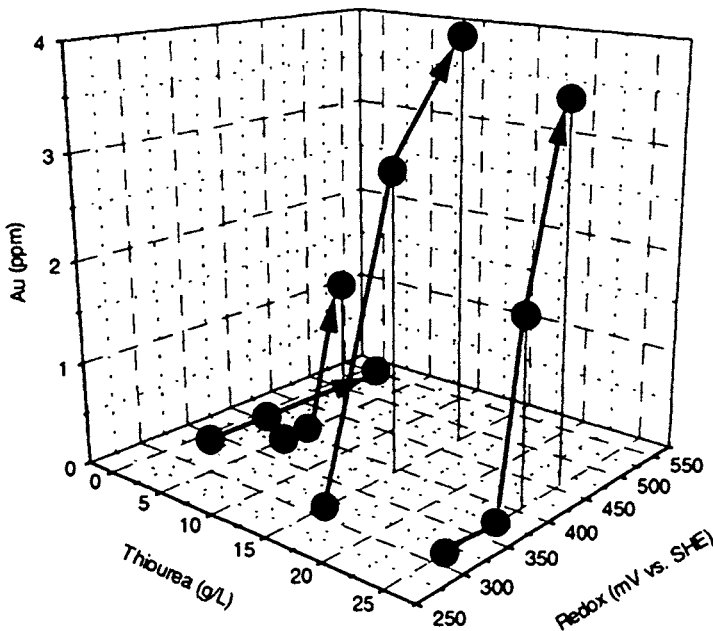


Figure 7.38. Dissolution of gold in thiourea solution (Sheng and Etsell, 1998))

Ion exchange resins have been investigated to recover precious metals from their acid leach solution (Goriaeva *et al.*, 2000). Low and high basic anion exchangers as well as complex forming resins have been tested, with promising results. Up to 99% platinum group metals are adsorbed.

7.8.1.2.1. Chlorine Leaching (Hoffmann, 1992b)

Precious metals in oxidic scrap can be done by chlorination. It may be done by chlorine water, or the oxidic scrap is slurried in water and chlorine gas sparged into the slurry. Along with gold, platinum and palladium are also dissolved completely if they are present in the elemental state. The oxides of these metals are extremely resistant to chemical attack. After separating the gold cyanide complex by filtration, gold is extracted by solvent extraction. A reagent, which is found very selective to gold is dibutyl carbitol or diethylene glycol dibutyl ether $C_4H_9-O-C_2H_4C_2H_4-O-C_4H_9$, which is characterized by a distribution coefficient for gold in chlorine media of approximately 1000 (Hoffmann, 1992). Scrubbing of the loaded organic phase by 1-1.5 M hydrochloric acid, which removes any extracted tin into the aqueous phase produces a higher purity gold product. From the organic phase gold is recovered by reduction. A variety of reducing agents can

be used. Sulfur dioxide is probably most economical. Hoffmann (1992b) has suggested hydrazine (N_2H_4) because of the speed of its reaction and also as the reaction products are nitrogen and water, which makes it a clean operation.

Chlorine leaching is a high cost process. Further, chlorine rapidly reacts with virtually all metals in the scrap. The process can be justified only on material, where the metallic components are already oxidized. This includes ceramic elements plated with gold or other precious metals. Acid concentration must be kept low to avoid excessive acid consumption by reaction with the oxide phase.

7.8.1.2.2. Other Leach Processes

A 3-stage leaching process has been developed by the U.S. Bureau of Mines (Kleespies *et al.*, 1969). The feed from a high tension separator is leached with sodium hydroxide to remove most of aluminum, then pressure leached with nitric acid at 150 °C for copper, nickel and silver. Silver is precipitated as chloride and copper recovered by cementation with steel. Almost all gold and silver and about 90% copper are recovered.

In an alternative process aluminum is dissolved in caustic soda and the residue incinerated to destroy residual organics. The residue is leached with sulfuric acid to remove base metals, mainly copper, and then treated with 50% (by volume) nitric acid to recover silver, and with aqua regia to leach gold, with several percent palladium. The impure silver and gold plus palladium products represent about 1.5% of the initial high-tension separated concentrate. Each step produces an upgraded product of progressively smaller volume from which metals can be recovered. The product of each step may either be sold to a precious metal refiner or used as feedstock for the next operation (Hilliard *et al.*, 1985).

7.8.1.3. Pyrometallurgical Processes

Pyrometallurgical processing includes incineration to remove organics and to concentrate metals. This is followed by smelting in a plasma arc, or a blast furnace, drossing, preferential melting (sweating) and preferential oxidation. In one operation, the scrap is shredded, the product incinerated, physically separated, smelted and the cast or granulated metals refined electrolytically. Up to 90% or sometimes higher recovery of gold, silver and palladium has been reported (Setchfield, 1987).

At Noranda smelter in Canada, feed enters a reactor where it is treated at 1250 °C in a molten metal bath, agitated by oxygen-enriched air (up to 39% oxygen). Iron, lead and zinc are oxidized and enter the slag. Copper sulfides containing the precious metals enter a matte at the bottom of the reactor. The slag is treated for metal recovery, and the copper matte then enters the copper circuit, where gold, nickel, palladium, platinum, silver and tellurium are recovered by electrolysis. About 125 ton silver, 5.1 ton gold and 5 ton platinum and palladium have been recovered from about 100,000 t of scrap (not all of which are electronic scraps) (Veldhuizen and Sippel, Noranda; Henstock, 1996, p. 285).

Similar procedures with desired modifications have been adopted for reclaiming metal values from computer scrap. Incoming circuit boards are clipped to remove excess plastics and reusable components, and the material granulated. Incineration is precluded on environmental considerations. Metal is separated from plastic either by smelting or by chemical methods. The refined gold is produced on site or in other refining companies.

The residues produced in the manufacture of electronics hardware or otherwise redundant electronic equipment contains components like printed circuit boards with

copper and precious metals. Copper is recovered from these boards by leaching with aqueous cupric chloride, followed by reaction with aluminum to recover copper and aluminum chloride. Printed circuit boards are estimated to contain 80-1500 g/t gold and 1.35-1.85 kg/t silver (Henstock, 1996, page 283).

The principal advantages of hydrometallurgical methods over pyrometallurgical ones are environmental benefit of operation at relatively low temperatures, easier separation of the main scrap components, and reduced process costs arising from lower energy consumption and with recycling of chemical agents. Disadvantages include the inability to accept electronics scrap without physical pretreatment to reduce its bulk and to separate it into material fractions, and the large volumes of leach solution and effluent, which may be corrosive and toxic.

7.8.2. Electronic Scrap

Electronic scrap, derived from discarded telecommunications equipment and telephone contacts and computers is a rich secondary source of precious metals. In addition to obvious economic motivation, as precious metals fetch high price, environmental consideration is an additional major incentive for the recycling of electronic scrap, as disposal is a serious problem. It forms an important and increasing part of the feed to many smelters, up to one quarter in some cases.

Electronic scrap is of variable composition, often containing 30% plastic, 30% refractory oxide and 40% metals. Such a deposit may be exposed or it may be enclosed within a component (Sum, 1991). The precious metals in electronic scrap include gold, silver and some PGMs, usually in the form of plating on base metal pins and laminates. The treatment usually comprises three stages: pre-treatment, upgrading, and refining. Generally, all electronic scrap containing precious metals is hand sorted followed by incineration to volatilize the plastics and other organic materials. (A drawback of incineration is the presence of precious metal chlorides which also volatilize). Physical separation of components is also done by air classification, magnetic separation, screening, eddy current separation and high tension separation (Ambrose and Dunning, 1980). Ferrofluid separation in a kerosene-based medium, first at a specific gravity of 2 to separate non-metallic detritus and then to 3, to produce an aluminum concentrate float and a sink fraction containing heavier metals like copper, lead and tin is sometimes applied when the cost is justified by high value of components to be recovered (Reimers *et al.*, 1976). Size reduction is used to liberate the precious metal-bearing materials from other components, thereby exposing the precious metals to increase the recovery rates of the subsequent extraction processes. Size reduction is also essential to obtain a representative sample of scrap for valuation.

7.8.2.1. Cyanidation Process

Recovery of precious metals from electronic scrap by hydrometallurgical processing requires cyanidation and solvent extraction. As in primary gold production, cyanide dissolves the precious metals. The metal-bearing liquid is then separated from the barren phase, and the pregnant liquor is contacted with zinc metal (cementation) to precipitate the precious metals. The overall reaction is represented by



The leaching is accelerated by a suitable oxidizing agent. Copper and silver present in the scrap also dissolve forming the corresponding cyanide complexes. The gold is usually recovered by zinc cementation, which produces a mixture of copper, silver, and gold in the cementation product. After washing and dewatering, the cementation product is melted in a small induction furnace. If necessary, any zinc present is acid leached. The final product generally contains 60% to 85% gold. This process is usually the choice of small scrap processors whose profitable operation is not contingent upon complete recovery of the gold content from the scrap.

7.8.2.2. Physical Separation Methods

Metal recovery from electronic scrap by applying mineral processing physical separation methods has been investigated by Distin (1995). Scrapped integrated circuits containing 25 weight percent copper pins in a ceramic base are crushed in a cone crusher to - 20 mesh. Size reduction of the ceramic is done with a ball mill, where the particle size distribution of the copper is essentially unaltered. By gravity separation using a Mozley shaking table (see Chapter 3 for description) 80-84% copper is recovered. Concentrate grades improve from 46% (with no grind) to 75% Cu (10 minutes grind) with increasing size reduction of ceramic. Up to 50% of the copper is recovered by flotation using sodium isopropyl xanthate collector. Scrapped plug connectors, containing 760 g Au/t in a plastic matrix, are crushed with a cone crusher producing 87% -6 mesh material containing 96.5 gold. By gravity separation, 96% of the gold is recovered from the -6 mesh to + 20 mesh fraction. The recovery is only 76% from - 20 mesh feed.

7.8.3. Computer Circuit Boards

The composition of computer scrap can vary significantly from model to model and for the same part in different units of the same model number. In general, mainframe computers manufactured before 1980 have a high precious metal content, averaging 2-55 troy oz of gold, depending upon the make and size of the system. The silver to gold ratio can range between 1:1 and 2:0. Precious metals can be found throughout electronic equipment in such components as pin connectors, contact points, silver-coated wire, terminals, capacitors, plugs, and relays. The precious metal content of the equipment ranges from relatively high concentrations (up to 2000 troy oz) to insignificant values.

Precious metal content per unit has decreased sharply with the development of new models of computers. Combined with the fact that the newer models are smaller in size, opportunities for precious metal recycling from computer scrap has been decreasing.

7.8.4. Photographic Waste Technologies

Two principal sources of photographic wastes are: X-ray film, graphic arts film, microfilm and related processing solutions; and black and white film, color film and paper.

Developer/fix solutions are treated in small electrolytic units, which produce an impure silver flake. This can be sold to refineries for upgrading to market specifications. The remaining solution can be treated by precipitation as silver sulfide or by passing through wire-wool recovery units. X-ray plates are collected from hospitals and burnt to recover the silver from the ash by smelting, or the silver can be removed by wet chemical means followed by electrolysis of the dissolved silver. The incineration of the film requires an incinerator protected by after-burners and venturi scrubbers. The temperature

must be controlled to prevent volatilization of silver.

Black and white or color film is typically shredded, sent to incineration or chemical treatment, to be followed by electrolysis or precipitation to recover silver sulfide, which may be further refined. The residual shredded material contains tri-acetate or polyester and may cause contamination of the site. Large effluent volumes may be generated and the characteristics of the effluent vary due to many types of photographic processes used. Technologies used for silver recovery include:

- metal replacement (often cementation by iron using wool cartridges) applicable to fixers and bleach fixes as well as final effluent;
- electrolysis - applicable to fixer and bleach-fix solutions but not to wash waters or dilute effluent;
- ion exchange - applicable to fixers and bleach-fixes as well as final effluent;
- sulfide precipitation - using caustic soda and sodium sulfide or hydrogen peroxide;
- electrochemical sulfide precipitation.

Where it is not possible to regenerate or re-use the solution, the amount of effluent and wastes may be reduced by regenerating the various solutions such as color developing reagents, couplers, ferrocyanide, chromium, and phosphate (Myslicki, 1981)..

A novel method of recovering gold and silver from photographic wastes by depositing the metals on an oxidized polymeric material, polyaniline (prepared by electrochemical oxidation of aniline, $C_6H_5NH_2$) has been described by Savic and coworkers (2000). Deposition of gold is kinetically favored under the experimental conditions. Up to 99% extraction of gold has been reported. Removal of the metal from the polymer has not been explained. One possibility is to combust the organic polymer and recover gold.

Specific examples of precious metal recoveries from different kinds of process wastes will be described in Chapter 10.

The following Sections will describe recycling of some of the less widely used. Many of them are used for specific applications in limited quantities. The main incentive for recycling is environmental concern as most of these metals are toxic and there are stringent regulations to ensure that they are effectively contained before discharge of disposable matter.

7.8.5. Platinum Group Metals from Automobile Catalysts

Catalytic converters have been an integral component of automobiles for many years to facilitate reduction in the level of hydrocarbons emitted in exhausts. The converters use platinum group metals, platinum (0.08%), palladium (0.04%) and rhodium (0.006%) to catalyze the oxidation of hydrocarbons. Scrapped automobiles are, therefore, a rich source of PGMs. This secondary resource is specially valuable as the concentrations of PGMs in catalysts are, in general, higher than those of the richest ore bodies. It is estimated, in the U.S. alone, about 20 million kg of catalyst containing 8.4 million g platinum, 3.5 million palladium and 0.6 million g rhodium are available in scrapped automobiles (Hoffmann, 1988).

Catalytic converters are routinely collected in scrap yards because of their high value. The first step in processing is the separation of the stainless steel outer shell. The catalyst substrates form the feed stock for the recovery of precious metals. Various leaching agents, both acid and alkali media, are used to separate precious metals from their alumina, silica, and carbon substrate in automotive catalysts. After primary extraction,

the precious metals are separated from base metals by standard chemical refining techniques including dissolution, solvent extraction, and selective precipitation. Alternatively, the ceramic substrate of some catalysts can be dissolved in acid (alumina in sulfuric acid) leaving behind a concentrated residue of precious metals. Some of the technologies used to recover PGMs will be described.

7.8.5.1. Soluble Substrates

This process is used to recover PGMs from catalysts with an alumina substrate. It comprises the following steps:

wet grinding - the catalysts are ground to $<74\ \mu\text{m}$ in a rod or ball mill;

catalyst dissolution and filtration - the catalysts are dissolved in dilute sulfuric acid;

fuming digestion - the remaining catalyst substrate is digested in concentrated sulfuric acid;

filtration - the acid is filtered out and returned to catalyst dissolution;

cementation - the filtrate from catalyst dissolution is treated for the removal of platinum group metals and lead by cementation on aluminum in the presence of tellurium. The cementate is filtered and the aluminum sulfate filtrate is evaporated to produce alum for use in water treatment plants;

leaching - the cementate is combined with the residue from fuming digestion and leached with chlorine and hydrochloric acid to recover PGMs;

precipitation - PGMs are precipitated by sulfur dioxide in the presence of tellurium.

7.8.5.2. Insoluble Substrate

This process is used to recover PGMs from catalysts with a cordierite substrate and comprises the following steps:

- 1) crushing to 25 mm;
- 2) alumina removal by dilute sulfuric acid;
- 3) decantation and washing;
- 4) PGM precipitation by scrap aluminum and tellurium from the solution (cementation);
- 5) decantation and washing;
- 6) PGM precipitation by sulfur dioxide in the presence of tellurium;
- 7) the solids from aluminum precipitation are mixed with the solids from sulfur dioxide precipitation and filtered;
- 8) the PGMs are redissolved in chlorine and hydrochloric acid ;
- 9) the tellurium is extracted by a tributyl phosphate solvent extraction; PGMs are precipitated from the raffinate.

7.8.5.3. Plasma Fusion

In this process the catalysts are fused with iron at a temperature, which may exceed $2,000\ ^\circ\text{C}$. The fused charge is allowed to settle to enable the slag and metal phases to separate, taking advantage of the large density difference between the slag and metal phase. The iron is leached in sulfuric acid to leave a residue of PGM.

7.8.5.4. Copper Collection.

This process is similar to plasma fusion to some extent as PGMs are collected in a metal matrix; but the temperatures are much lower, the slags less aggressive, and the conditions less reducing, which averts the possibility of reduction of silica. The catalysts

are ground and fluxed with silica, lime, iron oxide, and copper substrate. The charge is then smelted, the metallic copper is air- or water-atomized to provide an extended surface for leaching, and the copper is leached with sulfuric acid using air as an oxidant. PGMs are recovered from the residue, to leave a PGM residue. Results of laboratory research at high temperatures have shown PGM recoveries of 85-97%.

Hoffmann (1988) has suggested a logical extension of the copper collection process, whereby catalyst is directly introduced into a copper or nickel smelter. Catalyst would be crushed, ground and mixed with the required fluxes before combining it with the copper concentrates. Depending on the type of smelting process and composition of the concentrate, additional lime or silica may be required. The PGMs report virtually completely in the copper matte, which makes copper recovery a good bench mark of the recovery of PGMs.

Table 7.5 summarizes the advantages and disadvantages of various PGM recovery processes for automotive catalysts (Hoffmann, 1988).

Table 7.5. Recovery Processes for Platinum Group Metals (PGM) from Auto Catalysts

Process	Percent Recoveries			Advantages	Dis-advantages
	Platinum	Palladium	Rhodium		
Soluble substrate	88-94	88-96	84-88	Good recovery; cheap reagents;	Complex process, economics depends on by-products
Insoluble substrate	85-92	85-93	78-95	Low acid concentration; no salts	Decant washing less effective than filtration, poor extraction, water balance problems
Plasma Fusion	80-90	80-90	65-75	Rapid throughput, easily disposable slag	Lead emission problems, high power cost
Copper Collection	88-94	88-94	83-88	Metal product saleable, low smelting temperature, easily disposable slag	Lead emission problems, high power cost

7.8.5.5 Recovery of Platinum Group Metals (PGMs) by Metal Vapor Treatment

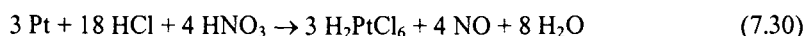
A novel method to recover platinum group metals (PGMs) from spent automotive catalyst by reacting with hot metal vapors of magnesium or calcium has been investigated by Kayanuma and coworkers (2004). It is based on the finding, magnesium is better than

calcium. At temperature $> 900^{\circ}\text{C}$ magnesium reduces the catalyst substrate and the mass of the treated catalyst increases due to the deposition of magnesium. After the reactive metal (magnesium) treatment the catalyst scraps are dissolved in aqua regia by heating at $50\text{--}60^{\circ}\text{C}$ or without heating for 1 hour. The untreated catalyst scrap is separated from the acid liquor. Up to 88% platinum, 81% palladium and 72% rhodium are recovered. The method is still in the developmental stage.

7.8.5.6. Recovery of Platinum from Spent Catalyst Dust by Hydrometallurgical Processing

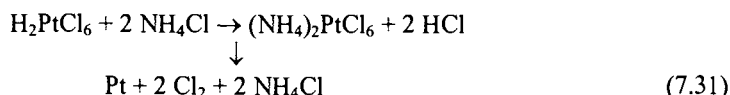
Platinum gauze is used as a catalyst in the manufacture of nitric acid by oxidation of ammonia. In the production process, part of the platinum is lost as fine dust, which is deposited on the internal reactor walls and cooling coils. It is collected during shut down and is stored for the recovery of platinum group metals. Such fine dust can be processed by leaching in aqua regia and the metal recovered by precipitation or solvent extraction. The two methods have been described by Barakat and Mahmoud (2002).

A catalyst dust containing 13.7% Pt is leached in aqua regia (mixture of nitric and hydrochloric acids in 1:3 (approximate) molar ratio) forming chloro-platinic acid:



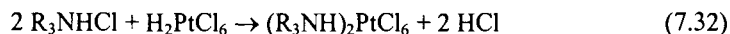
At acid ratio of 2.5, about 77% of the platinum is recovered; with acid ratio of 10, at the boiling point (109°C) almost 98% is recovered in about 2 hrs. The high consumption of acid is attributed to the refractory nature of the platinum content.

In the precipitation method for separating platinum, saturated ammonium chloride is added to the leach solution to precipitate ammonium chloro-platinum complex, which is then ignited to produce the metal:



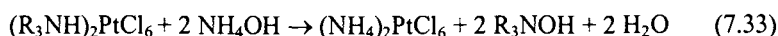
Precipitation efficiency of 99.5% is achieved at optimum temperature of 25°C . Higher temperature causes partial decomposition of the precipitate. The platinum complex is then ignited at 250°C to produce platinum powder of 97.9% purity with a recovery of 97.5%.

In the solvent extraction method, trioctylamine (TOA) is used as the extractant. It forms the corresponding aminium chloride with hydrochloric acid. This combines with chloro-platinic acid forming the platinum amine complex as shown in the equation:



where R stands for octyl chain, C_8H_{17} .

Best separation from iron (percent as ferric chloride) is obtained using 0.01 M hydrochloric acid. The platinum amine complex precipitate is then stripped by ammonium hydroxide to recover the amine in the organic phase:



The platinum amine complex is ignited to produce platinum metal as described before. The flow diagram of the entire process is shown in Figure 7.39.

In place of aqua regia, platinum carrying dust can also be leached in sulfuric acid in presence of sodium chloride. At high temperature ($\sim 125^\circ\text{C}$) sodium hydrogen chloride is produced by the acid decomposition of sodium chloride and the mixture (of sulfuric and hydrochloric acids) leaches platinum group metals forming chloro-complexes. A laboratory study Mahmoud and coworkers (2002) on a spent catalyst dust containing 16.8% Pt, 1.9% Rh and 0.14% Pd (similar to the one studied by Barakat and Mahmoud (2002) described before) has shown that leaching of the three PGMs is influenced by sodium chloride concentration. Palladium is leached most readily, 85% with 0.02 M NaCl, with less than 20% rhodium and about 40% platinum. Higher concentration, up to 0.1 M NaCl is required to reach maximum extraction of platinum (95%) and rhodium (85%). Effect of sulfuric acid concentration showed that the extraction follows the order $\text{Pd} > \text{Pt} > \text{Rh}$. The results indicate potential for partial selective separation of the three PGMs, but further study is desirable to refine the method for possible industrial application.

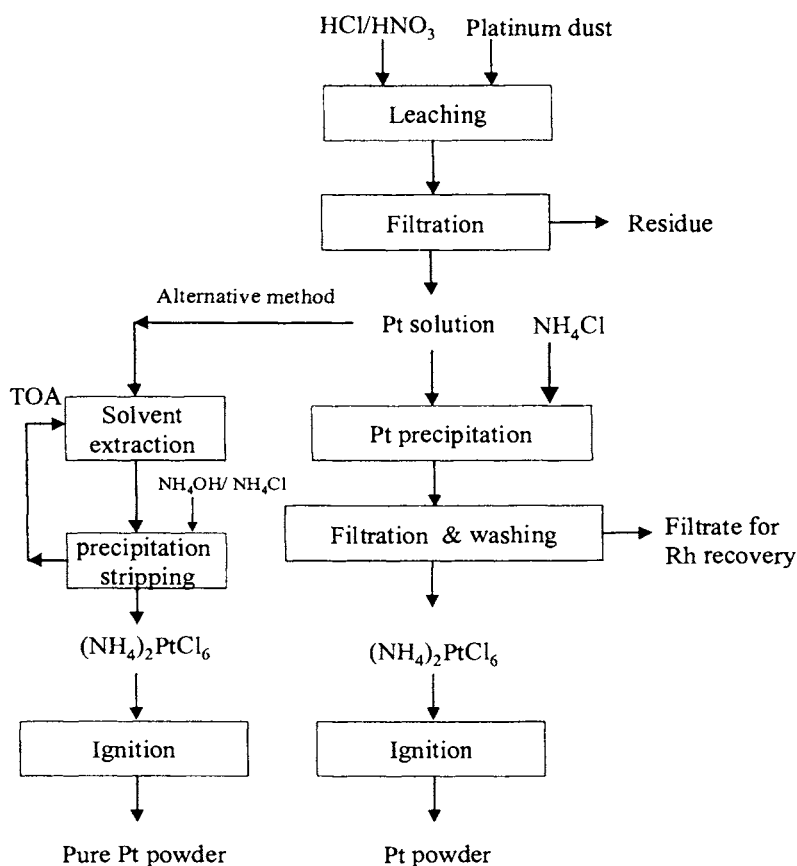


Figure 7.39 Process flowsheet to recover platinum from catalyst dust (Barakat and Mahmoud, 2002)

7.8.5.7. Recovery of Platinum Group Metals (PGM) by Pyrometallurgical Processing

Platinum, palladium and rhodium are recovered from the spent automobile catalysts by a pyrometallurgical process called “Rose Process” in Japan (Izumikawa, 1999). The ground catalyst is combined with cupric oxide, coke, lime, silica and iron oxide as additives and smelted in an electric furnace. The PGMs are extracted in the molten copper, which acts as a solvent. The ceramic carriers are melted with the flux components of lime, silica and iron oxide to form a slag. The copper carrying PGMs is sent to an oxidation furnace where the copper is oxidized and the PGMs are separated. They are concentrated in three stages. The concentration of the product is increased to 75% Pt, which is refined by a PGM producer. The oxidized copper is recycled to the primary electric furnace where it is reduced by coke and re-used. The flow sheet is shown in Figure 7.40.

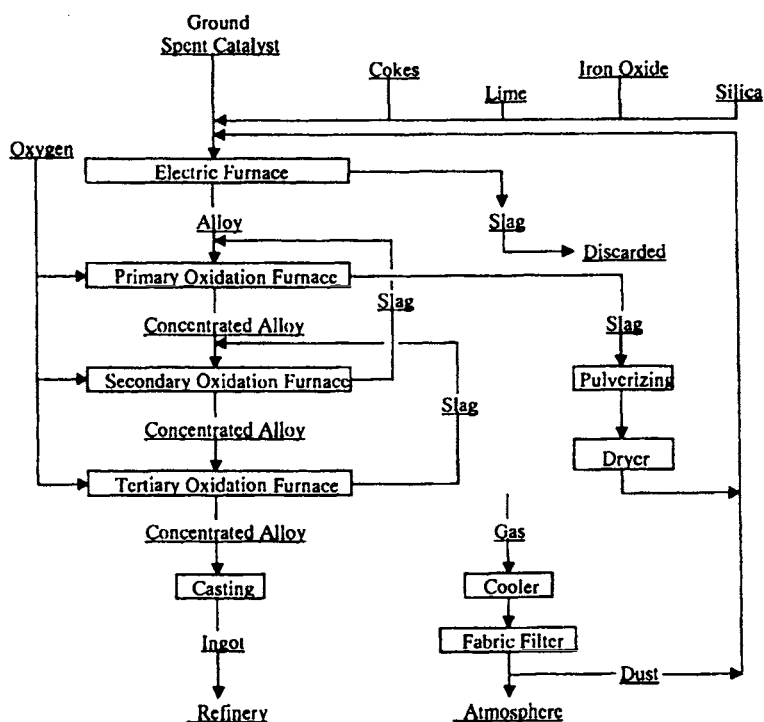


Figure 7.40. Pyrometallurgical Process (“Rose Process”) for recovery of platinum group metals from automobile catalysts (Izumikawa, 1999)

7.9. Gallium and Indium

In addition to common precious metals, materials coming into use in electronics and semiconductor industries contain, in small proportion, rare metals of very limited availability, such as gallium, germanium and indium. The potential demand is seen as greater than supply (Jacobson, 1988). There is thus a great incentive for the recycling of these metals. Scrap selenium contaminated with elements such as tellurium, arsenic and chlorine is converted to a mixture of oxides to recover high purity selenium (Badesha, 1985). In another method, granulated scrap alloy containing arsenic and selenium is

treated with caustic soda, followed by oxidation to recover the valuable constituents (Henstock, 1996, p. 287)).

7.9.1. Gallium has been recovered from residue containing both gallium and arsenic by treating with chlorine gas to form crude gallium and arsenic chlorides. By electrodeposition very high purity (99.9999%) gallium is obtained (Kubo, 1987). Gallium is also used for growing semiconductor single crystals of gallium arsenide for light emitting diode (LED) and laser diode (LD). Recycling of gallium from the arsenide scraps is of great practical interest as there are very few natural occurrences of this metal.

A cost effective process to recover high purity gallium from gallium arsenide scrap has been developed (Kubo *et al.*, 1990). It comprises a series of steps, as depicted in Figure 7.41.

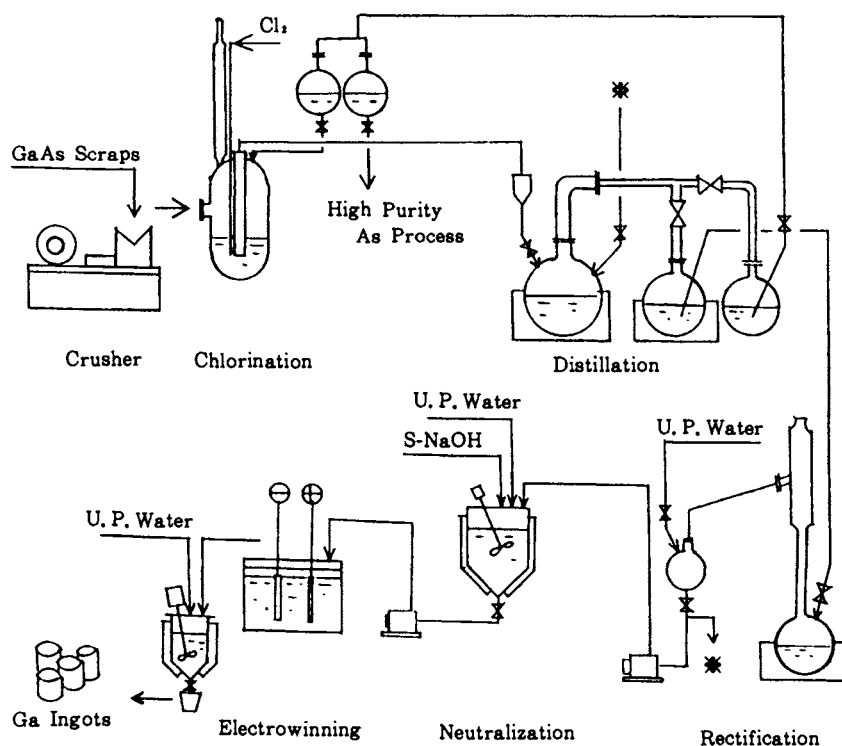
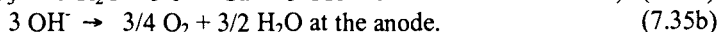
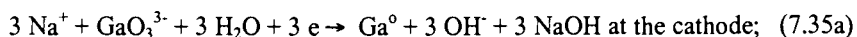


Figure 7.41. Flow Sheet of Process for Gallium Recovery from Scraps (Kubo *et al.*, 1990)

Various types of scrap are crushed to 2-5 mm size. The crushed scraps are placed in a quartz cell and chlorinated by chlorine gas. Mixture of chlorides, principally of gallium and arsenic, is produced. This is transferred to a distillation column where the metal chlorides are separated by fractional distillation. Arsenic chloride has a lower boiling point and distils at 130°-190° C. Gallium chloride is then distilled at 200° C. A second distillation step removes the residual arsenic chloride. The refined gallium chloride is treated with sodium hydroxide to form sodium gallate:



The gallate formed is electrolyzed in a cell with titanium plate as cathode. The electrode reactions are



The process leads to the production of very high purity gallium (total percent of impurities is < 0.3%).

7.9.2. Indium is used as an alloying agent in electronic solders. It is a trace metal occurring in some tin, lead, copper and zinc ores. However, industrial production of indium is based on processing metallurgical residues, wire scrap, slag and flue dusts. The feed stock is first leached with sulfuric or hydrochloric acid. Most metals including indium dissolve. Indium is then separated by cementation on zinc or aluminum sheets Barakat, 1998).

7.10. Cadmium, Mercury and Tin

7.10.1. Cadmium has low volatilization temperature, which is taken advantage of in separating and recycling this metal from its alloys by distillation and subsequent condensation. The distillate is acid leached and impurities are selectively precipitated and cadmium recovered by electrolysis.

Cadmium is also recycled from electric arc furnace (EAF) dust and from discarded nickel-cadmium batteries. These topics will be discussed in Chapters 8, 9 and 10..

7.10.2. Mercury is found in solid wastes in elemental form and as amalgams, organic mercury and mercury salts. It is recovered from electronic devices such as rectifiers, relays, switches and thermostats; and on a smaller scale from dental amalgams, batteries, lamps and broken thermometers. As it is a volatile element, mercury is recovered by distillation in steel retorts, followed by condensation. The product is then redistilled to remove base metal and other impurities. Triple distillation is done for obtaining a high purity product.

A vacuum retort system to recover mercury from broken or discarded mercury containing devices has been developed (Boyle, 1995). The retort unit is a batch system. The scrap received is first sorted to obtain a uniform material;. This requires crushing to break the higher strength glass containing mercury to allow the metal to be vaporized. The method is based on taking advantage of the liquid nature of mercury at room temperature and with boiling point of 357 °C. A vacuum equivalent of 25 inches of mercury column is maintained in the retort. By heating elements radiating heat onto the drum of materials a temperature almost the double the normal boiling point of mercury is maintained. The mercury vapor is drawn through a condenser where the saturated vapor stream is condensed and collected in a reservoir. It is then pumped to a quadruple distillation process. The residual material is non-hazardous.

The method has been used to recover mercury from fluorescent lamps, glass switches, thermometers and arc lamps. The residual material in the drum is non-hazardous.

A processing scheme to recover mercury from used dry battery cells has been developed in Japan (Hirayama *et al.*, 1987). The total system comprises three major subsystems; pretreatment, thermal processing and post-treatment. In the pretreatment system, the various dry battery cells are sorted according to their shape, size, and weight.

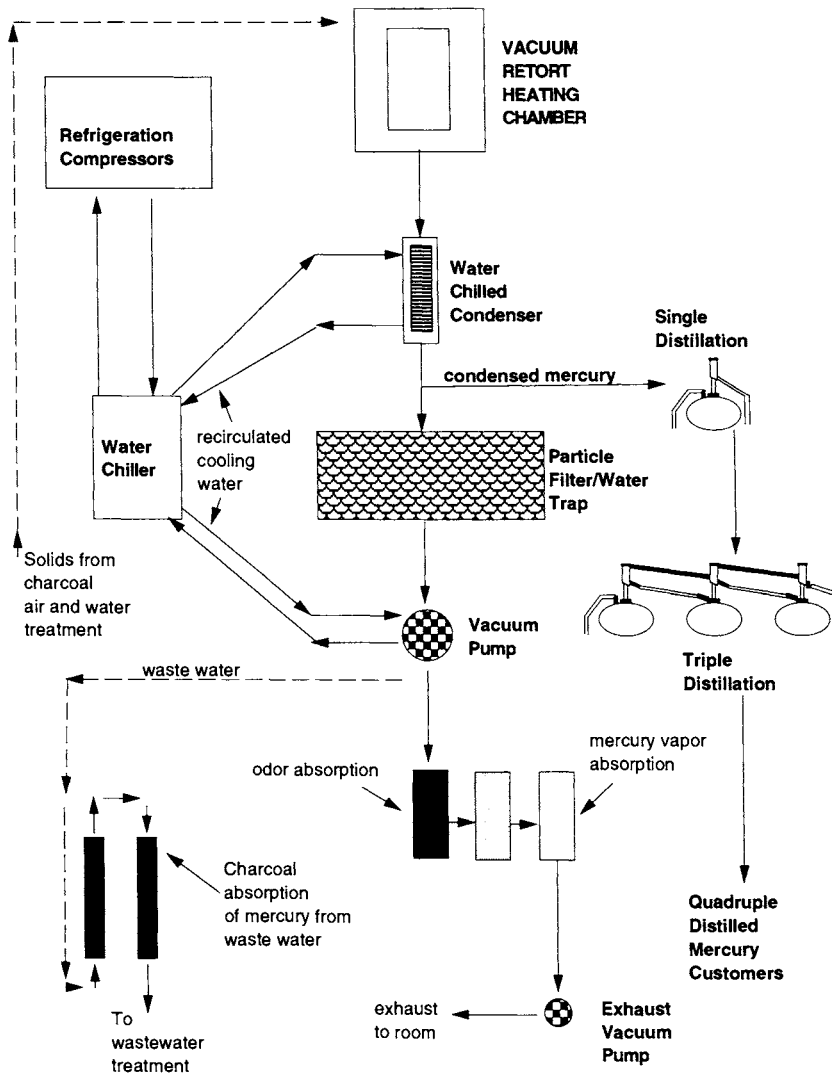


Figure 7.42. Mercury vacuum retort system (Boyle, 1995)

The cylindrical battery cells are then dismantled. The pre-processed batteries enter the thermal processing system where they are heated with a LPG burner at temperatures of between 600 and 800 °C whereby mercury is evaporated. The gases and vapors are led to the gas treatment process for condensation of mercury. The residues are then sent out to the following after-kiln where evaporation and cooling are completed without further heating. The gases and vapors then go through a dust remover or an electrostatic precipitator and then enter the condensing unit, which is cooled below the boiling point of mercury. In the post-treatment subsystem, dross material from the after-kiln is first cooled, then crushed to facilitate recovery of ferrous metals from them by a magnet

separator incorporated into this unit. In the recycled product, 70-98% mercury, 28-38% zinc and 90-95% scrap iron are recovered.

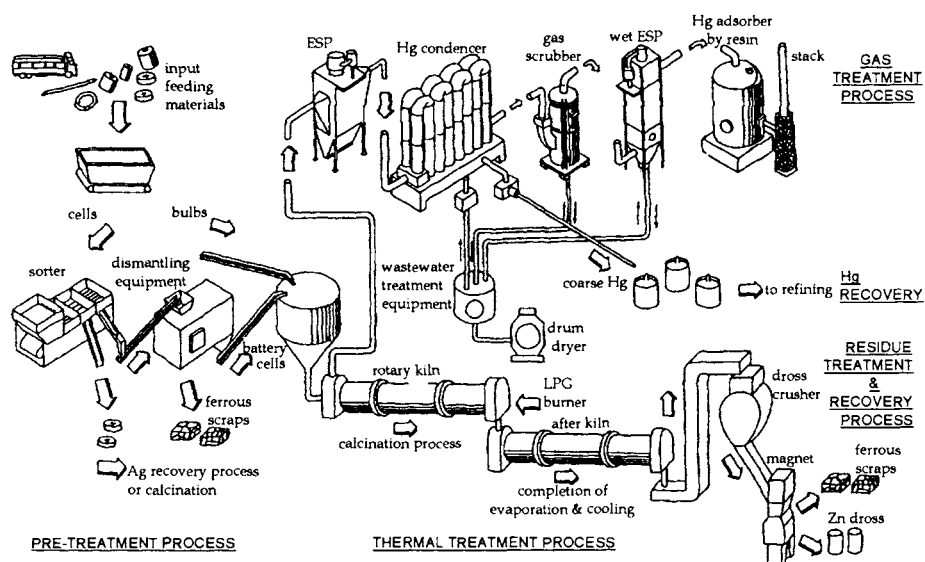
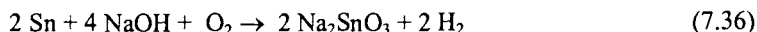


Figure 7.43. Schematic diagram of plant for disposal and recycling of mercury-containing wastes (Hirayama *et al.*, 1987)

7.10.3. Tin is found in recyclable form in scrap bronze (an alloy of tin and copper) and tinplate scrap. Scrap is used mostly for remelting into ingot or is processed in copper refineries. Tin is recovered from oxidized materials by reduction by carbon in rotary or reverberatory furnaces. The impurities, antimony, copper, iron and nickel are removed by oxidation and drossing similar to the operations applied for lead. Zinc and cadmium are removed by selective oxidation or by reaction with chlorine. Arsenic is removed by sodium hydroxide (producing soluble arsenite). Tin may be refined by electrolysis process similar to the silicofluoride process used for lead (Section 7.5.4.2).

Another secondary source of tin is tin cans. The cans are shredded to remove most of the dirt and associated aluminum. The tin is then leached in caustic soda at 70-90°C to form sodium stannate by the reaction:



Tin is deposited on a tinplate anode (Neenan, 1994)

7.11. Chromium, Molybdenum, Tungsten

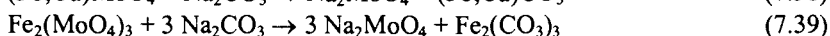
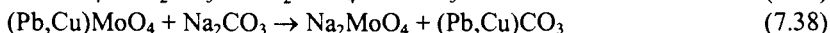
7.11.1. Chromium is a constituent of certain specialty alloy steels, their obsolete products and scrap are the principal secondary sources. Chromium is not generally separated, the steel itself is processed and recycled as described in Section 7.2.

Chromium is also a component of some catalysts. Recovery of metals from such industrial products will be described in Chapters 9 and 10.

7.11.2. Molybdenum is also a constituent of specialty steels and super alloys. Their

scrap is not treated specifically for recovering molybdenum. Steel scrap is recycled as described in Section 7.2.

Recovery of molybdenum from metallurgical residues containing lead and calcium molybdates and molybdenum oxide (MoO_3), by grinding the residue to 100 μm size and leaching with sodium carbonate has been described (Yang *et al.*, 2001). Fine grinding helps to reduce the amount of sodium carbonate required and enhances the leaching rate. The leach reactions are as follows:



Optimum pH is 8.5. Up to 95% molybdenum is recovered as molybdate salt.

Another secondary source of molybdenum is spent catalysts; see Section 7.16.

7.11.3. Tungsten is also used in alloy steels. In addition, it is used extensively for cutting and wear-resistant applications. This generates most of the recoverable obsolete tungsten scrap. It is recycled by a technique called cold stream process. A high speed (> 1000 km/h) air stream is used to entrain the scrap and to smash it on a carbide target. The powder formed is then air-classified and screened at 10 μm to produce a usable undersize and an oversize that can be reprocessed. The final product is offered in five basic grades.

7.12. Magnesium

The principal secondary sources of magnesium are its own alloys and aluminum alloys in the used beverage can (UBC). New magnesium-based scrap comes from castings, gates, drippings, machining swarf and drosses. Old scrap comes from aircraft parts, deactivated military hardware, and discharged power tools; die-castings are the largest source.

As received at the secondary smelter, magnesium scrap is usually mixed with some aluminum-based scrap and separated by hand-sorting. The scrap is then melted in a steel crucible at 675 $^{\circ}\text{C}$, with a flux to cover the surface and to prevent ignition. The composition is adjusted by alloying additions before the metal is cast into ingots. Certain types of clean magnesium swarf can be ground into fine powder for use in iron and steel desulfurization.

A fluxless recycling system for magnesium scrap has been developed (Berkmortel *et al.*, 2001). The system can handle 5,200 MT magnesium scrap annually. It consists of scrap feeding, melting, refining, ingot casting and stacking as shown in Figure 7.44.

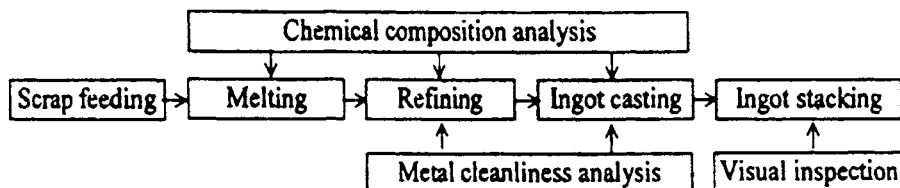


Figure 7.44. Continuous fluxless recycling system (Berkmortel *et al.*, 2001)

The recycled ingots and the chemical composition of die cast specimens from recycled materials meet ASTM specification and contain low oxides and chloride. Properties of die cast specimens from recycled materials are equivalent to those of primary metals (Berkmortel *et al.*, 2001).

Magnesium can also be recovered in the production of titanium. In the Kroll process to produce titanium metal, titanium tetra-chloride is reacted with magnesium to form titanium metal and magnesium chloride. After separating the titanium from magnesium chloride, the magnesium chloride is reduced in an electrolytic cell to form magnesium metal and chlorine gas.

7.13. Tantalum, Niobium, Titanium

7.13.1. Tantalum, known for its excellent corrosion resistance is used in chemical and pharmaceutical industries in surgical implants, screws and other components that are left resident in the human body, and in electrical capacitors. From its natural ore concentrate, tantalum is extracted by leaching in sulfuric and hydrofluoric acids. As it is a very expensive metal, with price in the range \$45-85 per kg of tantalum powder, the leach residues from the extraction of tantalum are recycled and subjected to a further metallurgical upgrading, process called internal recycling.

Old tantalum scrap occurs as used cutting tools and in alloy scrap. Tantalum capacitors, which are no longer useful, are an important secondary source for recycling. The metal is recovered from hard metals by grinding and acid leaching (Hoppe and Korinek, 1995).

7.13.2. Niobium, also known as columbium, is mainly used as a microalloying element, in specialty steel. Because of its refractory nature, significant amounts are used in the form of high-purity ferrocolumbium. Nickel-niobium is used in cobalt-, iron-, and nickel-base superalloys for heat resisting and combustion equipment, jet engine components, and rocket subassemblies. In superalloys, niobium strengthens the alloy at high service temperatures as in aircraft components.

Niobium is recycled from iron and steel and alloy scraps. The scrap is melted in basic oxygen and electric furnace furnaces.

7.13.3. Titanium, widely used in aerospace sector, is recycled from metallurgical scrap or processed scrap. Metallurgical scrap is material, which has failed for some reason; whereas processed scrap is material that has been found acceptable.

7.14. Rare Earth Metals

These metals, 15 of them, form a close knit family of elements in the Periodic Table. They are used in minor, yet significant, proportion in several industrial products such as catalysts and ceramics for automobile converters, batteries (lanthanum-nickel), fluorescent and incandescent lighting, glass additives, permanent magnets (e.g., cobalt-samarium magnet and neodymium-iron-boron magnet), fiber optics, and high temperature superconductors (Hendricks, James B. 'Rare Earths', Mineral Yearbook, vol.1 1990, USBM (1993), pp. 903-922). Some rare earth elements are used in nuclear industry as moderators. Very little work has been published on recovering rare earth elements from secondary sources. In view of increasing demand and small quantities of rare earths finding their way as tramp elements into other metals, (for example, steel), make their recycling attractive.

7.14.1. Rare Earths from Spent Optical Glass

A hydrometallurgical process comprising acid leaching, precipitation of hydroxides and solvent extraction has been applied by Jiang and coworkers (2004) to recover three rare earth (RE) metals, lanthanum, yttrium and gadolinium from spent optical glass containing 43.1% lanthanum oxide (La_2O_3), 9.4% yttrium oxide (Y_2O_3) and 4.6% gadolinium oxide (Gd_2O_3).

The glass is a type of amorphous body with the RE elements occurring in amorphous borosilicate, zirconate and niobate. In the first stage, the RE elements are converted to RE hydroxides by hot concentrated aqueous sodium hydroxide. The optimal parameter determined by the investigators is to use a 55% aqueous sodium hydroxide at a liquid to solid ratio of 2 and a temperature of 140 °C for 1 hour. This completely transforms the RE elements to a new solid phase. In the second stage, the solids are leached in 6 M hydrochloric acid at a liquid to solid ratio of 4 and a temperature of 95 °C for 30 minutes. To the leachate 1 M sodium hydroxide solution is added to adjust the pH to 4.5. At this pH zirconium and niobium are selectively precipitated and separated from the solution. The pH of the filtrate is raised to 9.5–10.0 by sodium hydroxide. This precipitates all three RE hydroxides. The precipitates are separated and dissolved in 1 M hydrochloric acid, which produces a colorless transparent solution containing dissolved RE chlorides.

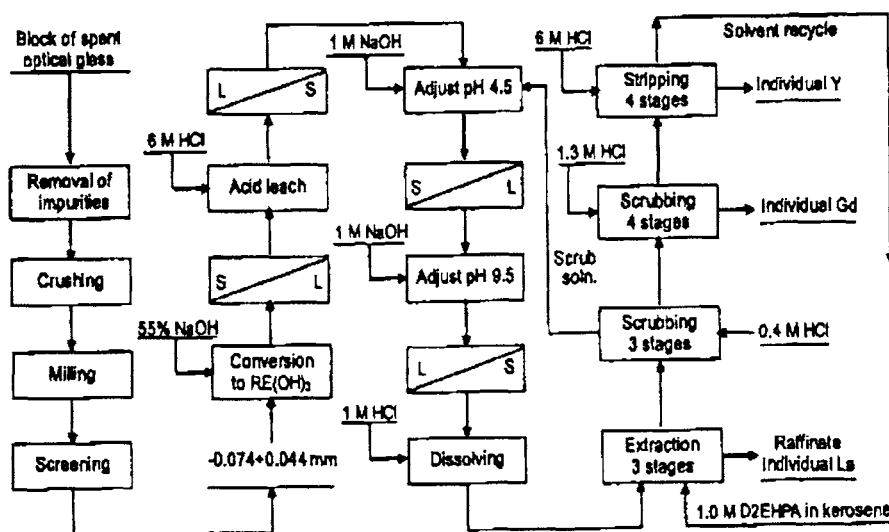


Figure 7.45. Schematic flow diagram of process to recover rare earths, lanthanum, gadolinium and yttrium, from spent optical glass (Jiang *et al.*, 2004)

In the final stage, the RE elements are separated by solvent extraction using D2EHPA (see chapter 4 for the formula and chemistry of this compound). This reagent has been shown to extract the heavier REs, but the light REs are not extracted (Thakur, 2000). In the present system, lanthanum is light RE; yttrium and gadolinium are the heavy REs. By conducting the extraction using 1.0 M D2EHPA in kerosene in multistage countercurrent operation, yttrium and gadolinium are almost 100% extracted. Small amounts of lanthanum are extracted in the organic phase. This is scrubbed by 0.4 M hydrochloric

acid. By increasing the concentration of the acid to 1.3 M gadolinium is scrubbed. Three-stage countercurrent scrubbing operation is required to scrub lanthanum entirely and separate from gadolinium and yttrium. The scrubbed organic phase is then scrubbed in a four stage countercurrent scrubbing using 1.3 M acid to separate gadolinium in the aqueous phase. The scrubbed organic phase is then stripped with 7 M hydrochloric acid to recover yttrium. By this multistage operation, 98-99% individual RE elements are recovered. The flow diagram is shown in Figure 7.45.

7.14.2. Samarium and Neodymium

Samarium is recovered from scrap cobalt-samarium magnet by leaching, followed by crystallization as a double salt of cobalt and samarium, which yields 96-100% recovery of Sm_2O_3 at 98.5% purity (Henstock, 1996; p. 290). Neodymium is recovered from Nd-Fe-B scrap by sulfuric acid leaching, followed by precipitation of recyclable neodymium-sodium double salt, which may be converted to various useful products (Morrison and Palmer, 1990). Recovery from contaminated Co_5Sm and Nd-Fe-B grinding swarf has been achieved by flotation and 2-stage leaching. The ground swarf consisting of samarium-cobalt alloy SmCo_5 and neodymium iron boride (NdFeB) is leached in 2M sulfuric acid. Neodymium and iron are leached. The neodymium rich solution along with boric acid produced and the tailing of the grinding medium are recovered in the tailing. The SmCo_5 alloy is hydrophobic and is recovered in the froth. This yields a high value SmCo_5 product (Lyman and Palmer, 1993).

Neodymium is a rare metal and is a constituent of $\text{Nd}_2\text{F}_{14}\text{B}$ magnet used in electromechanical and electronic devices. A process to recover neodymium from magnet scrap has been described by Lyman and Palmer (1991). The magnet scrap is leached in sulfuric acid controlling the pH to 1.0 at which both iron and rare earths dissolve. The pH is then raised to 1.5, at which neodymium sodium double salt $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is formed. Iron remains in solution as long as the pH does not exceed 2.0. This double salt is converted to neodymium fluoride (which can be easily filtered) by leaching in hydrofluoric acid solution. Following rare earth precipitation, oxygen is bubbled through the leach solution containing iron at 90 °C to form a yellow jarosite compound, which is easier to filter than ferric hydroxide. Jarosites are compounds of the type $\text{MFe}_3(\text{SO}_4)_2(\text{OH})_6$ where M is K, Na or NH_4 , or a metal ion such as Ag or 1/2Pb. Iron occurs in the ferric state. Jarosite precipitation is often preferred to precipitation as ferric hydroxide as it is more readily separable. Further, it can be converted to by-product like hematite, which will be described in Chapter 10. The original magnet material contains boron, which does not precipitate and remains in solution with jarosite. After the jarosite separation, some of it may be recovered as a form of zinc borate by raising the pH. The flow sheet of the process is shown in Figure 7.46.

7.15. Recovery of Metals from Spent Catalysts

Catalysts are indispensable in many industrial chemical processes such as petroleum refining, production of petrochemicals like gasoline, diesel oils, jet fuels, heavy oil hydrocarbons and plastics. Conversion of crude oil into these petrochemical products requires hydro-desulfurization (hydrogenation and removal of sulfur). During processing, catalysts get contaminated with impurities in the crude oil feed and become deactivated. They can be regenerated up to a point. Ultimately, however, they get contaminated with

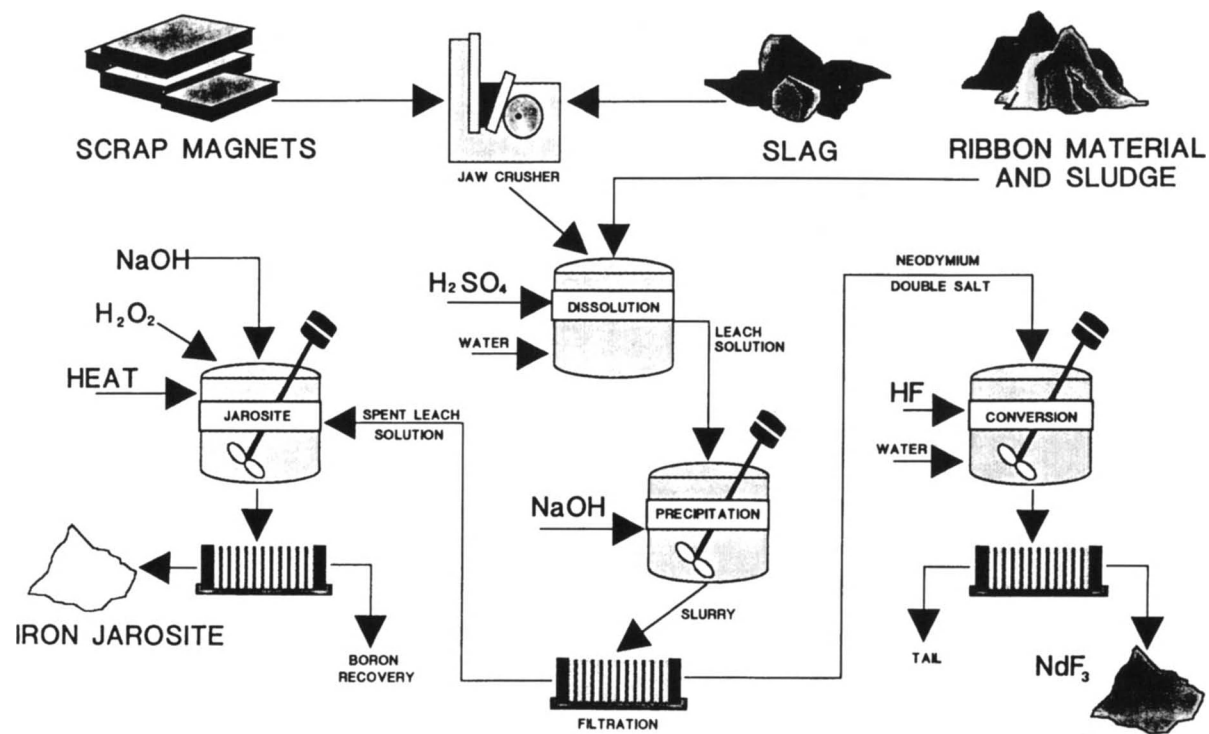


Figure 7.46. Recovery of neodymium from magnet scrap (Lyman and Palmer, 1991)

coke, sulfur, vanadium and nickel at such levels that makes regeneration impractical. At this stage, they are considered to be “spent catalysts” and present serious environmental problems, as land fill is no longer accepted as good practice. The spent catalysts contain significant quantities of molybdenum, vanadium, nickel and cobalt and are a potential secondary source of these metals.

7.15.1. Metal Recovery from Spent Petroleum Catalysts

The process for recycling spent petroleum catalysts uses a 2-stage oxidative pressure leach; the first for the separation of vanadium and molybdenum and the second for the separation of alumina and Ni/Co/Cu. Organics are oxidized during this procedure. The spent catalyst components are separated into four products: molybdenum trioxide, vanadium pentoxide, alumina trihydrate, and nickel-cobalt-copper concentrate. Chromium is dissolved in an acid leach in chrome processing plant. The chromium is then precipitated by alkali as chromic oxide. The remaining constituents from the plating wastes are transferred to the spent catalyst circuit to recovery. Plating wastes containing mainly chrome go into alumina recovery circuit while those containing nickel and copper are reprocessed through the spent catalyst circuit.

In some nickel extraction plants the spent catalyst containing nickel is mixed with the primary smelter feed consisting of iron, copper and nickel sulfides. The nickel oxide in the spent catalyst is converted to sulfide by high temperature reaction with iron sulfide or copper sulfide ((Thapliyal *et al.*, 1996):



7.15.2. Recovery of Cobalt, Nickel, Vanadium and Molybdenum from Spent Catalysts: Hydrometallurgical Process

Desulfurization of crude oil is done by a catalytic process, which uses a molybdenum trioxide catalyst promoted with cobalt and nickel oxide on a carrier of alumina. During the process, such metals as nickel and vanadium present in the crude oil are deposited on the catalyst together with hydrocarbons, carbon and sulfur. The last three are burnt off, and the catalyst is reused, but after a number of cycles, the catalytic activity is reduced to the extent that the catalyst has to be renewed. The spent catalyst contains recoverable cobalt and nickel, together with molybdenum, vanadium and aluminum. A solvent extraction process for the separation and recovery of these metals has been described by Inoue and Zhang (1995). The spent catalysts are first leached in sulfuric acid. Molybdenum and vanadium are recovered by using organophosphinic acid like Cyanex or α -hydroxy oxime like LIX as the extractant. These extractants exhibit excellent selectivity for molybdenum and vanadium over aluminum, cobalt and nickel at pH 0-2. The molybdenum is then separated by stripping with 5% aqueous ammonia solution, which forms ammonium molybdate with molybdenum oxide and forms a separate organic phase. The vanadium is then recovered from the scrub solution. by treatment with acid. In the second stage, nickel and cobalt are extracted at pH 3-4 and subsequently separated from the loaded solvent by stripping with acid.

7.15.3. Recovery of Nickel from Spent Catalysts: High Temperature Process

A high temperature process has been developed to recover nickel from spent catalysts

Hanewald *et al.*, 1995). It is done in a rotary hearth furnace with carbon as reducing agent. The gas produced is discharged to a wet scrubber system. The off-gas system is then treated in a wastewater treatment plant and is recycled. The scrubber water is also separately treated in wastewater treatment plant, where zinc, lead and cadmium are precipitated and pressed into a cake, which is mixed with dust from the system's baghouse also containing zinc, lead and cadmium. This byproduct is used to process the metals. The hot reduced material from the rotary furnace is transferred to the electric arc furnace for smelting to produce the metal. The metal and slag are tapped periodically from the furnace. The slag is collected and transported to a separate area. It is non-hazardous and can be processed, sized and used for building roads and other uses (see Chapter 9). In the final step, the molten metal is cast into pigs, which are sent to specialty steel mills to be used as remelt alloy. See Chapter 6 for a description of INMETCO process.

The process has been applied to reclaim copper, chromium, and cobalt besides nickel. The feed specifications are Ni >1.3%, Cu <2.0%, Cr >5.0% and Co <2.0%.

7.15.4. Combined Pyro- and Hydrometallurgical Processes to Recover Molybdenum, Vanadium, Nickel and Aluminum Products

In a combined process described by Wang (2000), the feed first undergoes a devolatilization step in a rotary kiln at 300-350 °C to remove the hydrocarbons adhering to the spent catalyst. It is then leached in a mixture of 5% hydrogen peroxide and 5 to 7.5 g/L sodium carbonate solution in three stages. Maintaining a solid to liquid ratio in the range 10 to 20% leads to the extraction of 95% molybdenum and 85% vanadium. Hydrogen peroxide serves as oxidant to convert vanadium to pentoxide (V_2O_5) and molybdenum to trioxide (MoO_3). These are acidic oxides and dissolve in sodium carbonate forming sodium vanadate and molybdate. The extraction of nickel and aluminum is generally low, between 1.25 and 2.0%. The leach solution is acidified with hydrochloric acid to pH 1.5-2.0 and heated to 80 to 90 °C. Vanadium and molybdenum oxides are coprecipitated as their respective oxides. These are dissolved in ammonia solution to a pH of 9.0 to 9.5. Ammonium vanadate and molybdate are produced. Ammonium vanadate has lower solubility than the molybdate and is precipitated by mixing ammonium chloride (Precipitation occurs by common ion effect of ammonium ion). The ammonium molybdate is then precipitated using hydrochloric acid, washed by dilute nitric acid and then roasted to 500 to 600 °C to obtain molybdenum oxide.

In another method, described by Llanos and Deering (2000) spent catalysts are mixed with soda ash and roasted at 700-750 °C in multiple hearth furnaces. The furnace gases are sent to a post combustion chamber where residual hydrocarbons are incinerated at 900 °C. Particulates are removed from the off gases using electrostatic precipitators. During roasting, molybdenum, vanadium, phosphorus and sulfur for their respective sodium salts by reaction with sodium carbonate. Alumina and other metallic oxides remain unreacted. The calcine from the roaster is cooled and ground in ball mills. The slurry from the ball mills is treated by counter current decantation, filtration and washing in vertical pressure filters. The filter cake, containing approximately 30% moisture, consists of about 70% alumina and oxides of molybdenum, vanadium, nickel, cobalt and silicon. Depending on its metal content, the filter cake may be sold to cement manufacturers, nickel refineries or it may be treated in an electric arc furnace.

The leach solution loaded with molybdenum and vanadium is first treated to remove

recovered by solvent extraction. The molybdenum and vanadium are stripped by sodium hydroxide and the strip liquor is recycled and the raffinate is sent to ammonia recovery circuit. Ammonia is stripped from the raffinate using caustic soda and steam in a packed tower. The ammonia gas is recovered by scrubbing with dilute acid to regenerate ammonium chloride and sulfate. The stripper tailings, depleted of metals and ammonia, are adjusted in pH, cooled and filtered and discharged.

The principal final products from this process are vanadium pentoxide (>98% purity), molybdenum trioxide (>99% purity) and ammonium molybdate solution with 16% Mo.

7.16. Recovery of Alloy from Industrial Scrap

Many alloys of base metals are commonly used in industrial equipment and domestic appliances. Two well known ones are brass and bronze. Brass is an alloy of copper and zinc extensively used in small fittings in competition with other metals and plastics.

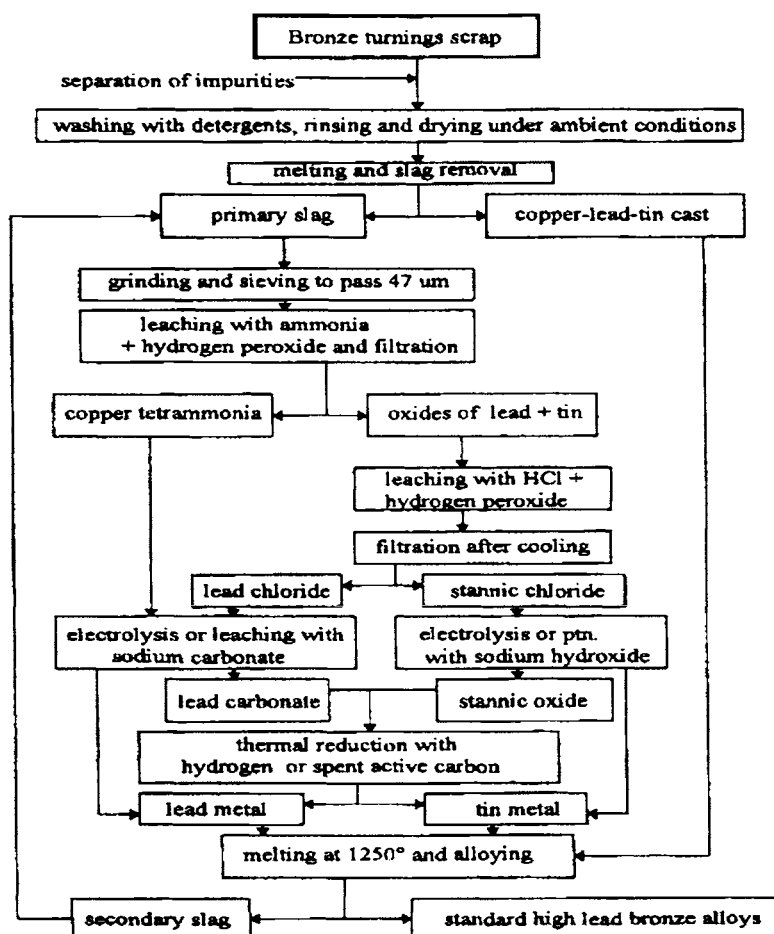
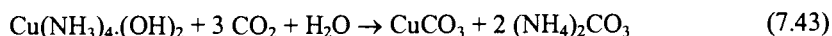


Figure 7.48. Conceptual flowsheet to recover lead and tin from bronze turnings (Rabah, 1998)

Bronze is an alloy of copper and tin used for household utensils. It is also used in ships propellants.

Industrial scrap containing lead, tin and copper (together with their oxides and some minor impurities) has been processed to recover a high lead/tin/bronze alloy by a process which combines hydro- and pyrometallurgical treatment (Rabah, 1998; Rabah and El-Basir, 2001). The flowsheet shown in Figure 7.48. The scrap is subjected to hydrometallurgical treatment. Copper is selectively leached by ammonia (forming cupric ammonium hydroxide, as explained in Chapter 2) in presence of hydrogen peroxide. The function of hydrogen peroxide is to partially oxidize copper as this enhances the reaction rate with ammonia. An optimum dose of 25% peroxide in 4 M ammonia solution at 50 °C leads to almost complete dissolution of copper, leaving lead and tin in the solid phase. These metals are leached by 4 M hydrochloric acid at 75 °C for 3 hours. Upon cooling insoluble lead chloride precipitates while stannous chloride remains in solution. In the next, carbonation step, carbon dioxide is bubbled through cuprammonium hydroxide to produce cupric carbonate:



The reaction is favored at 50 °C.

Conversion of lead chloride to carbonate is done under similar conditions by mixing sodium carbonate solution. The tin, leached to form stannic chloride, is recovered as stannic oxide by adjusting the pH to 2.6 by sodium hydroxide.

The copper and lead carbonates and stannic oxide are reduced using hydrogen gas. In place of hydrogen spent active carbon can be used (which will make the process more economic). The optimal temperatures for tin, lead and copper are 800, 1000, 1200 °C respectively. In the final step, bronze alloys are prepared by melting the product obtained from the pyrometallurgical treatment. Deficiency of any metal below the level required for the alloy composition is compensated by metals obtained by the thermal reduction step.

In the pyrometallurgical route, bronze turnings are melted and the slag skimmed off. The metal component (copper-lead-tin cast) is sent to pyrometallurgical treatment (melting at 1250 °C and alloying). The slag is subjected to hydrometallurgical treatment. The slag formation (due to the formation of metal oxides) can be minimized by starving the system of atmospheric oxygen by using a suitable flux. A sodium borate/carbon mixture is found to be most suitable.

7.17. Recovering Metals from Automobile Scrap

Automobile scrap is one of the richest secondary sources of several metals, besides non-metals like plastics, glass and fuel. Recovery of individual metals from automobile scrap is explained in the preceding sections. The present section will describe methods developed to process automobile shredder scrap to recover several non-ferrous metals.

Economic life cycle of a car usually ends with an average age of 10 years. Millions of cars, which enter into the junkyard every year has become an important secondary source of metals and materials. Steel is the obvious most common metal in car scrap. In recent years, however, the proportion of iron and steel is being replaced by lighter metals, such as aluminum and synthetic materials, as is seen from Table 7.6, to increase energy efficiency.

Table 7.6. Car Composition (Daimler-Benz) (Dalmijn and van Houwelingen, 95)

Material Year →	1965	1985	1995	
Steel		76.0	68.0	63.0
Non-ferrous metals		6.0	7.5	9.5
Polymers		2.0	10.0	13.0
Balance		16.0	14.5	14.5
Total		100	100	100

Recovery of steel and a few non-ferrous metals from obsolete automobiles and the treatment required are described in Sections on specific metals. The present Section describes the various treatment methods adopted to recover steel and non-ferrous metals from car scrap.

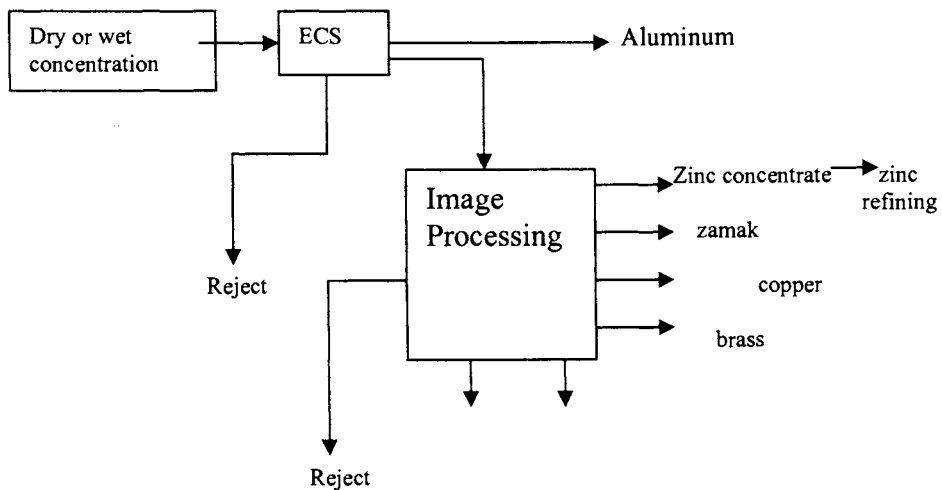


Figure 7.49. General flow sheet for the recovery of metals from car scrap. (Dalmijn and van Houwelingen, 1995)

Selective dismantling is the first step in car processing as it reduces the land filling fraction and improves the quality of the different fractions after processing. After separating the plastic materials the metal components are recovered. They are reduced in size in a shredder and classified in different size fractions. Magnetic fraction, mainly steel, is then separated. The non-ferrous metal fraction is separated from non-metallic components by a rising current separator and a density separator. The aluminum fraction is then separated from other non-ferrous metals by eddy current separation. Further cleaning of the aluminum fraction is done by drying, magnetic separation, screening and another eddy current separation. These steps lead to over 99% aluminum product. The heavy non-ferrous fraction is processed for the recovery of zinc, copper and brass. This is done by technique called image processing. It is based on color detection of the particles on a transport belt, and the final concentrate is obtained by an air blasting array in the free

fall of the particles. By this process, copper, brass and zinc products of over 98% purity are obtained. The general flow sheet is shown in Figure 7.49.

Another gravity method based on separation in a water elutriator was developed by the U.S. Bureau of Mines (Bilbrey *et al.*, 1979). It is schematically shown in Figure 7.50.

Water is pumped into the column at the desired flow rate and the feed (non-magnetic shredder residue from which the -0.5 cm residue material has been recovered) is dropped into the tank, where the first separation is made. Light materials are washed over the discharge lip of the feed tank with a portion of the water, while heavier components sink into the upflowing column of water. At the side arm, materials of intermediate density are carried out as middling product with the balance of the water, while the heavier ones sink to the bottom of the column where they are caught in the bucket elevator and discharged as a sink product. A flow diagram illustrating the use of the water elutriator for the recovery of metals from automobile shredder residues is shown in Figure 7.51.

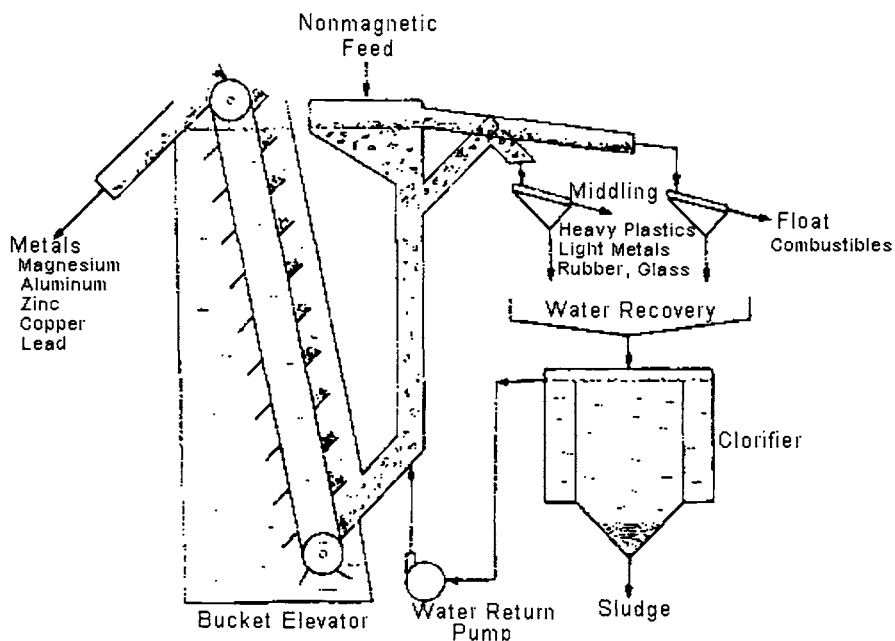


Figure 7.50. Diagram of water elutriator to process automobile shredder residues (Bilbrey *et al.*, 1979)

The inside diameter of the water column of a laboratory model is 20 cm, which gives it the capacity to separate about 1 ton/h of non-magnetic residue. Feed rates of up to 1.6 tons/h have been reached, but the separation efficiency of the elutriator can be changed by controlling the velocity of the water flow through the column.

The major effect of increasing the velocity of water is to increase the metal concentration of the sink fraction at the expense of the metal recovery. A rapid increase in the metal content of the middling fraction at higher velocities is observed. Increasing the water velocity also affects the analysis of the metal mixture of the sink and middling fractions. At the higher water velocities, more light aluminum trim and insulated copper

wire are recovered in the middling fraction. This is shown graphically in Figure 7.52.

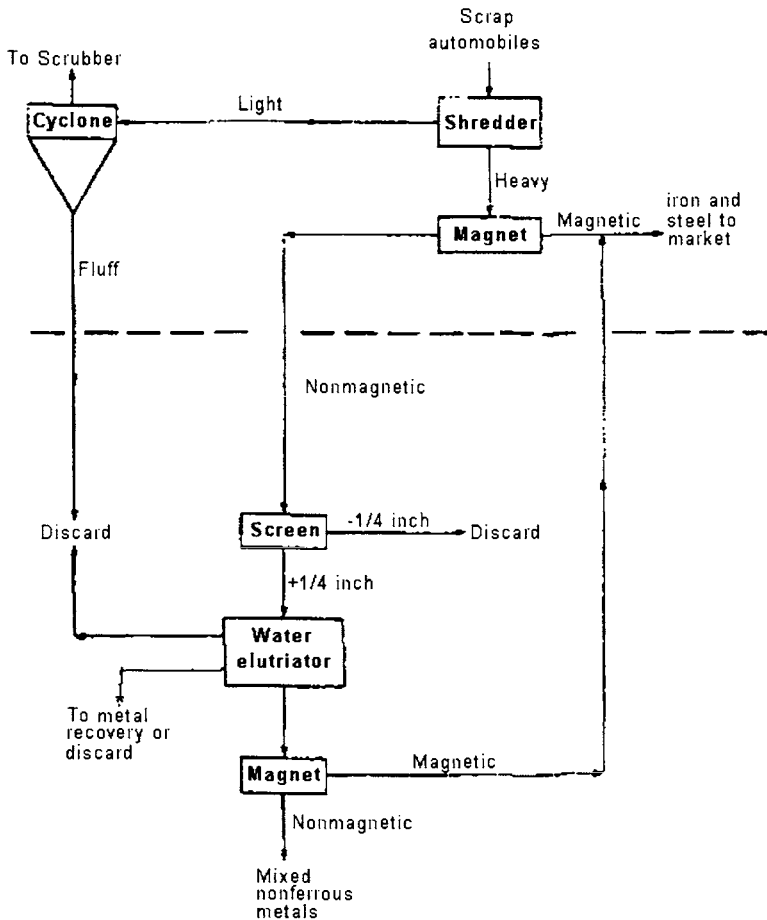


Figure 7.51. Flow diagram to recover non-ferrous metals from auto shredder residues (Bilbrey *et al.*, 1979)

Individual metal fractions from the metal mixture recovered from the elutriator sink fraction are separated in a novel heavy media separator, designed at the US Bureau of Mines; see Figure 7.53. The separator uses barite (barium sulfate) as the medium, which goes into the slag when the products are melted. The operation is as follows: barite-water slurry, made up to the desired density, is pumped through the separator trough at a preselected velocity, and the mixed metals from the sink product of the water elutriator are dropped into the slurry at the upstream end. The aluminum and lighter materials float to the discharge end of the trough where they are separated from the slurry by screening; the slurry is recycled. Materials heavier than aluminum sink to the bottom of the trough, where they are collected in perforated pans and removed at intervals. Slurry adhering to the metal is removed by water washing. Barite separates from water when slurry is diluted and is thus recovered from the wash water by settling and decantation. product at

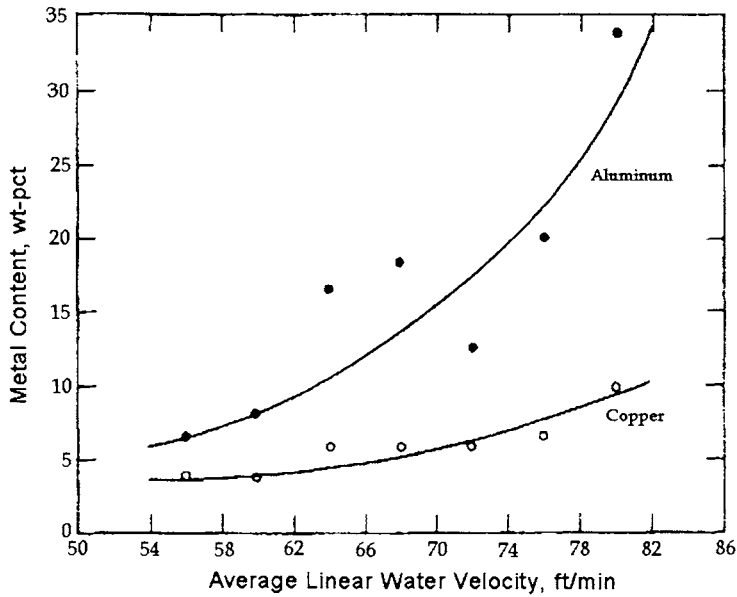


Figure 7.52. Metal content of middling fraction as a function of elutriator water velocity (Bilbrey *et al.*, 1979)

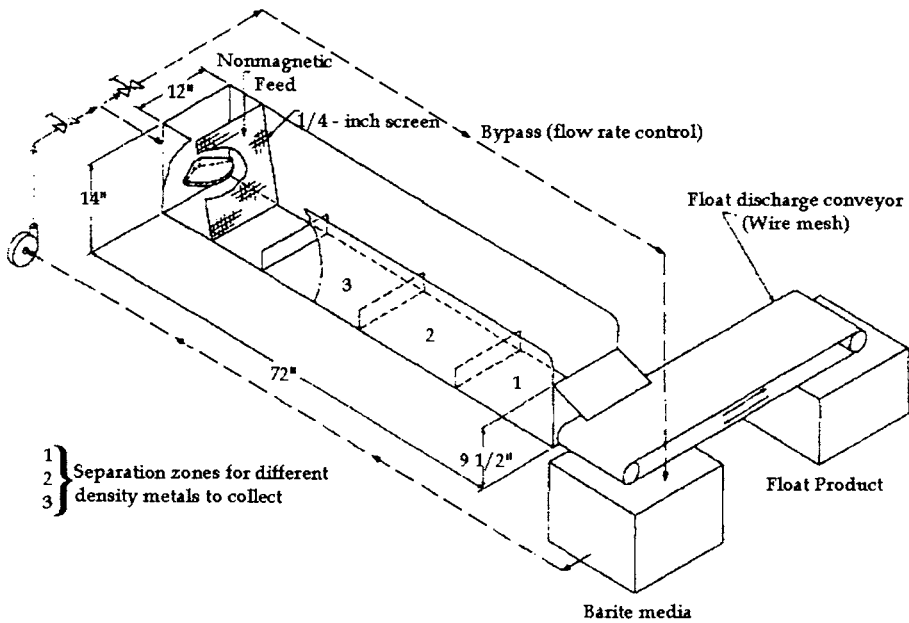


Figure 7.53. Barite media separation process (Bilbrey *et al.*, 1979)

ferrous metals and alloys, containing zinc, lead, antimony, tin, etc. melt forming two immiscible phases, zinc base alloy on top and lead base alloy under, according to the difference in densities.

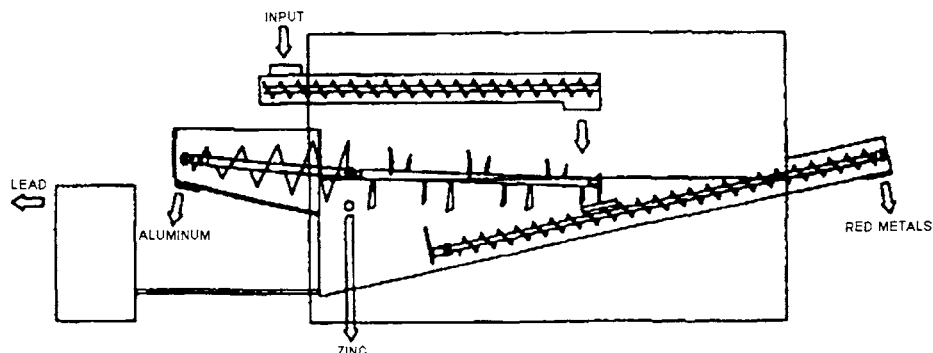


Figure 7.55. Thermal gravity classifier cross-section (Lindroos and Stout, 1987)

A laboratory model of the separator recovers 95-98% of the aluminum in the float difference in densities. Zinc is poured into sow molds by letting it overflow from the vessel. Lead is poured from a well using a siphon type arrangement. The unmelttable red metals and stainless steel sink through the molten phase and end up floating on the molten lead phase. This fraction is taken out by a screw conveyor. The flotables, magnesium, if present, aluminum and zinc dust are conveyed by paddle type screw conveyors to the rear of the vessel. The paddles gently agitate the floating material to ensure all heavier material is immersed into the molten bath. The unmelttable aluminum and red metals fraction are discharged on to screens to remove dust, H, J. The dust is taken to the bag house K. A general arrangement of thermal gravity classifier is shown in Figure 7.55.

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Chapter 8

METALLURGICAL SLAGS, DUST AND FUMES

Slags, dust and fumes are common products in almost all extractive metallurgical operations. Left to themselves, they pose serious hazard, both environmental as well as human health. Dust and fumes may contain toxic metals in fine particle size and as such are a potential environmental and health hazard. They are a potential secondary source of many metals and also can be converted into useful by-products of practical value. The present chapter will discuss the properties and metal recycle from these materials. Their conversion to other by-products of use will be described in Chapter 9.

8.1. Slags

In extractive metallurgical operations a slag phase is generated, formed mainly from the addition of mixtures of oxides and fluxes and is also composed of reaction products like those resulting from the oxidation of charge materials and the dissolution of refractories. Primary purpose is to refine the liquid metal by removing impurities such as sulfur and phosphorus. Steel making operations, such as Basic Oxygen Furnace Process (BOF) and Electric Arc Furnace (EAF) process produce slags of different compositions.

The main slags are classified in three types; ferrous slag, including iron and steel slags, non-ferrous slag and incineration slags. They usually contain a quantity of metals and are, therefore, a valuable secondary source of metals. In addition, they contain valuable material and are potential secondary sources to manufacture products of practical use in cement industry and road construction. Some slags contain significant quantities of toxic heavy metals causing potential environmental hazard. There is a great incentive to exploit the useful properties of slags and recover metals to minimize their disposal in land filling sites.

Ferrous slag, generated in iron blast furnace has been processed for many years. Approximately 200 kg ferrous slag is generated per ton of iron. It is almost all granulated and used as a cement supplement. In Hamilton, Ontario, Canada, for example, well known steel company Dofasco markets their slag locally to the City of Hamilton for use as aggregate on city streets. Details of applications and utilization of slag will be described in Chapter 9.

The non-ferrous slag produced in smelting often contains residual metal, which, in most cases inhibits their use without further processing. The long haul between smelters and urban markets is also an inhibitory factor except where high value added can justify the freight cost. Therefore, most slag is stockpiled adjacent to the smelter pending favorable economic conditions for slag recycling or new technological developments,

which will lead to economic utilization of such slag. Such technological advances will be discussed in the present Chapter and in Chapter 9.

8.1.1. Blast Furnace Slag

Blast furnace slag is a nonmetallic coproduct produced in the process in the production of iron from iron ore or iron scrap. It consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates. The molten slag, which absorbs much of the sulfur from the charge, comprises about 20 percent by mass of iron production. Figure 3.1 presents a general schematic, which depicts the blast furnace feedstocks and the production of blast furnace coproducts (iron and slag).

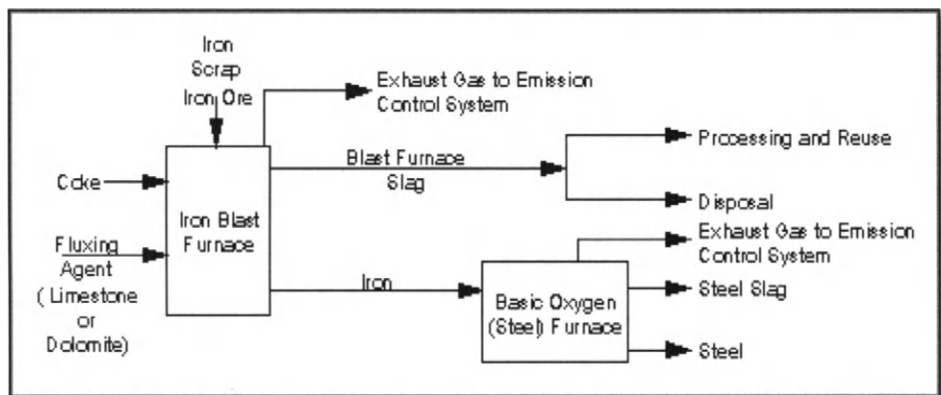


Figure 8.1. General schematic of blast furnace operation and blast furnace slag production (courtesy, Mr. M. P. Sudbury)

Different forms of slag product are produced depending on the method used to cool the molten slag. These products include air-cooled blast furnace slag (ACBFS), expanded or foamed slag, pelletized slag, and granulated blast furnace slag.

8.1.1.1. Air-Cooled Blast Furnace Slag.

If the liquid slag is poured into beds and slowly cooled under ambient conditions, a crystalline structure is formed, and a hard, lump slag is produced, which can subsequently be crushed and screened. Crushed ACBFS is angular, roughly cubical, and has textures ranging from rough, vesicular (porous) surfaces to glassy (smooth) surfaces with conchoidal fractures. There can, however, be considerable variability in the physical properties of blast furnace slag, depending on the iron production process. For example, some recently produced ACBFS was reported to have a compacted unit weight as high as 1940 kg/m^3 (120 lb/ft^3). (Szoke, 1995) Higher unit weights that are reported are generally due to increased metals and iron content in the slag and tend to occur in slags that are generated from blast furnaces with higher scrap metal additions.

The water absorption of ACBFS can be as high as 6 percent. Although ACBFS can exhibit these high absorption values, ACBFS can be readily dried since little water actually enters the pores of the slag and most is held in the shallow pits on the surface.

8.1.1.2. Expanded or Foamed Blast Furnace Slag.

If the molten slag is cooled and solidified by adding controlled quantities of water, air, or steam, the process of cooling and solidification can be accelerated, increasing the cellular nature of the slag and producing a lightweight expanded or foamed product. Foamed slag is distinguishable from air-cooled blast furnace slag by its relatively high porosity and low bulk density. Crushed expanded slag is angular, roughly cubical in shape, and has a texture that is rougher than that of air-cooled slag. The porosity of expanded blast furnace slag aggregates is higher than ACBFS aggregates. The bulk relative density of expanded slag is difficult to determine accurately, but it is approximately 70 percent of that of air-cooled slag. Typical compacted unit weights for expanded blast furnace slag aggregates range from 800 kg/m^3 (50 lb/ft^3) to 1040 kg/m^3 (65 lb/ft^3).

8.1.1.3. Pelletized Blast Furnace Slag

If the molten slag is cooled and solidified with water and air quenched in a spinning drum, pellets, rather than a solid mass, can be produced. By controlling the process, the pellets can be made more crystalline, which is beneficial for aggregate use, or more vitrified (glassy), which is more desirable in cementitious applications. More rapid quenching results in greater vitrification and less crystallization. Unlike air-cooled and expanded blast furnace slag, pelletized blast furnace slag has a smooth texture and rounded shape. Consequently, the porosity and water absorption are much lower than those of ACBFS or expanded blast furnace slag. Pellet sizes range from 13 mm (1/2 in) to 0.1 mm (No. 140 sieve size), with the bulk of the product in the minus 9.5 mm (3/8 in) to plus 1.0 mm (No. 18 sieve size) range. Pelletized blast furnace slag has a unit weight of about 840 kg/m^3 (52 lb/ft^3) (Emery, 1980).

8.1.1.4. Granulated Blast Furnace Slag.

If the molten slag is cooled and solidified by rapid water quenching to a glassy state, little or no crystallization occurs. This process results in the formation of sand size (or frit-like) fragments, usually with some friable clinkerlike material. The physical structure and gradation of granulated slag depend on the chemical composition of the slag, its temperature at the time of water quenching, and the method of production. When crushed or milled to very fine cement-sized particles, ground granulated blast furnace slag (GGBFS) has cementitious properties, which make a suitable partial replacement for or additive to Portland cement. Granulated blast furnace slag is a glassy granular material that varies, depending on the chemical composition and method of production, from a coarse, popcorn-like friable structure greater than 4.75 mm (No. 4 sieve) in diameter to dense, sand-size grains passing a 4.75 mm (No. 4) sieve. Grinding reduces the particle size to cement fineness, allowing its use as a supplementary cementitious material in Portland cement concrete. It is estimated that approximately 14 million metric tons (15.5 million tons) of blast furnace slag is produced annually in the United States.⁽¹⁾

Table 8.1 lists some physical properties of air-cooled, expanded, and pelletized blast furnace slags. Typical composition is shown in Table 8.2.

In addition to the typical properties, blast furnace slag aggregates have lower thermal conductivities than conventional aggregates (Noureldin and McDaniel, 1990). Their insulating value is of particular advantage in applications such as frost tapers (transition

treatments in pavement subgrades between frost susceptible and nonfrost susceptible soils) or pavement base courses over frost-susceptible soils.

Table 8.1. Typical Physical and Mechanical Properties of Blast Furnace Slag (From American Association of State Highways and Transportation Officials, Standard Specifications for Materials “*Blended Hydraulic Cements*” AASHTO M240-85, Part I, 1986)

Property	Slag Type and Value		
	Air-Cooled	Expanded	Pelletized
Specific Gravity	2.0 - 2.5	—	—
Compacted Unit Weight, kg/m ³ (lb/ft ³)	1120 - 1360 (70 - 85)	(800 - 1040) (50 - 65)	840 (52)
Absorption (%)	1 - 6	—	—
Angle of internal friction	40-45		
Hardness (Moh’s scale of mineral hardness)	5-6		

Table 8.2. Typical Chemical Composition of Blast Furnace Slag (Ontario Ministry of natural Resources, Toronto, Canada, *Mineral Aggregate Conservation, Re-use and Recycling.*)

	CaO	SiO ₂	Al ₂ O ₃	MgO	FeO/Fe ₂ O ₃	MnO	S
Mean	39	36	10	12	0.5	44	1.4
Range	34-43	27-38	7-12	7-15	0.2-1.6	0.15-0.76	1.0-1.9

8.1.2 Composition and Mineralogy of Steelmaking Slags

Chemical composition of the slag varies with the stage in the process in which it is generated. Steel slag occurs in four classes: basic converter slag, which includes low phosphorus and high phosphorus pig iron slags; electric furnace slag; pig iron desulfurization slag; and in-ladle processed steel slag. Table 8.3 shows average analysis of slags from these processes

Table 8.3. Chemical Composition of Calcium Phosphate Slags from Various Converters (Akbari and Pickles, 1998)

Process	Weight %						
	Fe _{total}	Fe ²⁺	CaO	SiO ₂	P ₂ O ₅	MgO	MnO _n
Thomas	12.2	8.4	48.3	6.6	19.5	19.5	2.3
BOF	15.6	6.1	49.3	5.9	13.3	13.3	1.9
Ladle processed – first slag	6.8	3.4	52.2	8.0	20.5	20.5	3.6
Ladle processed- second slag	23.4	11.0	47.2	4.6	2.5	2.2	3.5

The slag occurring with low phosphorus pig iron or scrap is rich in lime and silicates. Typical compositions of such slags are shown in Table 8.4. Table 8.5 describes mineralogical phases in the slags.

Table 8.4. Chemical Composition of Calcium Silicate Slags (Akbari and Pickles, 1998)

Process	Weight %							
	Fe _{total}	Fe ³⁺	CaO _{total}	CaO _{free}	SiO ₂	MgO	MnO	P ₂ O ₅
BOF								
Steel, <0.1% C	20.0	8.4	49.8	4.5	12.2	1.3	4.4	2.5
Open Hearth								
Steel, <0.1% C	13.8	9.7	47.5	8.5	12.8	9.3	6.7	2.1
Steel, <0.1% C	20.0	14.0	41.4	4.5	12.6	6.8	7.5	2.3
EAF				1.4				
Steel, <0.1% C	17.3	9.8	39.9		12.8	6.4	9.3	0.7

Table 8.5. Mineralogical Phases Identified in Steelmaking Slags (Bjoerkman *et al.*, 1996)

Identified phase	Chemical composition	BOF slag	EAFslag	Ladle slag
Dicalcium silicate-calcium phosphate	Ca ₂ SiO ₄ -Ca ₃ (PO ₄) ₂	X	X	
Dicalcium silicate	Ca ₂ SiO ₄			x
Tricalcium silicate	(Ca,Mg,Mn,Fe) ₃ SiO ₅	X		x
Wustite	(Fe,Mg,Ca,Mn)O	X	X	
Magnesiowustite	((Mg,Fe,Mn,Ca)O	X	X	
Dicalciumferrite	Ca ₂ (Fe,Al) ₂ O ₅ - Ca(Ti,Si)O ₃	X	X	
Magnetite	Fe ₃ O ₄	X		
Calcium ferrite	CaFe ₂ O ₄	X		
Mervinite	3CaO.MgO.2SiO ₂		X	x
Spinel	(Mg,Fe)(Cr,Al) ₂ O ₄		X	x
Lime	(Ca,Mg,Mn)O	x	X	
Fluorspar	CaF ₂			x

8.1.3. Composition and Metal Contents of Non-Ferrous Slags

Non-ferrous slags cover a wide range of composition with a corresponding range of physical properties. An illustrative analysis is shown in Table 8.6. The slags can be broadly divided into high iron (copper and nickel sulfide smelters), high magnesia (laterite, a complex nickel silicate ore), high lime (lead smelters) and platinum group elements in an intermediate position.

Analyses of base metal content in non-ferrous slags vary widely depending on the smelter feed characteristics and operating practices. Oxygen potential of the main smelting system is often a key determinant of the residual metal content combined with provision for slag cleaning. Table 8.7 shows analyses, and typical (not necessarily the best) practice.

Table 8.6. Variability of Non-ferrous Slag Composition (Sudbury and Kemp, 2006).

Component	% SiO ₂	% FeO	% MgO	% CaO	% Al ₂ O ₃	% Cr ₂ O ₃	Sum
Smelter Type							
Copper Sulphide	36	47	1	2	4	-	90
Nickel Sulphide	36	46	3	3	6	-	94
Nickel Laterite	54	11	32	-	2	1	100
PGM Nickel	42	12	19	15	5	2	95
Lead Sulphide	22	35	1	20	4	-	82

Table 8.7. Examples of Residual Base Metal Content of Non-ferrous Slags (Sudbury and Kemp, 2006)

Component	% Cu	% Ni + Co	% Pb	% Zn
Copper	0.9	-	0.3	3
Nickel	0.34	0.36	-	-
Ferro-nickel	-	0.16	-	-
PGM	0.15	0.15	-	-
Lead	-	-	1	7

8.1.4. Slag Treatment Technologies

Slag is a high volume intermediary product, which is generated as part of the iron and steel making process. It is primarily non-metallic and contains impurities liberated by the melting of the ore and scrap. The rate of generation and treatment practice associated with various slags are summarized in Table 8.8.

Most steel mills process the slag as follows:

- the slag is allowed to cool;
- cranes with magnets sweep the slag to recover the large pieces of steel which are recycled back to the furnace.;
- the remaining swept material is fed into magnetic separator and screened to further recover residual metallics for recycling;
- the remaining slag is sold as aggregate, landfilled or stockpiled.

8.1.5. Metallurgical Applications

Slags from different metallurgical processes, including blast furnace, steel making, non-ferrous contain many useful components used for various industrial and construction purposes. For example, steelmaking slag contains valuable components like iron, manganese, silica, magnesia and alumina. It is a potential secondary source of these metals and has been exploited as such, which will be discussed in this Chapter. In addition, it could also be employed as a low-cost substitute in many metallurgical processes and also as a secondary source of iron. The properties of slag including mineralogical composition play important roles in determining specific applications. They can be altered by methods of modification to make the slag suitable for specific applications.

Table 8.8. Slag Treatment

Process Source	Generation Rate (Percent of steel produced)	Treatment/Reuse/Disposal
Blast Furnace	17 to 20	Metal in slag is recovered by magnetic separation and remaining slag is sold for cement and cement block production, and used as a roasted aggregate. Otherwise land-filled or stockpiled.
Basic Oxygen Furnace	12 to 18	Metal recovered by magnetic separation and some remaining slag is recycled to the BF. Production of cement blocks are recharged to a blast furnace as fine source or recycled to sinter plant. Also used as roadbed aggregate. Otherwise land-filled or stockpiled.
Electric Arc Furnace	4 to 10	Metal recovered by magnetic separation and recycled. Remaining slag is sold as roadbed or land-filled.

8.1.5.1. Blast Furnace Recycling

In view of their high iron content as shown in Table 8.2, the low phosphorus slags can be considered as a low grade iron ore. It is possible to use such slag to recycle back to the blast furnace resulting in savings in iron ore and also flux materials like limestone or dolomite; however, this also results in increased consumption of blast furnace coke and sinter fuel and leads to much higher phosphorus content in the pig iron. The maximum quantity of reclaimable slag is determined by the acceptable phosphorus content in the pig iron, which depends mostly on the phosphorus content of the iron ore. In some cases, the presence of chromium oxide could limit the application of slag recycling as it could increase the chromium content of the steel produced.

8.1.5.2. Sinter Production

Use of steelmaking slag in sinter production conserves charge materials for pig-iron smelting. One ton of converter slag in the production of pig iron is estimated to save 300-480 kg iron ore, 530-620 kg limestone, 110-120 kg dolomitic limestone, 140-180 kg manganese ore, and 80-120 kg coke (Xiao and Feug, 1990). To save coke and increase productivity, the converter slag should be charged into the sinter-machine and the blast furnace in small size fractions. It requires the construction of crushing-screening operations in the plant.

8.1.5.3. Slag Regeneration

The possibility of recycling slags inside a steelmaking plant is an attractive proposition as it would result in a waste-free steelmaking process. In practice, however, it is limited by the high phosphorus content in the steelmaking slags.

Li and coworkers (1995) have investigated the possibility of using slag regeneration in the production of high carbon and high manganese steels. Manganese ore is charged

into the converter with fresh flux and scale. The slag from the converter is first totally recycled to the pre-dephosphorization furnace. The slag is then transferred to the regenerator and the phosphorus removed. The slag from the regenerator, with low phosphorus content, is totally or partially recycled to the pre-dephosphorization stage and/or to the desiliconization furnace. The composition of the dephosphorization slag is adjusted by adding ferrous oxide (FeO). Coke is supplied to compensate for the amount consumed by the reduction of iron oxide and phosphorus pentoxide. In the slag regenerator, the ability of the hot metal to extract phosphorus from the slag decreases with increasing phosphorus in the hot metal. When the phosphorus content reaches a certain limit, the hot metal is dephosphorized at a low temperature by using a high phosphate capacity slag. After this treatment, the hot metal from the final dephosphorization stage is returned to the regenerator. The final dephosphorization slag could be used as a fertilizer.

8.1.6. Properties of Slag of Interest in Their Application

As will be described in Chapter 9, metallurgical slag has been found to have a number of applications besides their direct use in metallurgical processes. However, such applications require the slag to be available with specific properties for each application. Properties of a slag vary depending upon the source and the temperature through which it has been cooled and the rate of cooling. It is possible to modify properties by appropriate controls. Some important characteristics of slag will be discussed.

8.1.6.1. Mineralogical Changes During Solidification

During cooling of the liquid slag, based on liquidus temperatures of steel slags, the silicate phases appear first, followed by the ferrites and the wustite solid solutions (see Table 8.3). The silicate groups are comprised of two types of minerals: tricalcium silicate (alite, $3\text{CaO} \cdot \text{SiO}_2$, abbreviated as C_3S) and dicalcium silicate (larnite: $2\text{CaO} \cdot \text{SiO}_2$, abbreviated C_2S). the calcium ferrites consist of a wide range of solid solutions which vary from $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (calcium ferrite; CF) to $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ (dicalcium ferrite, C_2F) to $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (brownmillerite, C_4AF) and the wustite phase consists of FeO with MgO, CaO and MnO in solid solution.

Dicalcium silicate (larnite) is the most common silicate mineral in slags; tricalcium silicate (alite) appears at high alkalinity. Upon cooling dicalcium silicate undergoes a series of complex phase transformations. The C_2S phase is first formed during cooling and is surrounded by liquid phase at high temperature. Tricalcium silicate also solidifies early in the cooling process, but at 1200°C the structure becomes thermodynamically unstable and decomposes into larnite (C_2S) and lime (CaO) (Wachsmuth *et al.*, 1981). The transformation is suppressed by rapid cooling.

8.1.6.2. Production of Granulated Slag by Rapid Cooling.

Granulated slag can be produced by rapid cooling. In a Swedish industrial operation with electrical smelting furnace (Borell, 2005), the fumed slag is trapped from the fuming furnace into a settler furnace, where the remaining metal and sulfide droplets are separated in the liquid phases and are recycled to the metal smelter or sold for further treatment. The cleaned slag is rapidly cooled in water, which results in a stable granulated product, which is found to be amorphous (glassy) by X-ray studies. The mixture of water and granulated slag is then pumped for dewatering. The product has been named "Iron

sand” and has a particle size 0.25-3.0 mm and a compact density 3.38 g/cm³. Environmental characteristics determined by leaching tests (see Chapter 2) has shown the product to be inert and is suitable as material in road construction (Borel, 2005). Granulation of slag after melting and reduction increases the glass content of the slag to 24% (from only 3% in the reduced slag) (Yang *et al.*, 2005). Glassy slag has low coefficient of expansion. Chemical nature of glassy slag is discussed in Section 8.1.8. Read also particle size enlargement discussed in Chapter 6.

8.1.6.3. Modification of Slag

Several treatment procedures have been suggested to enhance to properties of the steelmaking slag for incorporation into asphalt.

1. Control of the cooling rate, either a very rapid cooling to forms a glassy slag or a controlled slow cooling (Fujita and Iwasaki, 1988; Freguea-Wu and Iwasaki, 1995). Quenching the slag prevents the disintegration of dicalcium silicate. This is practiced in many steel works.
2. Addition of various components to the molten slag to stabilize the impurities and the hazardous elements or extraction of these elements into phases that can be separated (Chiang *et al.*, 1988).
3. Reduction of BOF slag with carbon to obtain a metal phase containing most of the impurities and a slag that can be recycled back to the steelmaking process (Hatton and Pickles, 1994).
4. Oxidation of the slag to form dicalcium ferrite from the free lime present in the steelmaking slag (Meadowcroft *et al.*, 1996).

The addition of a boron-containing mineral to the slag to prevent powdering during cooling has been suggested by Ishizaka and coworkers (1987). Typical boron minerals are kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$), colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$). Harada and Tomari (1991) suggest using boron-containing compounds, which can release B_2O_3 in amounts equal to 0.1 to 0.4 of the slag. A silicate-containing modifier such as foundry waste sand and coal ash can be added after the boron compound to bring the slag alkalinity in the range 1.6-1.9. A second and exothermic modifier, consisting of aluminum, aluminum dross, magnesium or magnesium slag, is then added in powdered slag. It has also been shown that boron oxide or titanium dioxide can effectively lower the fusion temperature of dicalcium silicate, preventing its precipitation and enhancing the dissolution of lime (Bronson and St, Pierre, 1985). Borate also serves as a stabilizer by promoting the formation of B-type dicalcium silicate. This form of silicate possesses hydraulic properties that are preferable in the application of slag as aggregate for road construction (Viklund-White and Ye, 1999).

Alkalinity of the slag can also be reduced by external desulfurization. The use of liquid blast furnace slag for the stabilization of excess amount of lime in steel slag has been proposed (Akbari and Pickles, 1998).

Chemical stability of slags can be enhanced to minimize the leaching of vanadium and chromium by remelting in combination with added olivine, magnesia and silica. Magnesium oxide and chromium oxide form a stable compound $\text{MgO} \cdot \text{Cr}_2\text{O}_3$, reducing the leachability of chromium. Leachability of vanadium is reduced by addition of lime to maintain a $\text{pH} > 12$ (Viklund-White and Ye, 1999).

Chemical stability of slag is determined by leachability tests described in Chapter 2.

8.1.6.4. Reduction of Slag in DC Furnace

Reduction in a DC furnace has been used to process slag. The slag is fed together with a reductant through the hollow electrode, which exposes the slag to the very high temperature of the arc, which provides desired conditions for fast and complete reactions. Heavy metals contained in the slag are reduced and recovered in the metal phase yielding a slag product with low concentrations of unwanted elements. The slag product can also be designed to suit various purposes by the addition of other slag forming materials and inorganic by-products (Viklund-White and Ye, 1999). When reduction is followed by granulation (Section 8.1.5.2), the metal produced by reduction forms spherical droplets (Yang *et al.*, 2005). They can be recycled for the production of steel.

8.1.7. Recovery of Metal Values from Slag

Both iron and steel slag as well as non-ferrous slag carry considerable quantities of metals originated from the feed material, which is usually a complex mineral composite of several metals in addition to the principal metal, which is sought to be extracted. Slag is an important secondary source of metals, which could be recovered by appropriate technology. Some of the example will be described in the present section.

8.1.7.1. Recovery of Iron and Iron Concentrate

The first step in slag processing is size reduction to liberate metallic iron and iron-bearing minerals. This is done by crushers or by autogenous grinding, that is, the slag is ground on its own in the grinding mill without any balls. The latter process yields higher quality product as the iron product discharged from grinding mill contains as high as 80% Fe (Shen and Forssberg, 2003). Metallic iron and iron minerals are separated by magnetic separation. The phosphorus-bearing minerals occurring in steel slag are removed in the tailings of high gradient magnetic separation. The flow diagram is shown in Figure 8.2.

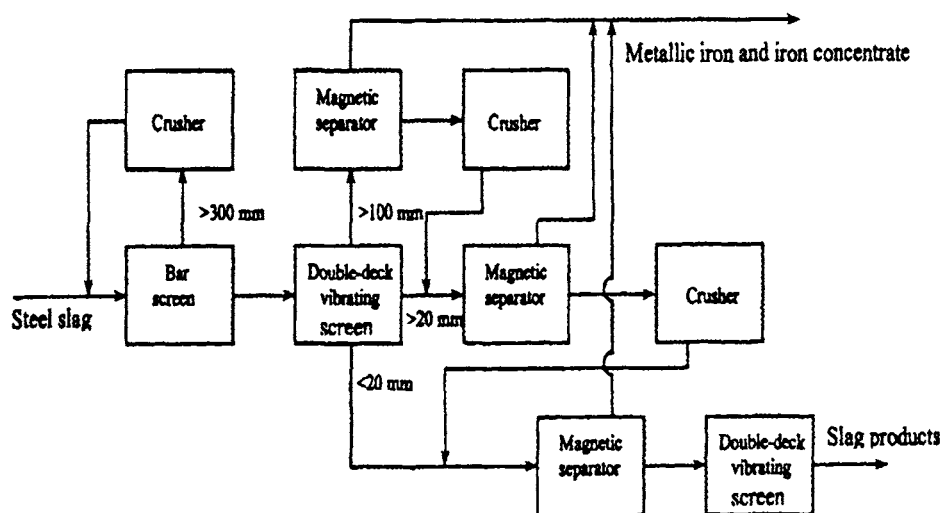
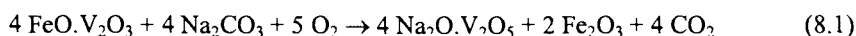


Figure 8.2. Recovery of iron and iron minerals from steel slag (Shen and Forssberg, 2003)

Reduction of iron oxide at high temperature has been shown to be an attractive low energy cost process (Ol'ginskij and Prokhorenko, 1994). The iron-free mineral residue is suitable for applications in construction industry. An alternative route applies microwave heating with carbon and the recovery of iron by magnetic separation (Hatton and Pickles, 1994).

8.1.7.2. Vanadium

Recovery of vanadium value from a ground slag (-100 mesh) has been described by Suri and coworkers (1992). The process consists of thorough mixing with requisite quantity of soda ash and roasting at suitable temperature in the presence of small quantity of potassium chlorate (KClO_3) and air in a rotary furnace. Sodium vanadate is produced by the following reaction and leached in hot water.



The optimum conditions for roasting to achieve maximum leaching of 98 % of the vanadium value present in the slag are, 20 % soda ash and 5 % potassium chlorate by weight of the slag, 800 °C temperature and reaction time of 2 hours.

Yu and coworkers (2004) have attempted to recover vanadium from converter slag by slow cooling which causes the vanadium compounds to concentrate in a distinct phase, from which they are recovered.

8.1.7.3. Manganese, Niobium and Tantalum

A process to recover niobium, manganese and phosphorus from steel slag and convert them to make an alloy and process the remaining slag for use as construction material has been described by Rong (1994). The slag is reduced in a blast furnace, which produces liquid iron containing high grade niobium, manganese and phosphorus. It is taken to a revolving furnace for smelting. The rich slag discharged from the revolving furnace is taken into an electric furnace where it is melted into alloy. The byproduct blast furnace slag is used as cement material and firming agent. The electric furnace slag is used as raw material of refined manganese. The process diagram is shown in Figure 8.3

Recoveries of niobium and tantalum from tin slags by chlorination has been described (Gaballah *et al.*, 1997). Iron, calcium, manganese and aluminum are first removed by leaching. (acid or successive acid and base). Then, the niobium and tantalum concentrate is subjected to chlorination at 500-1000 °C for 24 h with (chlorine + nitrogen) or (chlorine+ carbon monoxide + nitrogen). Niobium and tantalum oxides in the concentrate are converted into respective chlorides, which are volatile and separated from the residue. Chlorination of high grade concentrate with (chlorine + carbon monoxide + nitrogen) niobium and tantalum chlorides of very high purity.

8.1.7.4. Chromium from Chrome Slag

Gravity separation has been applied to process chrome slag by steel researchers in India. Heavy media separation (Choudhury *et al.*, 1996) and crushing and jigging (Khan *et al.*, 2001) are the principal techniques used. The slag is subjected to 2-stage crushing to reduce the size to -10 mm and then screened into -10 +1 mm and -1 mm fractions. The coarse fraction is subjected to jigging and the fine one to tabling. The jigging produces

59% chromium with 6.7% yield, while the tabling produces a low grade concentrate containing 29.25 chromium.

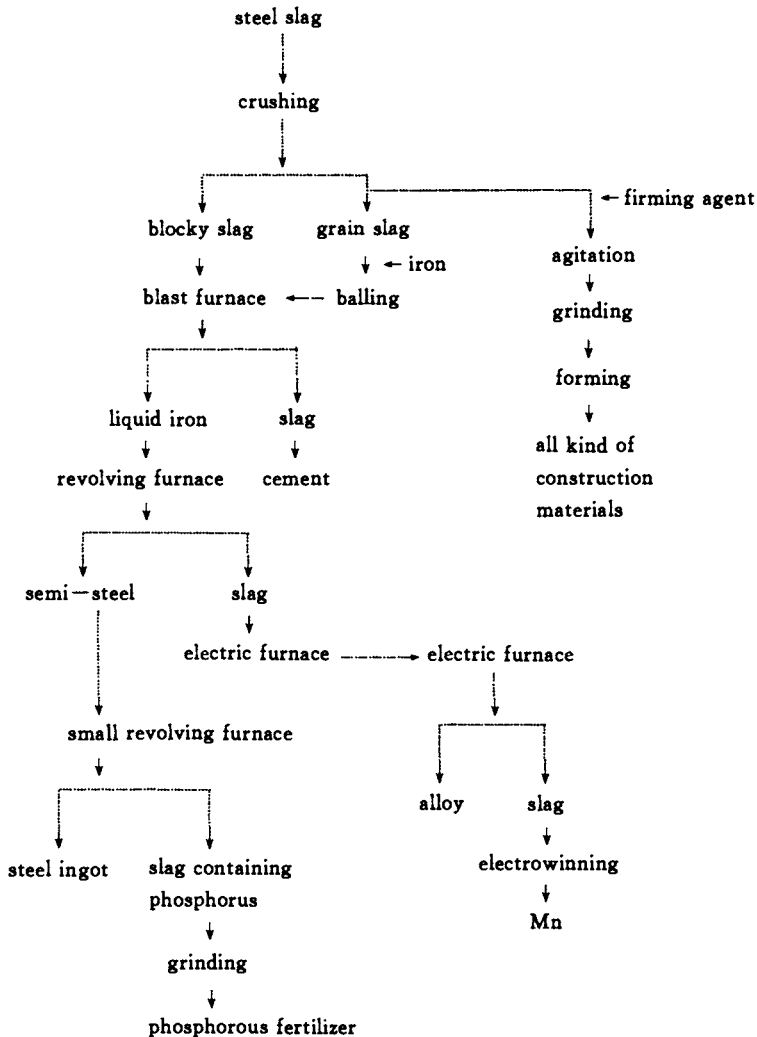


Figure 8.3. Recovery of niobium and manganese from steel slag (Rong, 1994)

8.1.7.5. Cobalt and Copper from Smelter Slag

Selective recovery of cobalt and copper from waste slag requires controlling the quantity of reductant added or equivalent oxygen partial pressure. When carbon is used as the reductant the amount is found to be about 5 % of the total slag feed in a laboratory study by Banda and coworkers (2002). These researchers have also found that the base metal recovery can be significantly improved by certain slag modifiers. The modifiers investigated are lime (CaO), fluorspar (CaF_2) and rutile (TiO_2). Rutile has a more selective effect on the recovery of cobalt than lime and fluorspar, but it leads to lower

overall recoveries of cobalt at various levels of addition than in corresponding cases with fluorspar and lime. The ratio of cobalt recovered to iron recovered increases when rutile is added, but the increase is not found with lime and fluorspar.

8.1.7.6. Heavy Metals from Zinc Fumer Slag

Zinc fumer slags, also known as tail slags or barren slags, are generated from slag fuming furnaces in zinc and lead production. Several industrial processes are in operation. All are based on a reduction step, which carries zinc and lead from lead refining slag into a gas phase. The tail slag from fuming furnaces still contains about 3 percent of zinc and some significant quantities of elements such as lead, indium and germanium. At present these slags are not processed further and are sold as road fill or cement raw material or sent to land fill, often at a net cost to the producer. Although the metal contents are low in absolute terms, there is still the potential to extract considerable value from the remaining metals, especially the rarer element, indium and germanium. As well, the removal of these metals and the residual zinc and lead will help to ensure that the slags can be used as cement additives or roadbed material without negative environmental consequences.

Two possible methods to recover metals from slag have been explored by Zhang and coworkers (2004). They are equilibration with a metal “getter” and electroreduction into a metal cathode. The use of a metal to extract the trace elements is enhanced if the activities of the trace elements of interest are low in the metal and the activities of the undesirable elements are high. Copper is chosen as the low cost metal. The ionic nature of the slag melts, previously established by Mackenzie (1962) and Diaz (1974) indicates the possibility of electroreduction of metals from slag. The expected half cell reactions are:

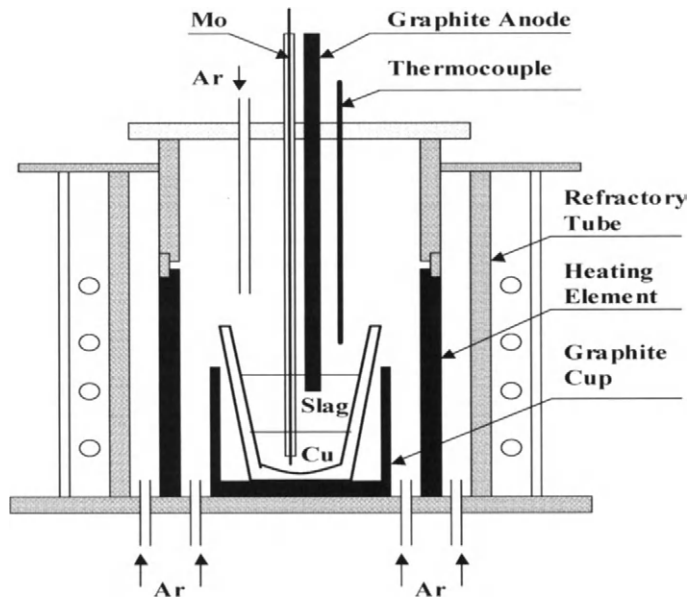
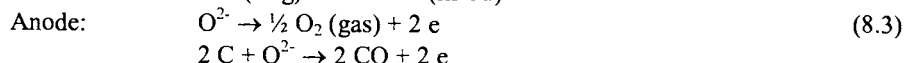
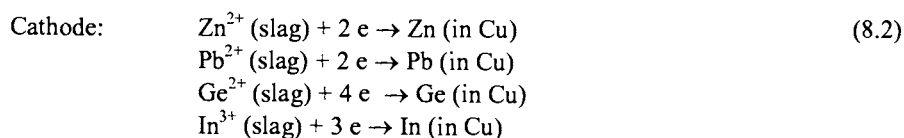


Figure 8.4. Crucible Set-up for the Recovery of Metals from Fumer Slag (Zhang *et al.*, 2004)



The crucible set-up used by Zhang and coworkers is shown in Figure 8.4. It is made of fire clay material analyzing 36 % Al_2O_3 and 57 % SiO_2 with Fe_2O_3 and TiO_2 as the major contaminants.

8.1.7.7. Smelting Redox Process of Slag Treatment

The process known as HSR (Holchim Smelting Redox) developed in Switzerland (Tschudin *et al.*, 2002) treats the slag both to reduce metals and convert the silicate fraction of the slag into materials, which can be used in construction industry. The HSR converter in which slag is treated contains an iron bath with carbon. The intense mixing of metal bath and slag, in combination with the reducing action of carbon, leads to a rapid, effective reduction of metal oxides. Hot air is blown into the metal bath, which promotes the oxidation of carbon monoxide produced to dioxide in post combustion process generating energy, which is used for the overall process. The non-reduced oxides are transferred to the process slag on top of the metal bath. The CaO/SiO_2 ratio is adjusted by addition of either acid or basic material to obtain a product of the desired composition. Treatment of steel slag by this process leads to the production of molten iron with lower chromium content.

8.1.7.8. Recovery of Metal Values from Copper and Brass Slag

The principal components of copper slag are iron and silica, 25-50% of each. Almost all copper slags contain 0.4-3.7% copper (Pavez *et al.*, 2004), which is close to or even higher than in copper ores. Depending on their original source, some slags contain cobalt and/or nickel at levels enough to be recovered. Toxic elements like arsenic and lead occur in some copper slags. Brass melting slag contains recoverable copper, zinc and lead.

Slow cooling facilitates formation of various components in crystalline form. In such slags the principal mineral species are silicates, oxides of nickel and cobalt and copper minerals chalcocite (Cu_2S), covellite (CuS), bornite (Cu_5FeS_4) along with metallic copper.

Recovery of metal or mineral species from copper and brass smelting slag has been done by one of the three methods, flotation, leaching and roasting.

Copper slag flotation is similar to the flotation of sulfides (see Chapter 3). The copper sulfide minerals and metallic copper are floated and the oxides (of cobalt, nickel and silicates) go into the tailings. The slag is ground to 80% -74 μm and conditioned with sodium secondary butyl xanthate as collector and methyl isobutyl carbinol (MIBC) as frother. The process produces a concentrate grading 40-45 % Cu with a recovery of about 80% from the slag containing 3.7% copper (Rao and Nayak, 1992; Barnes *et al.*, 1993).

Metal recovery by leaching is done by treatment of the slag with leachants sulfuric acid, hydrochloric acid, ferric chloride or ammonia (Anand *et al.*, 1980; Basir and Rabah, 1999). Leaching efficiency can be enhanced in some cases by the addition of hydrogen peroxide. For example, in the leaching of brass smelting slag containing 6.3% copper

metal, 14.4% copper in oxide form, 11.4% zinc (oxide form) and 1.3% lead (oxide form) by hydrochloric acid, addition of hydrogen peroxide greatly increases the extent of metal extraction, especially in the hydrochloric acid leaching (Basir and Rabah, 1999). The role of hydrogen peroxide seems to be to oxidize any free metal present to oxide, thus enhancing the rate of leaching. With dilute sulfuric acid leaching Anand and coworkers (1983) have extracted 90% copper and more than 95% each of nickel and cobalt, with only 0.8% extraction of iron from a copper converter slag containing 4% copper, 2% nickel and 0.5% cobalt.

Roasting process converts the metals in the slag into soluble sulfate. This is done by sulfating agents like sulfuric acid, ammonium sulfate or ferric sulfate at temperature in the range 200-600 °C. (Tumen and Bailey, 1990; Hamamci and Ziyadanogullari, 1991) Hydrogen sulfide has also been used. In this case, the metal sulfide is first formed, which is then oxidized to sulfate by air at high the temperature (Ziyadanogullari, 1992). Sulfuric acid or ammonium sulfate directly convert metal or oxide to sulfate. In the case of ferric sulfate, it is decomposed to ferric oxide and sulfur trioxide, which reacts with slag metal oxides to form soluble sulfate.

Zinc recovery from brass ash by carbothermic reduction has been described by Kahvecioglu and coworkers (2002). The reducing agent is graphite at 1000 to 1200 °C with a time interval of 0-180 min. Zinc recovery increases with increasing time and temperature in the range indicated. Metallic zinc and zinc oxide are collected in condenser powder form. The lead content in the condensed powder increases with increasing temperature. Copper remains in the residue and is considered to be adequate for smelting.

8.1.8. Ladle Slag - Special Characteristics

Ladle furnaces have been constructed in significant numbers only since 1980s. As such, there has been much less work on the potential application of ladle slag. In addition, the main technical obstacle to extensive reuse or recycling of ladle slag is its unique property called '*falling slag*' phenomenon. This refers to the breakdown of slag upon solidification to a fine powder, which results in difficulty with handling, moisture retention, and emission problems due to dusting.

A possible mechanism of the 'falling slag' phenomenon has been described by Pinhey and Kunz (1995) based on studies of phase diagram of CaO-MgO-SiO₂ for 30 % Al₂O₃ (Muan and Osborn, 1965). Under slow cooling conditions, slags with 15 % silica will precipitate dicalcium silicate Ca₂SiO₄ (C₂S), which experiences a volume change on cooling, as it is transformed from α -phase to γ -phase. This is probably the origin of the dusting in high silica slags. It is also generally recognized that even slags with less than 40 % C₂S falls if the C₂S phase is at the grain boundaries as is the case with most ladle slags (Smith and Coley, 1998). The slags with lower silica content are less likely to break down as shown by the study of Pinhey and Kunz (1995). Such slags precipitate pure lime (CaO) and C₂S does not occur as one of the major solid phases for slow cooled, low silica slags.

The phase transformation causing the slag falling can be inhibited by fast cooling, although the mechanism has not been established. A glassy form in which no crystalline phase is present or the crystalline phase that does not form may have too small a particle size to nucleate γ C₂S. It may even be possible to encapsulate the C₂S in a glass thereby

preventing the transformation, but no evidence has been put forward (Smith and Coley, 1998).

8.1.9. Production of Non-Metalliferrous Slag

A novel system called “Para-Eco Incinerator Ash Processing System” has been developed by Takai and coworkers (2003) to produce non-metalliferrous slag and to improve recycling of ash produced from municipal solid waste. The system consists of four processing plant for feed preparation, “Para-Eco” furnace, slag preparation, and fly ash and flue gas treatment. It is schematically shown in Figure 8.5.

Clean dry ash with added flux of magnesium-calcium compound (e.g., dolomite), which better eliminates metalliferrous components from newly produced slag, and coke to maintain reducing atmosphere in the furnace is the feed material charged to the furnace made of graphite brick and consisting of an upper electrode of carbon, and a bottom electrode of iron metal. The dry powder feed melts at 1500 °C forming three products: slag, iron metal and fly ash. The molten slag is continually flows from the after-heating furnace adjoined to the furnace, and the molten iron is discharged intermittently. The slag produced has extremely low metalliferrous components and chlorine. The non-volatile metal oxides like copper, chromium are reduced to the metals and absorbed into the molten iron. The iron metal produced contains 10 % copper. Lead, zinc, and salts of sodium and potassium as well as chlorine, go into the fly ash component. The fly ash produced consists of almost 70 % salt containing 10 % zinc and 2 % lead. They can be recovered by hydrometallurgical treatment.

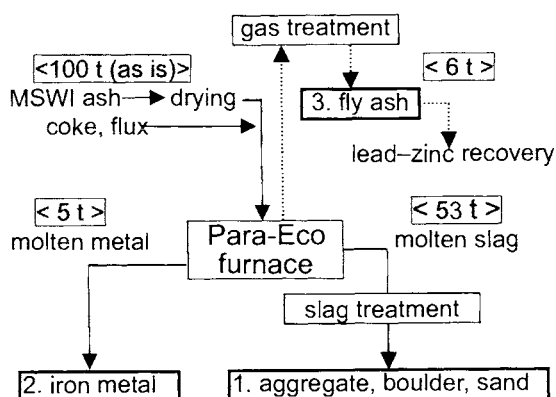


Figure 8.5. Summary of material flow in the para-Eco Incinerator Ash Processing System (Takai *et al.*, 2003)

8.2. Flue Dust

Metallurgical processes in furnaces generate large quantities of dust, which are potentially hazardous both for human health as well as for environment. Their disposal or possible internal re-use has been a serious concern for metallurgical industries. The iron industry has traditionally treated lump or sintered fines in integrated operations. Blast furnace dust could be readily recycled to the sinter strand. However, the adoption of pellet sintering (see under “Pelletization” in Chapter 6) in remote locations has made it uneconomic to recycle iron blast furnace dust to the pellet plant and this has led to

landfilling practice for blast furnace dust as the small tonnage and low value of the units do not justify installing a large agglomeration plant. In steel plants, the use of increasing tonnage of galvanize contaminated scrap leads to high levels of zinc in the dust. Such dust ends up in landfill. Electric furnace mini-mills melting 100% scrap generate much more zinc fume and the dust can run up to 30% zinc. Such dust may be processed in a Waelz kiln. In non-ferrous metal industry (Cu, Ni, Pb, Zn) the smelting dust contains major amounts of valuable metals and is almost always recycled. Treatment of the dust from various sources for resource recovery and to reduce their volume has led to several innovative developments in recycling.

Blast furnace (BF) flue dust generally contains low levels of zinc (1.5 %) and lead since only minor amounts of these elements are permitted to enter into the iron making process. Basic oxygen furnaces (BOFs) produce steel from molten iron (from the BF) and ferrous scrap metal. BOF flue dust generally contains higher levels of zinc (1.5 to 4.0 %) and lead. The zinc content is high enough to prevent its recycling to the last furnace, but not high enough to economically justify further processing of zinc recovery. Electric arc furnace (EAF) flue dust is very high in zinc (15 to 25 %), lead and cadmium due to the quantity and nature of the scrap consumed. EAF dust is therefore classified as hazardous waste. Mini-mills generate 13 to 18 kg of EAF dust per tonne of steel produced.

The present Section will consider the various recycle options to treat the dust generated in different classes of metallurgical industry.

Table 8.9. summarizes the characteristics and treatment practices associated with the various steel-making flue dusts.

Table 8.9. Flue Dust Treatment

Process Source	Characteristics	Treatment/Reuse/Disposal
Blast furnace: BF flue dust (from Furnace precipitators)	Non-hazardous	Sintered and recycled/ Used in cement production. Land filled
Blast furnace: BF Filter cake (from scrubbers)	Non-hazardous, very fine	Sintered and recycled. Used in cement production. Land filled
Basic Oxygen Furnace (BOF)	Non-hazardous, except with high zinc levels from melting galvanized scrap.	Sometimes sintered and recycled. Used in cement production. Land filled. Stockpiled
Electric Arc Furnace (EAF)	Mostly hazardous because of Zn, Pb and Cd levels from steel scrap in melting operation.	Used as supplement in cement production. Various treatment processes. Stockpiled

8.2.1. Electric Arc Furnace Dust (EAF)

Electric arc furnace (EAF) dust is generated during steelmaking from iron-containing steel scrap in an electric arc furnace. It is considered a hazardous waste as it fails toxicity test for lead, cadmium and chromium. The EAF's share of total steel output has been increasing at the expense of integrated iron and steel production (Smithyman, 1996;

Nyirenda, 1991; Kola, 1991). This is partly due to increasing environmental concerns. Resource conservation and economic benefits associated with EAF steelmaking have led to an increased recycling of scrap. As a result, the volume of EAF dust to be treated has been steadily increasing. Stockpiling used to be a common practice, but that is no longer viable as the sites available for stockpiling are steadily being depleted. In addition, by stockpiling valuable metal values still present in the EAF dust are lost. Landfilling has been another common practice for the disposal of EAF. This option is also becoming more expensive with depletion of the number of landfill sites. Most importantly, stringent environmental regulations are being put into effect. New technologies for the treatment of the EAF dust are emerging, motivated by economic and environmental concerns.

About 10-20 kg of EAF dust are generated per ton of steel produced (Akerlow, 1975; Barnes, 1976). In North America, the quantity of dust generated is approximately 700,000 tons per year. In the U.S. there are about 80 steelmaking plants producing roughly a total of 600,000 tons of EAF dust per year (Goodwill and Schmitt, 1994). The average amount of dust generated per plant is about 8,000 tons per year. In the western European countries, around 480,000 tons of EAF dust are generated annually (Kola, 1991); the corresponding figure for Japan is about 300,000 to 450,000 tons per year from about 50 steelmaking operations (Yasuda, 1991). In the production of steel, the major constituents of the EAF flue dust generated are iron (24 %), chromium (10 %), zinc (6 %) and nickel (3 %).

8.2.1.1. Properties and Composition

The particles in EAF dust tend to occur as aggregates consisting of very fine individual particles. Most individual particles are less than μm (Hogan, 1974; Pickles *et al.*, 1977), or the average particle size is 1.0-4.3 μm using a Microtrac instrument (Wu and Themelis, 1992).

The composition of EAF dust varies widely depending upon the scrap used, the type of steel being made, the operating conditions and procedures. The dusts from carbon steelmaking are rich in zinc and lead, while those from steelmaking are relatively low in lead and zinc, but richer in alloying elements, such as chromium, nickel, manganese, etc. Since the ratio of galvanized steel scrap used has been increasing, the composition of zinc and lead in the dusts has also been increasing. Besides zinc, the dust also contains a considerable percentage of iron and lesser percentages of lead, manganese, calcium, sodium and potassium as well as trace amounts of other elements, such as cadmium, chromium, nickel, copper, magnesium, silicon and chlorine. Table 8.10 shows the typical compositions of EAF dusts from the U.S., Spain and France.

Mineralogical phase distribution of elements in EAF dust has been extensively studied by several groups and are reviewed by Akbari and Pickles (1998). X-ray diffraction (XRD) measurements have shown that EAF dust consists of a predominant magnetite-franklinite-jacobsite solid solution, with lesser zincite, hematite and minor sylvite, carbon (coke) (Hagni and Hagni, 1993) and calcite as well as calcium and aluminum silicates (Lopez *et al.*, 1993, Cruelles *et al.*, 1992). New phases such as $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$ (Cruelles *et al.*, 1992) and $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (Li and Tsai, 1993) have also been determined in some EAF dust samples by XRD. The amount of zincite varies with the percent zinc present in the sample and increases with the zinc content. Mineralogical analysis is often useful in determining the applications of the slag.

8.2.1.2. Processing Options

The EAF dust treatment processes are grouped in six categories:

1. Thermal – requiring high temperature treatment of the EAF dust.
2. Recycling – involving modification of the dust so it can be added to the furnace.
3. Vittrification – where dust is vitrified or mad into a non-leachable product.
4. Chemical fixation – where the dust is encapsulated and made suitable for land fill.
5. Leaching – where zinc is removed from the dust hydrometallurgically
6. Sintering – to produce a compact mass of iron ore that will withstand the weight of charge when the sinter is placed in a blast furnace.

Table 8.10. Mean Composition of EAF Dusts (compiled from Lopez *et al.*, 1993; Keyser, 1981 (marked by superscript a; Little, A. D., 1993; Frenay *et al.*, 1985)

Element	U. S.(20)	France (21)	Spain (16)
Fe	28.5	21.8	25.90
Zn	19.0	21.2	18.6
Pb	2.1	3.6	3.63
Cd	< 0.01	N. A	0.10
Cr	0.39	0.37	0.31
Ca	1.85-10.0 ^a	12.8	3.50
Ni	0.01 - 0.02 ^a	0.10	0.07
Mo	< 0.02 - 0.08 ^a	N. A	N. A
Mn	2.46 - 4.60 ^a	2.5	2.81
Mg	0.77 - 2.93 ^a	N. A	1.53
Cu	0.06 - 2.32 ^a	0.25	0.54
Si	1.35 - 2.49	N. A	1.65
Cl	0.51 - 2.36 ^a	1.75	3.43
F	0.01 - 0.88 ^a	N. A	N. A
K	0.06 - 1.12 ^a	2.06	1.23
Na	0.29 - 2.31 ^a	2.23	1.27
Al	N. A	N. A	0.44

N.A. data not available

8.2.1.2.1. Thermal Treatment Processes.

Three principal technologies in current commercial practice are, HRD/ZCA Process (Waelz Kin); Berzelius Duisberg process; and INMETCO (to be described under secondary recovery of superalloys.)

HRD/ZCA Process (Waelz Kiln)

The process is so-called as it was designed by Horsehead Resource Development Co. Inc. (HRD) and Zinc Corporation of America (ZCA). The EAF dust is blended with water, coal, limestone, and fluxes as required. The mixture is fed to the Waelz kiln in which it is heated to 1,000 to 2,000 °C to produce an iron-rich slag which, after cooling, crushing and screening, is sold as aggregate.

The volatile metal oxides are reduced and fumed in the kiln. The metal vapors are re-oxidized by introducing induced air as they are drawn out of the kiln. A baghouse collects the crude zinc oxide containing cadmium, lead and halides. The zinc oxide is subsequently refined in a second rotary kiln to selectively volatilize cadmium, lead,

chlorine and fluorine. The calcined zinc oxide sold as a feedstock to a zinc pyrometallurgical plant. The condensed lead and cadmium fume is collected in a baghouse and is used as a feedstock by a zinc hydrometallurgical plant.

In the zinc hydrometallurgical plant, the condensed fume dust is leached and the leach residue containing lead as a silver-rich intermediate, can be sold to lead smelters. The leach solution contains the soluble cadmium and some zinc and is further treated to produce a cadmium cake, a zinc oxide and a brine. The metals are recovered in a conventional zinc hydrometallurgical plant. The spent leach solution is a brine, which is presently disposed of by deep well injection.

There are presently three HRD/ZCA Waelz plants in the U.S., (Rockwood, Tennessee), Palmerton, Pennsylvania) and Calumet, Chicago, Illinois), with total annual capacity to treat 410,000 ton EAF dust.

8.2.1.2.2. Berzelius, Duisberg Process

The technology is a variation of the Waelz process. The EAF dust is fed to a Waelz kiln, which produces an impure oxide and an iron-rich slag (used as aggregate). The impure oxide is then fed to a briquetting plant, which consists of preheating kilns and briquetting rolls. The briquettes are then fed into a smelting shaft furnace, which normally operates on 100 percent sinter feed but can also process 100 percent Waelz oxide or other secondary material briquettes. Typical Waelz oxides consist of zinc (56 to 60 %), lead (7 to 10 %) and cadmium (0.1 to 0.2 %). No effluent is produced by this process.

8.2.1.2.3. Tetronics/IMS Plasma-Based System.

The plasma reactor performs carbothermic reduction to vaporize the zinc, lead and cadmium contained in the EAF dust. Iron oxides are reduced to the ferrous state and combined with the remaining dust fractions, such as limestone and silica to form an iron-rich basic slag, which is periodically tapped from the vessel. The gaseous products of the reaction, consisting of carbon monoxide with high levels of zinc, lead, and cadmium vapors, pass into a splash condenser where the metals are condensed. The carbon monoxide and any uncondensed metals pass to an afterburner and then to a bag-house. The solids from the bag-house are returned to the process.

8.2.1.2.4. Dereco Process

The Dereco process treats EAF dust as well as swarf, mill scale and shot blast dust. The materials are mixed with a binder and briquetted, the briquettes are claimed to have a virtually unlimited shelf life and are fed back to the EAF. To handle the build up of metallic oxides in the dust, a thermal separation unit or a kiln has been used. A commercial plant, which processes all of the metallic wastes generated by a local steel maker is in operation at Midland, Pennsylvania.

8.2.1.2.5. ISI Solidification Process

The solidification process takes various secondary materials and dusts. They are reacted with a proprietary chemical reagent and water. The mixed materials are allowed to cure for several days, after which they are broken into lumps, and charged to the furnace. The solidification process is chemically adapted to ensure that the agglomerate of secondary materials is self-fluxing and pyrometallurgically compatible with the furnace.

melt. The zinc content of the bag-house dust is allowed to build up to 40 percent before it is shipped to a zinc reclaimer. The process is in operation at Atlas Steels in Ontario..

8.2.1.2.6. Sintering Process

Sintering converts fine sized raw materials (e.g., iron ore, coke breeze, limestone, mill scale, and flue dusts) into an agglomerated product, sinter of suitable size for charging into the blast furnace. The raw materials are sometimes mixed with water to provide a cohesive matrix, and then placed on a continuous, traveling grate called the sinter strand. At the beginning of the sinter, the coke in the mixture is ignited by a burner hood. The combustion is then self-sustaining. It provides sufficient heat (1,300 °C to 1,480 °C) to cause surface melting and agglomeration of the mix. On the underside of the sinter strand is a series of wind boxes that draw combusted air down through the material bed into a common duct leading to a gas cleaning device. The fused sinter is discharged at the end of the sinter strand, where it is crushed and screened. Undersized sinter is recycled to the cooler with water sprays or mechanical fans. The cooled sinter is crushed and screened for a last time, the fines are recycled and the product is sent to be charged to the blast furnaces. Generally, to produce one ton of product sinter, 2.5 tons of raw materials are required including water and fuel.

Currently available options for processing EAF dust could be classified as follows: hydrometallurgical, pyrometallurgical, hybrid pyro- and hydrometallurgical, stabilization or vitrification processes and some miscellaneous processes. Some of these have either been put into industrial practice or commercialized for a period of time and then abandoned. Many of the methods are at pilot plant stage. Some of the principal processing methods will be described in this chapter.

8.2.1.3. Pyrometallurgical Processes

Most of the industrial methods for the processing of EAF dust can be considered pyrometallurgical, in particular, the rotary kiln processes. They usually require large tonnages of EAF dust to be treated to be economically acceptable. Other technologies developed aim at processing the material on-site on a relatively small scale. Some of these processes, like most plasma processes are, however, too elaborate or energy intensive. They all require a well designed condenser for the recovery of zinc, lead, cadmium and salts such as sodium and potassium chlorides. Even with such elaborate operations, the efficiency of metal recovery is low. The major high temperature metals recovery (HTMR) processes include rotary kilns and plasma.

Three commercially available technologies used to recycle stainless steel flue dusts are, INMETCO process, Berzelius Lankstrona, Sweden Plasma Furnace; and Tetronics/IMS Plasma system.

Berzelius, Lankstrona, Sweden Plasma Shaft Furnace. The process is used to treat hazardous chromium and nickel-containing stainless steel flue dusts. The environmental burden appears to be low if adequate gas-cleaning equipment is used on the plasma furnace off-gases. The slag is inert and is either land filled or sold as aggregate.

The plant located at Lankstrona, Sweden has the capacity to treat 50,000 tons per year of EAF dust from stainless steel plants. The process recovers 350 to 450 kg per ton of metal per ton of dust.

Some of the widely used processes will be described. Southwick (1998, 2004) has written extensive reviews of many processes used for EAF dust processing.

8.2.1.3.1. Tetronics/IMS Plasma System

The process has been described in Section 6.5. When stainless steel flue dusts are being treated, anthracite is added to reduce the metallic oxides of chromium, nickel and molybdenum. These metals are recovered in the carbon-saturated "pigs" which are recycled during alloy steel-making.

8.2.1.3.2. HTMR-Rotary Kiln Processes

Waelz Kiln Process. This is a pyrometallurgical process for volatilization of zinc, lead and cadmium under reducing conditions, in Waelz kilns. It is performed in a long, slightly inclined refractory-lined rotary kiln (waelz kiln) (see Chapter 6 for description).. Feed materials to a waelz kiln are, for example, zinc- and lead-bearing EAF dusts. To ensure quality of the product, it is important to agglomerate the feed material. This is done by preparing the homogeneous mix in the form of pellets in a palletizing plant. Fine coke (<10 mm) is used as reductant. The feed mixture is slowly moved by the rotation of the kiln and heated by the off-gas stream leaving the kiln counter-current to the material flow. After drying and preheating, the current charge enters the reduction zone in which the iron and zinc oxides are reduced. At the bed temperature of 1200 °C zinc is vaporized and swept out of the kiln by the hot off-gases in a very finely divided form along with other volatilized metals, including lead and cadmium. The dust laden gases pass through a large dust settling chamber where coarse particles settle, then to a surface or water evaporation cooler and finally to a baghouse or electrostatic precipitator, in which the Waelz oxide is collected. This so-called pre-oxide, consisting of kiln back-flow material and dust from the settling chamber is recycled to the kiln inlet. The Waelz slag discharges by gravity from the lower end of the kiln at about 100 °C and falls through a chute into the wet slag extractor. After cooling, the slag is classified and separated on a magnetic separator for recovery of unburned coke.

An example of this is found in the treatment of about 80-85 % of the dust from carbon steel makers in the U. S. (Moser *et al.*, 1992). Typical Waelzing feed and product composition are given in Table 8.11.

Table 8.11. Typical Waelz Kiln Feed and Products (Moser *et al.*, 1992)

Element	Zinc Calcine	Pb/Cd Concentrate
Zn	55 - 66	5 - 10
Pb	0.5 - 1.5	35 - 50
Cd	0.05 - 0.15	1.2
Fe	4 - 9	0.5 - 1.5
Cl	0.15	15 - 25

Table 8.12. Percent Composition of Products and Calcining Kiln (Moser *et al.*, 1992)

Element	Zinc Calcine	Pb/Cd Concentrate
Zn	55 - 66	5 - 10
Pb	0.5 - 1.5	35 - 50
Cd	0.05 - 0.15	1.2
Fe	4 - 9	0.5 - 1.5
Cl	0.15	15 - 25

Further separation of the non-ferrous metals is achieved by employing a separate rotary kiln to selectively volatilize cadmium, lead, chlorine and fluorine from the zinc oxide (Kashiwada and Kumagai, 1970). Calcining kilns are essentially identical with the Waelz kilns, but the processing conditions are more oxidizing. The lead and cadmium are converted to oxides, sulfides, and halides, discharged as fumes and are condensed. Table 8.12 shows the typical composition for the zinc calcine and the lead/cadmium concentrate. Crude Waelz oxide contains substantial amounts of halides (chloride and fluoride), which seriously hamper electrolysis of zinc. Halides are also a potential environmental hazard. A method to remove or reduce the concentration of halides will be described in Section 8.2.1.9.

In the process, the Waelz slag occurs as a byproduct and contains all non-volatile components and the fluxes added. As a function of the Waelz process chosen, the slag may be acid or basic. To describe the slag properties, a basicity index is used, which is applied to Waelz slag in particular. The index is defined as

$$\text{Basicity (B)} = \frac{(\% \text{ CaO} + \% \text{ MgO})}{\% \text{ SiO}_2}$$

The acid process in which silica is added to the mix has a basicity between 0.2 and 0.5. the basic process, with the addition of lime, limestone or slaked lime, is operated at a basicity of between 1.5 and 4. the operation of a Waelz plant between these two basicity ranges is extremely difficult to control. At a slag basicity of about 1, accretions form and agglomeration may occur in the inlet zone of the kiln as well as the formation of an iron-rich ring at the Waelz kiln end.

The off gas is quenched with water and/or with air or is cooled in indirect coolers. The Waelz oxide itself is separated from the off gas stream at temperatures between 120 °C and 350 °C. The product filter may be a bag filter or an electrostatic precipitator.

The Waelz oxide product contains, aside from 55-60% zinc, some alkalis (1-2% Na, 1-2% K) and halides.(4.8% Cl, 0.4-0.7% F). These elements, which are also an environmental hazard, may be reduced to low concentrations by leaching in a 2-stage countercurrent wash. The double-leached Waelz oxide may be directly fed to electrolytic zinc plants. Waelz oxide and filtrate of the second stage are mixed with the addition of soda ash. At 80 °C and a pH of 9, more than 90 % of the alkalis and halides are dissolved. After the solid-liquid separation, the solids are washed with fresh water to remove any impurities adhering to the Waelz oxide. The filtrate of the second stage is heated in a Venturi scrubber installed in the off gas stream and returned to the first leaching stage. The first stage filtrate is routed to a water treatment plant for heavy metal separation. The solid residues produced by water treatment are processed in the Waelz kiln. More than half of the Waelz oxide output can be used as feed material for electrolytic plants (Mager *et al.*, 2000).

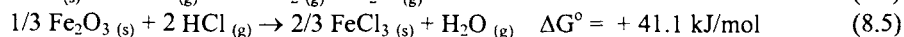
Other Rotary Kiln Processes. All rotary processes for EAF dust treatment are basically the same in terms of process physics and chemistry. Differences are in feed preparation and crude oxide treatment. The mixed EAF dust is introduced directly into the Waelz kiln in America, while it is fed into the kiln in the form of pellets or briquettes in Europe (Kola, 1991) and Japan (Tsuneyama *et al*, 1990). In America, most crude zinc oxide is further treated in rotary kilns to generate zinc calcine, which is sold to an electrothermic zinc smelter. In Europe, crude zinc oxide from Waelz smelters is either

sold to ISP (Imperial Smelting Process, described in Chapter 6) smelters directly (Kola, 1990) or dehalogenated in a hydrometallurgical process before it is sold to ISP smelters in Japan (Tsuneyama *et al.*, 1990). Another example of a modification of the Waelz kiln process is the Inclined Rotary Reduction Process (IRRP) (Kotraba and Lanyi, 1991). The major difference between the Waelz process and IRRP is that the mixed oxide recovered in the bag filters is pelletized with high quality powdered coal and binder, and then fed to a retort and recovered as zinc alloy (with < 1.5 % Pb) and lead alloy (about 10 % Zn and 1 % Cd) in an ISP condenser. The balance of zinc, lead and cadmium is recovered from the off-gas as a mixed oxide in a baghouse and is recycled to the retort.

HTMR-Plasma Processes. One process developed in the U.S. uses an elaborate process flowsheet for the preparation of the material to be treated (Eriksson *et al.*, 1986; Herlitz *et al.*, 1987).

Other HTMR Processes. Flame Reactor Process is an example of an industrial method designed specially for the treatment of EAF dust (Bounds and Pusateri, 1990). It meets demand for a small scale site specific waste processing facility and achieves results similar to Waelzing technology for zinc-bearing feeds. However, its high specific throughput makes possible economic operation at 10,000-50,000 TPY level, rather than the much higher feed rates needed for the Waelz kiln operation to be cost-effective (Moser *et al.*, 1992).

Chlorination Process. Chlorination of iron oxide and non-ferrous metal oxides leads to the formation of metal chlorides. A comparison of the Gibbs free energy values for the conversion of oxides to chlorides shows significant differences as noted from the following equations:



The chlorides of non-ferrous metals are more stable than their oxides whereas ferric oxide is more stable than ferric chloride.

The common chlorinating agents, chlorine, hydrogen chloride or metal chlorides will make the process more expensive. Tailoka and Fray (1997) have proposed the use of scrap polyvinyl chloride (PVC) as an alternative, cheap source of hydrogen chloride for chlorinating metallurgical dusts. The basic chemical structure of PVC is represented by $[-\text{CH}_2-\text{CHCl}-]_n$ where n is the length of the hydrocarbon chain. Upon combustion, PVC decomposes to produce mainly hydrogen chloride gas, carbon dioxide and hydrocarbons. The combustion also produces heat energy, as high as 34 kJ/kg of PVC. By directly heating a mixture of metallurgical residues (EAF dust, zinc-lead blast furnace slags, zinc-copper rich dusts from copper refining) with scrap PVC at a temperature range of 1166-1332 K, 80-90 % of zinc and lead could be recovered. Only negligible amounts of iron are observed in the aqueous solutions. For iron rich dust, a residue, highly rich in hematite is recovered. The concentrations of hydrocarbons after the process is reported to be typically less than 100 ppm. Dioxins and furans, possible products of thermal degradation of organic halo compounds are not found in the soot or the discharge gas (Tailoka and Fray, 1997). As these organic compounds are well known carcinogens, their absence or complete removal is an important environmental and health benefit. Further, as the process uses scrap material as a source of hydrogen chloride, cost savings could be significant.

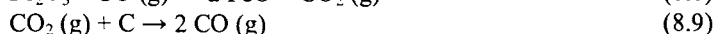
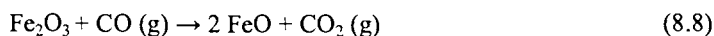
8.2.1.3.3. Enviroplas Process for Recovering Zinc

This process, developed at Mintek in South Africa (Schoukens *et al.*, 1995; Abdelatif, 2002), relies on a DC arc furnace and an ISP lead splash condenser for the direct recovery of the zinc contained in metallurgical wastes like EAF dust and lead blast furnace slag. EAF dust is first pre-treated in a rotary kiln or a DC arc furnace. This is to reduce the moisture content to $< 0.1\%$ and remove elements such as chlorine, fluorine, sulfur, potassium, sodium, arsenic, cadmium etc. while keeping the zinc loss to a minimum. The pre-treatment is followed by pelletization or induration. The product is charged to a fuming furnace. Metallurgical coke is used as reducing agent and is delivered to the fuming furnace at a controlled rate. Other carbonaceous materials like coal or charcoal can also be used as reductants. Zinc and lead oxides produced in the molten bath are reduced to metals at $1400\text{--}1500\text{ }^{\circ}\text{C}$ and report to the gas phase. The residual slag and any iron alloy that is produced, is tapped from the furnace. The volatilized zinc and lead exit the furnace through a refractory-lined duct and enter the lead splash condenser operated at $500\text{--}550\text{ }^{\circ}\text{C}$, where they are condensed. The lead-zinc solution is then cooled down to separate the zinc (at about $450\text{ }^{\circ}\text{C}$). The condenser off-gas passes through a combustion chamber, where any residual metal oxides are captured in a bag house. Condenser drosses and fumes are then pre-treated before recycling to the fuming stage. The process is schematically shown in Figure 8.6.

The following principal reduction reactions leading to the production of zinc have been recognized (Dal and Rankin, 1993):



As the smelting conditions in the furnace are very reducing, both ferric oxide and carbon dioxide are reduced to ferrous oxide and carbon monoxide:



These reactions ensure that the activity of ferrous iron is maintained at high level.

Kinetics of the process is influenced by the operating temperature (Rankin and Wright, 1990). Elevated temperatures favor the reaction rate by enhancing the diffusion rate of the reacting species. High temperature also helps to suppress possible formation of iron metal as the reduction of zinc oxide is thermodynamically favored. However, increased temperature could also contribute to refractory erosion by thermal degradation and slag attack. In addition, overall energy requirements increase with higher temperatures. Typically, a smelting temperature in the range $1500\text{--}1550\text{ }^{\circ}\text{C}$ is considered to be optimum for the treatment of EAF dust.

Some of the impurities in the feed could affect the process. The principal one is sulfur content of the feed. The reaction is retarded by sulfur, probably due to a surface blockage at the solid-gas interface caused by the surface-active nature of the sulfur on the solid (Dal and Rankin, 1993). If some of the zinc occurs as zinc sulfide that could end up in a segregated matte (of sulfide) phase building up above the metal bath. Additionally, sulfides of zinc and lead may be extracted into the gas phase, and collect in the condenser upon solidification. This increases the dross generated and represents loss of zinc and

lead. One way to minimize the impact of high sulfur content is to increase the alkalinity by the addition of lime. Zinc sulfide reacts with lime forming a double compound ZnCaOS . This is readily reduced by carbon monoxide forming zinc and calcium sulfide:

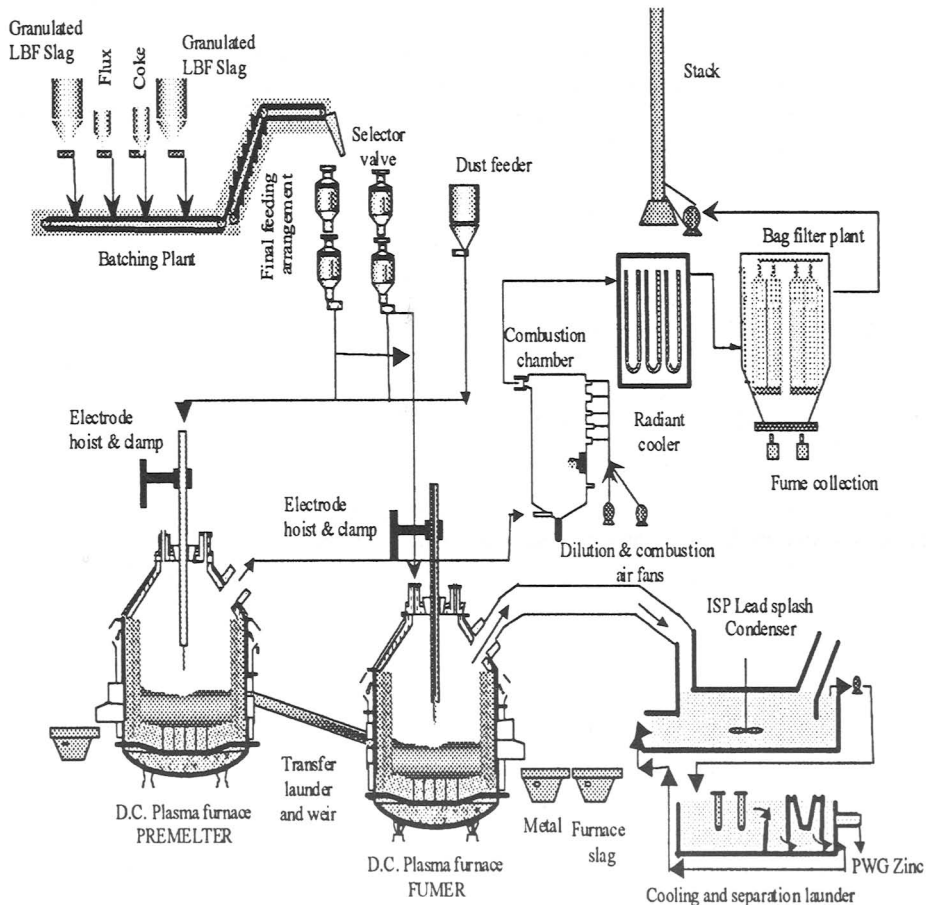
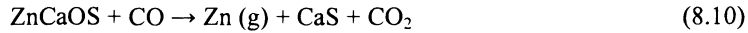


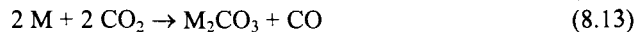
Figure 8.6. Enviropilas process diagram (Abdel-latif., 2002)

Other elements that could influence the overall zinc recovery include chlorine, fluorine, sodium, potassium, arsenic, etc. Their impact is believed to be more pronounced on zinc condensation as compared to its extraction.

A noteworthy feature of the Enviropilas process is its capability to recycle the condenser dross. About 90 % of the volatilized zinc is condensed. The rest reports to the dross together with an almost equal amount of oxidized lead. Generally, lead can be recovered from such material by reduction with coke or coal at 750-1000 °C. Dross generation is typically about 800-1000 kg per ton of zinc produced. The dross produced

contains about 35-45 % zinc oxide, 30-40 % lead oxide, with lesser amounts of ferric oxide, silica, and oxides of calcium, magnesium oxide and aluminum.

A method based on the same principle of reduction of oxide by carbon has been used by Wang and coworkers (1990) for separating zinc and iron from electric furnace dust. Most of the zinc is collected in the condenser. Its cadmium content is low (~ 0.5 %). Most of the iron is recovered in the crucible. It carries about 10% cadmium. An interesting observation is the catalyzing action of sodium or potassium carbonate on the reaction of the metals. It is suggested that the alkali metal carbonate is reduced by carbon to produce carbon monoxide, which then reduces zinc oxide producing zinc metal and carbon dioxide, which then reacts with alkali metal regeneration the alkali carbonate. The cycle of reactions is represented by the following equations:



8.2.1.3.4. Imperial Smelting Process

This process, originally developed for the extraction and refining of zinc and lead from their concentrates is now being applied to recover zinc from EAF dust. The furnace is described in Chapter 6. Zinc oxide is reduced to zinc by carbon in the furnace shaft. The metal is separated through the gas phase, and is therefore almost completely separated from accompanying elements. Both lead and zinc can be recovered. Lead collects all elements that are nobler, such as copper, which can also be recovered from secondary materials. The process has also been applied to recover zinc from zinc-containing batteries. An additional feature of this method is that organic materials like plastics, or impurities like dioxins, which can be found in EAF dusts, are completely decomposed to carbon dioxide and water, at the high temperature (> 2000 °C). (Schwab and Schneider, 2000).

8.2.1.3.5. Upgrading of EAF Dust by Injection into Molten Iron and Steel

The zinc and lead grades of EAF dust can be increased by reinjecting it into the steel furnace. The injection rates are in the range 0.4 to 1.5 kg dust per minute per tonne of steel. Upon injection, the dust is chemically transformed. The zinc content in the generated dust is 4 to 5 times higher than injected EAF dust, ranging from 60 to 80 % from 16 % zinc (Colbert and Irons, 2000). The iron content is lowered to 5 to 15 % compared to 45 % in the EAF dust. The zinc and iron are ejected from the melt as metal vapor, and most of the dust. About 49 % of the zinc injected dissolves in the iron, independent of the carbon content and temperature of the furnace. When no carbon is added to the dust, the carbon content decreases approximately from 0.22 % to 0.17 %. A study of the process by Colbert and Irons (2000) suggests that the probable mechanism is the reduction of zinc oxide by dissolved carbon. If, however, injection is performed with EAF dust plus added carbon, the mechanism for the reduction of zinc oxide is likely through the reduction of zinc oxide by carbon monoxide and the reduction of carbon dioxide by the injected carbon:



Virtually all carbon is consumed by chemical reactions as little carryover to the dust, and the carbon content of the steel does not significantly increase.

8.2.1.3.6. Recycling with CONTOP Technology

The CONTOP smelting cyclone described in Chapter 6 is used for processing EAF dust. A process flow sheet is shown in Figure 8.7.

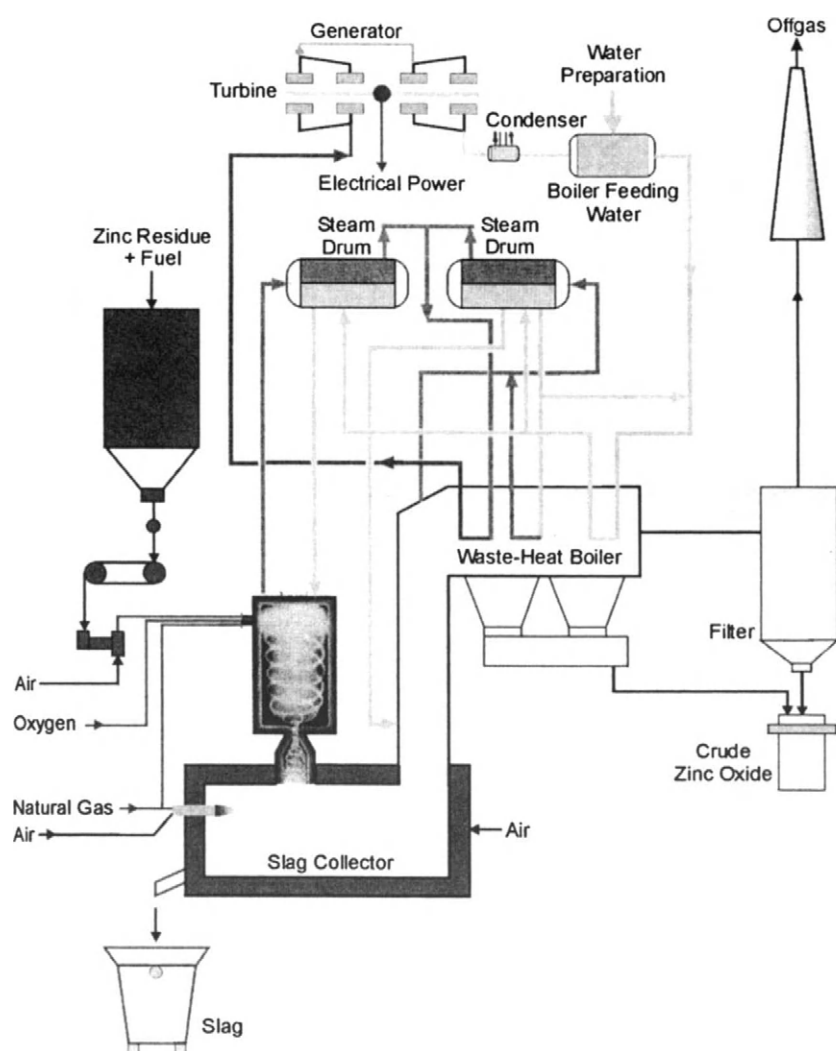


Figure 8.7. Process flow sheet for Processing EAF by CONTOP plant ((Sauert *et al.*, 2000)

The reactor is mounted on a chromium-magnesite-lined hearth of dimensions 6 m long, 3 m wide and roughly 1.9 m height. The settler is equipped with an auxiliary burner mainly required for heating-up after down times. The auxiliary burner is installed in the

side wall of the settler and operates with natural gas and enriched air. The EAF dust (or any furnace dust), coal and molding sand and lime (fluxes) are ground to below 2 mm and dried to <2 % moisture. The mixed feed is drawn from the storage bin by an adjustable rotary lock, and injected into the reactor burners. The slag and gaseous products are separated in the settler. The slag is tapped into two parallel ladles and allowed to cool for 2 to 3 days. During cooling, the matte precipitates at the bottom and is manually separated. The off-gas is cooled very slowly to 1000 to 600 °C. This facilitates the sulfating of zinc and lead oxides, which lowers the sulfur dioxide content of the gas. Off gas temperature is maintained at 120 °C by cooling air. The process leads to the reduction of metal oxides to form a matte consisting of approximately 22 % copper, 25 % iron, 8 % nickel and 20 % sulfur. The matte is sent for further processing in a copper plant. The slag produced meets the environmental requirements and is a useful byproduct for construction of waterways.

As compared to several other pyrometallurgical processes, it is claimed that CONTOP process results in low off-gas volume, the best slag quality, the least ecological harm and optimal energy recovery. The main product is crude zinc oxide (58-60% Zn), which is sold to a zinc processing plant. (Sauert *et al.*, 2000; Sauert, 2002).

The CONTOP smelting cyclone has been integrated with a process to recover and recycle automotive shredder, light fraction. Management of such material is called RESH (Residue Shredder) recovery. The RESH is mechanically treated in a special impact crusher to fit the grain size conditions of the smelting cyclone. It is mixed with fly ash from any residual material such as from a waste incineration plant and blown into a CONTOP smelting cyclone together with oxygen. A copper/iron mixed metal is formed in addition to the slag, which meets the leaching criteria. The reducing atmosphere in the smelting cyclone volatilizes the zinc, lead and cadmium, which can be further processed as metal oxides after post combustion. The waste heat of the smelting cyclone and of the boiler is derived as saturated steam. The saturated steam can be either used directly in other process or it is superheated and converted to electric energy turbine. The exhaust gas is cleaned in an exhaust gas cleaning process. The process is schematically described in Figure 8.8. It enables about 90% each of copper, iron and zinc recovery to be achieved.

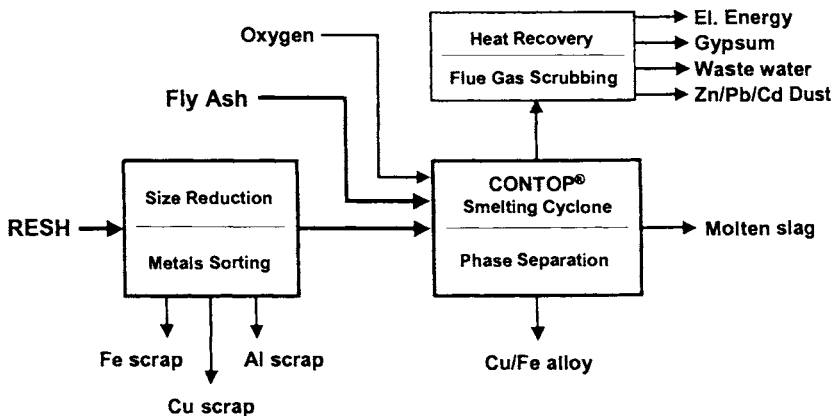


Figure 8.8. Functional diagram of shredder recycling (RESHMENT) process (Sauert, 2002)

8.2.1.3.7. EAF Dust Treatment by INMETCO Process.

In the INMETCO process (see Chapter 6) the wastes are blended with coke or coal in a screw conveyor. The mixture proceeds to a green pelletizer to produce pellets strong enough to resist disintegration in the subsequent thermal operation. In the second step, metal oxides are reduced in a rotary hearth furnace. Some of the carbon in the pellets reacts with oxygen in the waste to produce metal. A portion of the zinc, lead and halogens contained in the dust are exhausted into the off gas treatment system. The third major operation is done in a submerged electric arc furnace, where hot metallic sintered pellets are transferred in sealed containers. The pellet is melted and chromium oxides are reduced by the residual carbon in the pellet. Lime, silica, alumina and magnesia separate to form a liquid slag. Metal and slag are tapped from the furnace. The metal is cast into pigs and sent to the steel mills. The slag can be used in road building applications.

8.2.1.4. Hydrometallurgical Processes

The major impetus for the development of hydrometallurgical processes for the treatment of EAF dust is that a small scale, on-site process could be economic, because of its low capital and operating costs as well as the potential for the recovery of some valuable metal-containing products. There may also be some environmental benefits. While today's industrial EAF dust treatment processes are predominantly pyrometallurgical, they are gradually being replaced by hydrometallurgical processes..

8.2.1.4.1. Other Industrial Processes

EZINEX Process. In this process, the EAF dust is leached in ammonium chloride solution to solubilize the zinc, lead and cadmium oxides (Olper, 1993). Leach solution is filtered and treated with zinc powder to cement the lead and cadmium which can be sold. Zinc is recovered by electrowinning from the purified solution in the EZINEX process. the spent electrolyte is recycled to leaching. The iron-rich, zinc ferrite containing leach residue is dried, pelletized with coal, and recycled to the EAF. A mixed sodium and potassium chloride salt is recovered and can be sold as a flux. No other by-products requiring disposal are produced. Details are described in Section 8.2.1.4.3.

Modified Zincex Process. This was developed from the original Zincex process described in Chapter 7 (see Section 7.6.2). It consists of leaching, solvent extraction and electrowinning, to produce 99.99 % purity zinc cathodes or zinc ingots (Diaz and Martin, 1994; Diaz *et al.*, 1995). The zinc and cadmium oxides are dissolved in a dilute sulfuric acid solution under atmospheric pressure. The leached liquor is purified by precipitation to remove aluminum and iron prior to introducing it to the solvent extraction step. Zinc is extracted selectively from the pregnant liquor by a liquid cationic exchanger consisting of D₂EHPA complexing agent (see Chapter 3 for the chemistry of complexing agents; Section 3.1 and 3.2 for the chemistry of ion exchange and solvent extraction processes). Impurities including cadmium, chloride, fluoride and magnesium remain in the aqueous phase. A small fraction of this aqueous phase is bled-off to remove the impurities, while most of the aqueous solution is recycled back to the leaching step. Stripping of the zinc from the organic phase back to the aqueous phase is done by increasing the acidity of the zinc spent electrolyte. A loaded high purity electrolyte and an organic raffinate are produced. The raffinate is returned back to the previous extraction step. In the last step, zinc is electrowon with aluminum cathodes from the loaded electrolyte. Some results

from the pilot plant test are summarized in Table 8.13. The process is schematically shown in Figure 8.9.

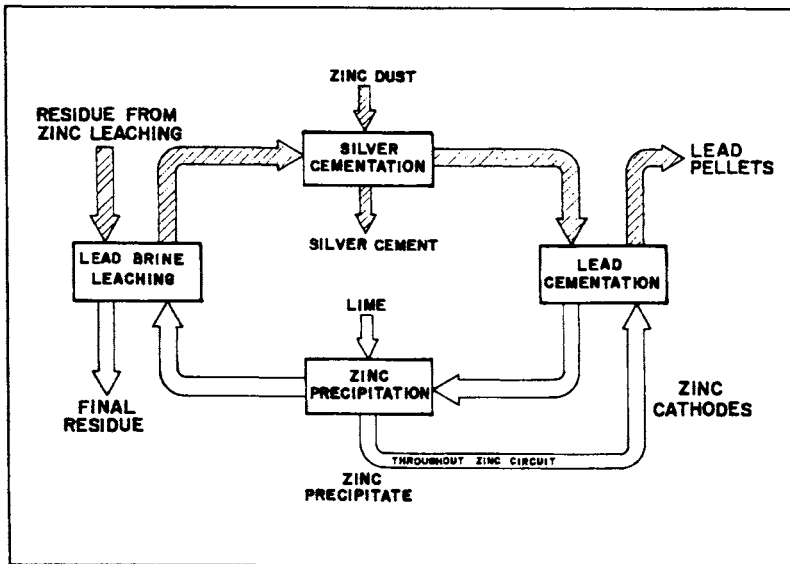


Figure 8.9. Zinc Recovery by Modified Zincex Process (Diaz *et al.*, 1995)

Table 8.13. Composition of Zinc Secondaries Used in Pilot Plant Tests and Zinc Recovery by Modified Zincex Process (Nogueira *et al.*, 1985)

Element/Compound	Waelz oxide	Galvanizing ashes	EAF Dust (Irish)
Zn	53.9	64.6	36.7
Fe	4.3	0.5	12.3
Cd	0.36	0.01	0.11
Cu	0.41	0.08	0.26
Al	0.16	1.5	0.29
Pb	7.8	1.0	8.1
Silica	1.2	0.9	2.2
Cl	4.3	8.2	9.2
Ag	-	-	-
Zinc Recovery, %	96	97	891

In addition to zinc, other metals such as silver, lead and copper can also be recovered by integrating another leach unit. The silver and lead in the EAF dust are recovered by hot brine leaching of the thickened pulp of zinc leaching residue. Leaching efficiencies greater than 92 % are obtained at 80 °C, leading to an overall silver and lead recovery greater than 90 %, even with low (6 %) lead content in the raw feed. A flocculant is mixed with the leach slurry to facilitate the solid/liquid separation. The underflow from the thickener is fed to a belt filter for final separation. The pregnant brine leach solution is treated with zinc powder (cementation) in a stirred vessel, followed by a filter press to

recover silver. The lead-containing filtrate is fed to a second cementation unit and treated with zinc cathodes from the zinc electrowinning section. The lead thus displaced is dried in inert atmosphere and melted, which produces 99.97 % lead ingots. Zinc dissolved during both cementations is precipitated by lime and recycled to the zinc recovery section. The spent brine is also recycled to the lead leaching step. The process is schematically represented in Figure 8.10.

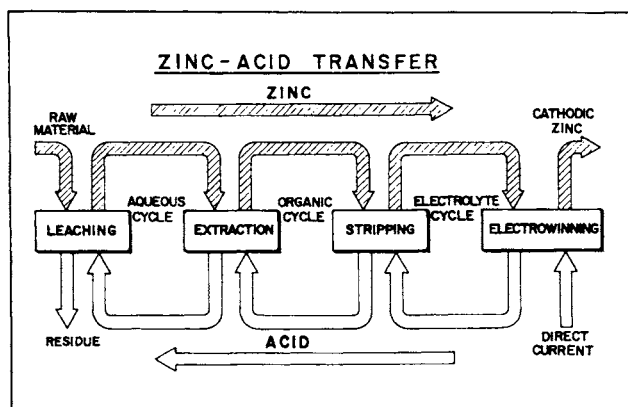


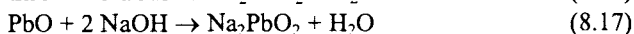
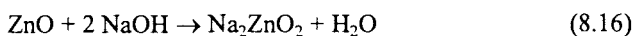
Figure 8.10. Recovery of silver and lead in the Modified Zincex process (Diaz *et al.*, 1995)

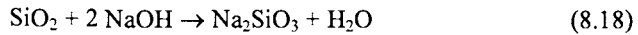
The yield of zinc depends on the amount of zinc ferrite in the EAF dust; higher proportion of ferrite leads to lower yield. The iron residue contains most of the lead of the original dust, and has to be further treated. The gypsum produced in the purification process, in most cases is a waste, and requires careful treatment before release into the environment.

Cashman Process. Originally developed for the treatment of arsenic-bearing ores, this method has been adapted for the treatment of EAF dust (Zunkel, 1996). The process, also known as Artech/Cashman process has been applied to copper smelter dust in Anaconda (Litz, 1991). It is a pressure leach process. Zinc, which is not in the zinc ferrite, along with lead and cadmium in the EAF dust are pressure leached with sulfuric acid in saturated calcium chloride solution. Arsenic is precipitated as scorodite (ferric arsenate), while the other metal oxides dissolve. The residues pass the TCLP test (Chapter 2). Lead, bismuth and silver are first removed, by hydrolysis and are recycled in a lead smelter. Copper is separated by solvent extraction and recovered by electrowinning. Cadmium and mercury are recovered by precipitation with zinc dust (cementation). The cemented lead and cadmium mixture is separated and treated to produce metallic lead and cadmium, using conventional procedures. The zinc in the solution is recovered as a zinc hydroxide/oxide product by hydrolysis.

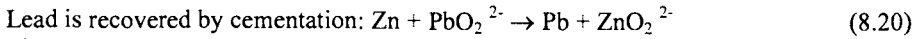
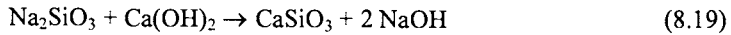
Another example of treatment of smelter flue dusts has been described by Kunter and Bedal (1991).

Caustic Leach Process. The oxides of zinc and lead and silica are leached in caustic soda to produce soluble zincate, plumbate and silicate:





The silicate is precipitated by lime:



Zinc is recovered by electrolysis:

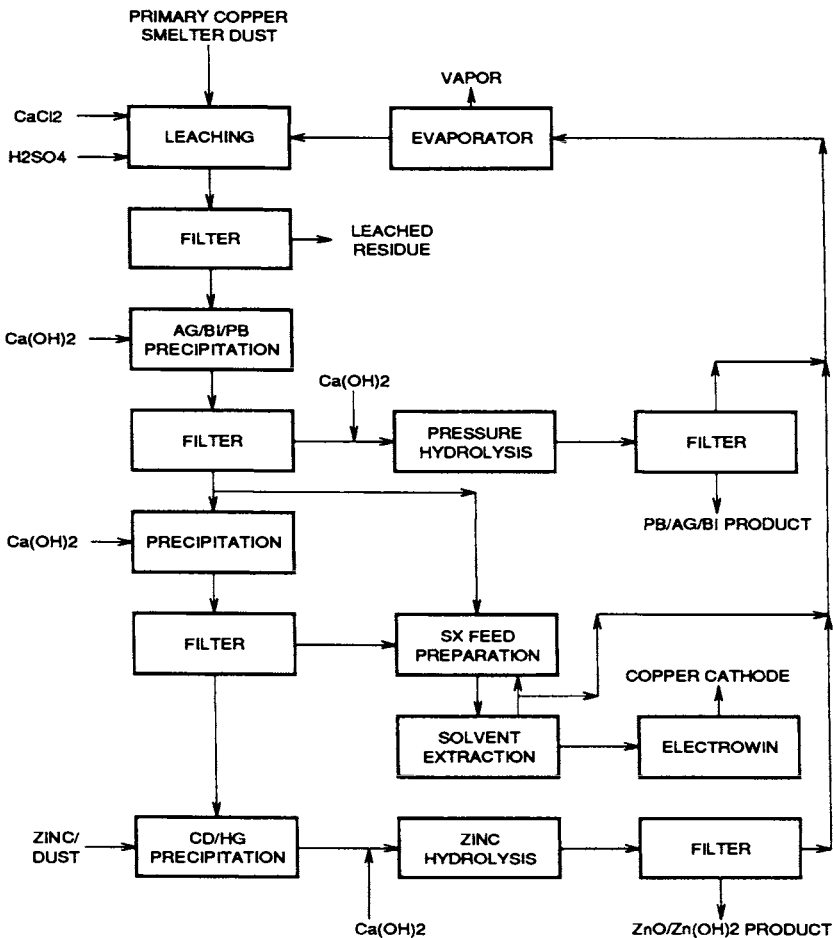
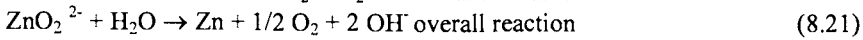
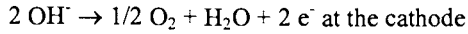
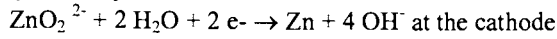


Figure 8.11. Artech/Cashman process (Litz, 1991)

Examples of the caustic leach process have been described by Frenay *et al.* (1986), Guetskens (1990) and Wheatley (1990).

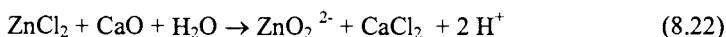
8.2.1.4.2. Other Hydrometallurgical Processes

Sulfuric Acid Leach Process. Leaching of zinc in sulfuric acid would be a relatively inexpensive process to recover zinc as sulfate. Up to 90 % zinc could be extracted at pH 2 and 80 % at pH 3 to 4. But the selectivity is not satisfactory as a good portion of iron also gets leached (Pearson, 1981). A method to convert dissolved iron to hematite (ferric oxide) at higher temperature in an autoclave has been reported (Ohtsuka *et al.*, 1978). The ferrous sulfate gets hydrolyzed forming ferrous oxide, which is oxidized to ferric oxide (hematite) by atmospheric oxygen at higher temperature. (Ohtsuka *et al.*, 1978).

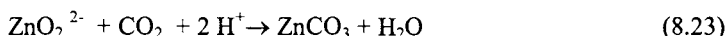
Sulfuric acid leaching is best suited for the type of EAF dust with low iron content. In the fumes produced from pyrometallurgically treated EAF dust iron content is reduced to about 5 % ferric oxide as most iron and lead were removed by this treatment. Lupi and coworkers (1996) have obtained high zinc recovery by leaching such a material in 1.5 M sulfuric acid. The remaining iron and lead, which are also leached, are separated by selective precipitation as hydroxides. The leach liquor containing zinc sulfate is sent to recover zinc metal by electrowinning.

The UBC-Chaparral Process. The process is schematically described in Figure 8.12. It has been applied to recover zinc from dust consisting of zinc oxide, carbonate and ferrite (ZnFe_2O_4); lead and cadmium also as corresponding compounds, and sodium, potassium and calcium chlorides. The process comprises five steps: (1) selective removal of chlorides by water washing with lime; (2) selective removal of calcium in an acetate lixiviant; (3) selective leaching of zinc in an ammoniacal solution; (4) cleaning up solids to render dust non-toxic; and (5) precipitation of final products in high purity.

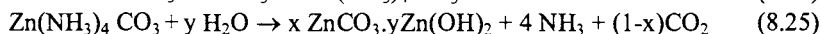
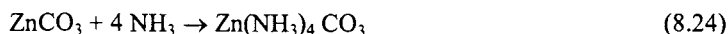
In the first stage, alkali metal and calcium chlorides dissolve in water, while zinc and lead form hydroxides with lime, which then dissolve to produce zincate and plumbate:



The zincate, plumbate are further treated with carbon dioxide to produce the respective carbonates;

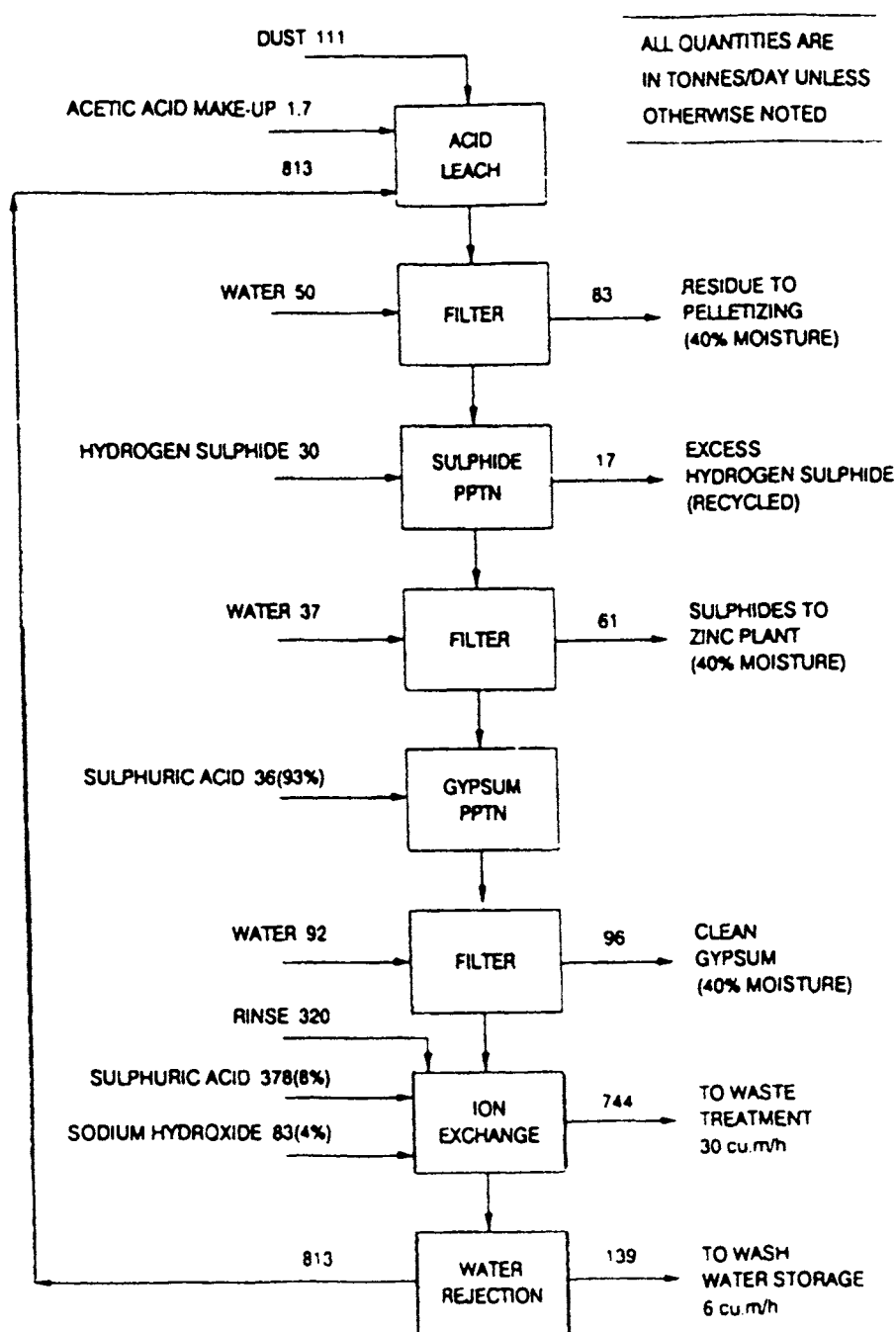


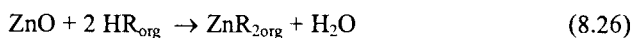
The calcium is also precipitated as carbonate. It is solubilized by treating with 3 M acetic acid, which selectively dissolves calcium carbonate forming acetate while lead and zinc carbonates are not leached. The lead and zinc acetates are treated with ammonia and carbon dioxide, which selectively leach zinc to form zinc ammonium hydroxide. The zinc is then precipitated as basic carbonate by hydrolysis in steam at pH 4.1:



For further purification, the zinc precipitate is dissolved and the lead and cadmium present in the solution are separated by cementation with zinc dust.

The process comprises many steps of processing and separation. Metal recoveries are of the order 60 % Zn and Pb, 85 % Cd.

Figure 8.13. Schematic representation of Acetic Acid Leach Process (Barrett *et al.*, 1992)



where HR represents the extractant or leaching agent and org is the organic phase. The versatic acid is a mixture of tertiary monocarboxylic acids with the simplified formula, $\text{R}_1\text{R}_2\text{C}_2\text{H}_3\text{COOH}$, where R_1 and R_2 are alkyls with 3 or 4 carbon atoms. In leaching applications, versatic acid is dissolved to 30 percent by volume in a paraffinic compound such as kerosene.

Table 8.14. Summary of Metal Extraction during Acid Leaching of Water-Leached Dust (Barrett *et al.*, 1992)

Element	Concentration in head liquor (g/l)	Extraction (%)	Element	Concentration in head liquor (g/l)	Extraction (%)
Zn	14.4	99.96	Fe	3.06	99.47
Pb	1.88	99.85	Cd	0.1	99.90
Cu	0.135	99.69	Mn	0.49	22.35
Mg	3.04	16.70	Ca	16.5	15.35
Ca	15.6	15.35	Al	0.102	27.28
SiO_2	0.369	63.31			

Table 8.15. Summary of Metal Extractions by Precipitation with Hydrogen Sulfide (Barrett *et al.*, 1992).

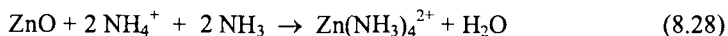
Leaching Reagent	L/S Ratio	Temp. K/°C	Time min.	% Leached				
				Zn	Cu	Fe	Pb	Cd
NaOH 5M	10	298 / 25	120	32.2	0.5	0.02	23.6	3.3
			240	41.6	1.0	0.02	49.1	5.6
NaOH 5M	20	298 / 25	120	47.7	1.0	0.05	29.3	8.9
			240	50.0	7.1	0.08	6.4	13.3
	10	298 / 25	120	32.2	0.48	0.02	23.6	3.3
			240	41.6	1.0	0.02	49.1	5.6
		323 / 50	120	52.5	1.9	0.04	39.6	8.9
			240	58.8	1.4	N. A	51.1	6.7
	373 / 100		120	58.8	1.4	N. A	51.1	6.7
			240	54.6	3.3	N. A	65.0	8.9

Zinc is recovered from the organic phase by stripping with sulfuric acid. This reaction generates leachant, which is returned to the previous leaching step. Zinc is recovered by electrolysis. The leach residue contains most of the lead present in the dust and also the zinc, which was present as ferrite. The residue needs no further treatment.

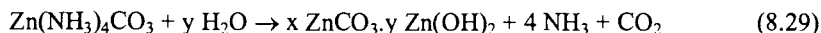
The Chloride Leach Process. In this process dilute hydrochloric acid is used as leachant (Duyvesteyn and Jha, 1986a). Leaching occurs at pH below 1. By increasing the pH to 2-4, dissolved iron and lead are precipitated. Zinc is recovered from the solution by solvent extraction, using alkylphosphoric acid or alkylphosphonic acid as extractants for zinc. (See, Chapter 4 for the formulae of the complexing agents). Zinc is recovered from the extract by electrolysis. The process produces cathode zinc, but the residue needs further treatment for detoxification. The precipitated oxides have to be washed in brine to eliminate any co-precipitated lead chloride.

The Chloride-Sulfate Process. In this process the dust is leached with hydrochloric and sulfuric acids at pH between 1 and 4 (Duyvesteyn and Jha, 1986b). The residue from the first leaching step is leached again using sodium hydroxide as leachant. Dissolved iron and aluminum are removed by precipitation at elevated pH. Zinc is separated from the pregnant solution by solvent extraction using phosphoric and phosphonic acids and zinc is then electrowon. The residue has to be detoxified to remove lead and cadmium before being discharged.

The Ammonium Carbonate Process. The dust is leached with ammonium hydroxide and carbon dioxide (Peters, 1978). Carbon dioxide neutralizes part of ammonia producing ammonium carbonate, which produces ammonium ions. The reaction is as follows:



The zinc is recovered as zinc ammonium carbonate in the purified solution:



Impurities such as lead, cadmium and copper are separated by cementation with zinc powder. The final residue contains zinc ferrite and lead, and needs to be treated.

The principle has been used for developing a process for the recoveries of metals from secondary smelter dusts; see Section 8.2.2.

Leaching EAF Dust in Various Media. Leachability of EAF dust in different leaching reagents has been studied by Caravaca and coworkers (1994). As seen from the results presented in Tables 8.16-8.18, the recovery of zinc is enhanced in acidic media compared to that obtained in alkaline media. However, a relatively clean and iron-free leach solution can be achieved by alkaline leaching as iron is not leached in alkaline medium, thus eliminating the complicated iron removal step. Zinc recovery is generally low except when very concentrated acid is used, which can leach the ferrite constituent of the EAF dust.

Table 8.16. Leaching of EAF Dust in Sodium Hydroxide Solutions (Caravaca *et al.*, 1994)

Leaching Reagent	L/S Ratio	Temp. K/°C	Time min.	% Leached				
				Zn	Cu	Fe	Pb	Cd
NaOH 5M	10	298 / 25	120	32.2	0.5	0.02	23.6	3.3
			240	41.6	1.0	0.02	49.1	5.6
NaOH 5M	10	298 / 25	120	47.7	1.0	0.05	29.3	8.9
			120	32.2	0.48	0.02	23.6	3.3
		298 / 25	240	41.6	1.0	0.02	49.1	5.6
			120	52.5	1.9	0.04	39.6	8.9
		323 / 50	240	50.0	7.1	0.08	6.4	13.3
			120	58.8	1.4	N. A	51.1	6.7
		373 / 100	120	58.8	1.4	N. A	51.1	6.7
			240	54.6	3.3	N. A	65.0	8.9

Microwave-Assisted Leaching of EAF Dust. A laboratory study on microwave-assisted leaching of EAF dust in sodium hydroxide has been described by Xia and Pickles (1998). The process is schematically shown in Figure 8.14. The reactor for leaching is

Table 8.17. Leaching of EAF Dust in Acidic Reagents (Caravaca *et al.*, 1994)

Leaching Reagent	L/S Ratio	Time min.	% Leached					Note
			Zn	Cu	Fe	Pb	Cd	
H ₂ SO ₄ 5M	10	120	71.7	66.7	14.9	----	88.9	In all cases initial Temperature was 25°C, but the reaction is exothermic and increases the temperature until 60°C - 70°C. The systems were allowed to evolve freely.
		240	71.7	66.7	25.0	----	91.9	
	20	120	79.4	71.4	15.7	----	95.6	
		240	80.4	71.4	15.7	----	97.8	
HCl 5M	10	120	74.4	80.9	41.5	42.2	95.6	
		240	76.3	83.3	41.5	42.2	95.6	
	20	120	94.8	95.2	31.5	100	100	
		240	97.6	95.4	27.0	100	100	
HNO ₃ 5M	10	120	70.6	69.1	14.5	100	100	
		240	71.6	71.4	30.0	100	94.4	
	20	120	71.1	76.2	11.3	100	96.6	
		240	71.1	76.2	11.3	100	95.6	

Table 8.18. Leaching of EAF Dust with Complexing Agents (Caravaca *et al.*, 1994)

Leaching Reagent	L/S Ratio	Time min.	% Leached				
			Zn	Cu	Fe	Pb	Cd
(NH ₄) ₂ CO ₃ 2M	10	120	44.9	38.1	0.3	17.8	44.4
		240	45.5	40.5	0.3	15.6	44.4
	20	120	47.4	43.8	0.5	32.0	51.1
		240	48.5	44.3	0.5	28.9	48.9
NH ₄ Cl 5M	10	120	34.5	35.7	----	48.2	71.1
		240	38.7	38.1	----	48.2	71.1
	20	120	43.3	40.9	----	74.4	80.0
		240	43.3	40.9	----	74.4	80.0
NH ₄ OH 5M	10	120	15.3	22.6	----	0.13	48.9
		240	17.9	26.2	----	0.27	50.0
	20	120	16.5	23.8	----	0.6	46.7
		240	21.7	29.6	----	0.6	51.1
(NH ₄) ₂ SO ₄ 4M	10	120	30.4	38.1	---	0.2	65.6
		240	30.4	38.1	---	0.2	62.2
	20	120	28.9	38.1	---	0.36	62.2
		240	34.4	38.1	---	0.36	62.2

constructed of teflon and with a diameter of 64 mm and a height of 64 mm. The leached solution is separated using a conventional vacuum system,

Some of the results obtained with 70 g/L solids in 10 M NaOH at 93 °C for 180 minutes leach time, are summarized in Figure 8.15 and Table 8.19. Under conventional conditions, the zinc recovery reaches a plateau in about 180 minutes with a maximum zinc recovery of about 72 %. In microwave leaching, the zinc recovery reaches a plateau within a few minutes, indicating a very fast dissolution rate, with a zinc recovery of nearly 80 %. The fast leaching rate with microwave treatment is thought to be due to one or more of the following factors: superheating, favorable interactions of microwaves with EAF dust solids, and the violent boiling of the leach solution.

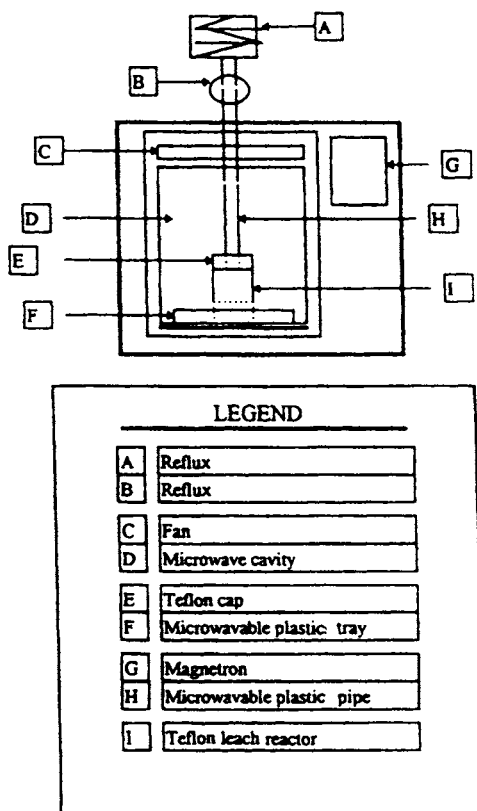


Figure 8.14. Schematic diagram of microwave leaching apparatus (Xia and Pickles, 1998)

The analysis of the leaching of other elements such as cadmium, chromium and iron has shown that dissolution rate of cadmium increases with increasing sodium hydroxide concentration and leaching time. Cadmium dissolves faster and more completely than zinc and lead, which implies that it may be present in phases which are more readily soluble in caustic solutions than those phases which contain zinc and lead. Cadmium may not be present as a substitute for zinc in zinc ferrite. Chromium is generally difficult to dissolve, thus it may be present mostly as a ferrite.

Leach slurry is filtered and the unleached iron oxide, containing zinc ferrite, is filtered, washed and recycled to the steel mill or stockpiled. Leach solution is treated with zinc dust to precipitate the dissolved lead and cadmium as cement, which is further separated into metallic lead and cadmium which can be sold. Clean solution passes to a crystallizer where high purity zinc oxide crystals are produced for sale. The ammonium chloride solution is concentrated and recycled to the leach process.

Roasting and Leaching Process. Research aimed at breaking down the zinc ferrite in the dust has been reported. The roast conditions are as follows: 10 % coke, 1223 K (950 °C), 2 hours reaction time in a carbon monoxide atmosphere. After roasting, about 83 % zinc and over 90 % chloride, sodium and potassium can be extracted in the caustic

leaching process, but the extraction of lead is zero. The zero lead recovery suggests that lead oxide under such roast conditions is readily reduced to metallic lead, which is insoluble in the caustic leach process. (Degliomni, 1983; progress report cited in Xia and Pickles, 1998).

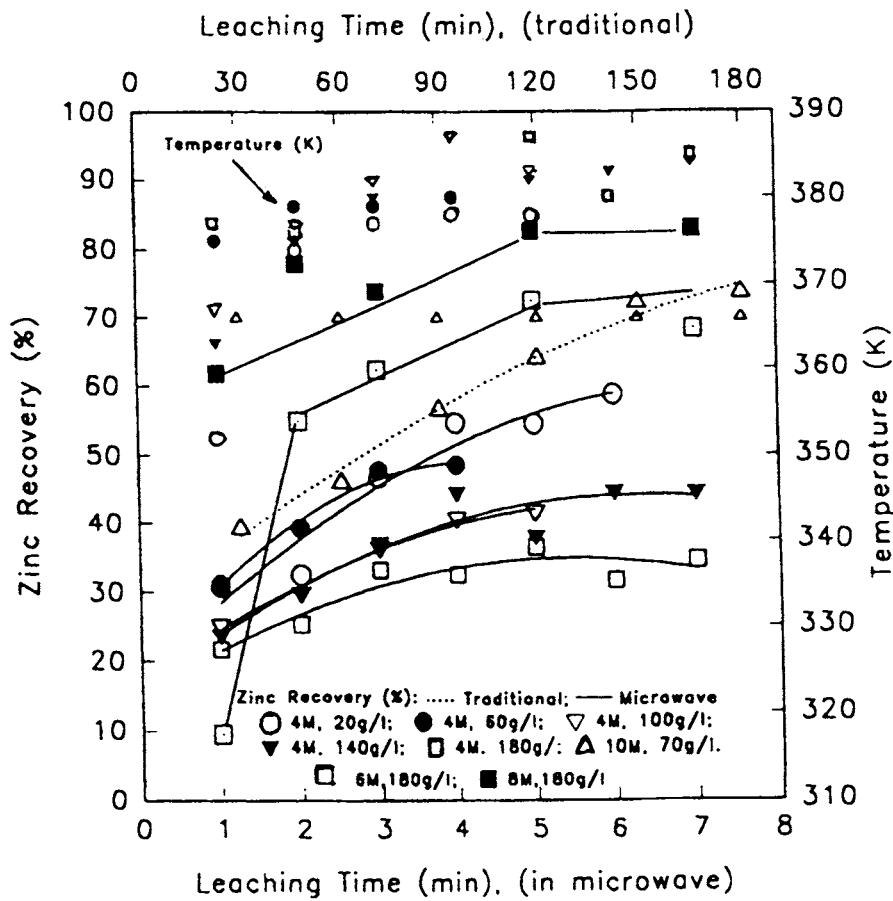
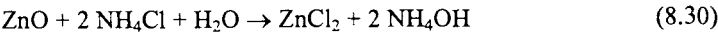


Figure 8.15. Comparison of conventional and microwave alkaline leaching of EAF dust (Xia and Pickles, 1998)

Table 8.19. Chemical Composition of Water Washed and Dried EAF Dust (Xia and Pickles, 1998)

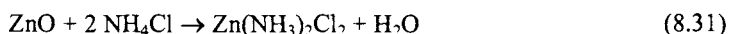
Element	Zn	Pb	Fe	Cd	Cr
Percent	24.9	2.3	12.8	0.3	0.1

MRT Process. In this process, dust is leached with hot ammonium chloride to dissolve most of the zinc, lead and cadmium oxides by the following reaction:

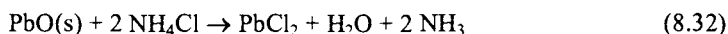


8.2.1.4.3. Ammonium Chloride Leaching Process

Concentrated ammonium chloride solutions react with metal oxides by a mechanism, which depends principally on the formation of complexes of chloride and amines with metals. Zinc oxide is leached in ammonium chloride forming zinc ammine chloride:



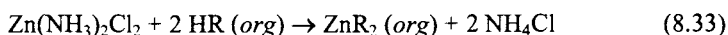
Similar reactions occur with cupric and cadmium oxides, while lead oxide is solubilized because of the high affinity of lead for chloride:



These reactions form the basis for recovering metals from brass foundry dusts and EAF dust (Ducati *et al.*, 1998). The leaching is done at pH 6-7 in a 200 g/L ammonium chloride solution at 60-80 °C.

The recovery of copper from leach solution may be done by cementation with zinc metal dust for low copper concentration. For higher copper concentration, metal recovery is done by solvent extraction with LIX 54, which is a β -diketone chelating extractant. (See Chapter 3 for the chemistry of LIX reagents). This reagent is selective towards copper.

The purified zinc solution containing mainly ammonium chloride and zinc chloride ammine complexes is sent to another solvent extraction process with a cationic extractant to produce a concentrated solution of zinc sulfate and, at the same time, regenerate ammonium chloride. The media exchange reaction is represented by



where HR represents the organic acid and ZnR_2 the extracted organic salt. Various industrial reagents have been used as solvent extractants. Mono (2-ethyl hexyl)-2-ethyl hexyl phosphonic acid and neodecanoic acid have been found most efficient (Ducati *et al.*, (1998). Zinc sulfate is recovered from the zinc extractant compound by stripping with sulfuric acid.

When the leach solution carries manganese (as sulfate), it is reduced to manganese dioxide by treatment with potassium permanganate and separated:



The flow sheet to treat brass foundry dust and EAF dust by this process is shown in Figure 8.16.

The process is also applicable to many other types of zinc oxide containing residues like Waelz kiln oxides and plasma smelting oxide.

The ammonium chloride leaching process is the basis for the development of an industrial process, EZINEX ("Engitec Zinc Extraction") process, to extract zinc from EAF dust (Olper, 1995b; Olper and Maccagni; 2000). The leach liquor is freed of other dissolved metals (copper, lead, cadmium, nickel and silver) by dosing metallic zinc powder, which reduces the metals more noble than zinc by cementation type reaction. ($\text{Zn} + \text{Me}^{2+} \rightarrow \text{Zn}^{2+} + \text{Me}$; see Chapter 4 for details)

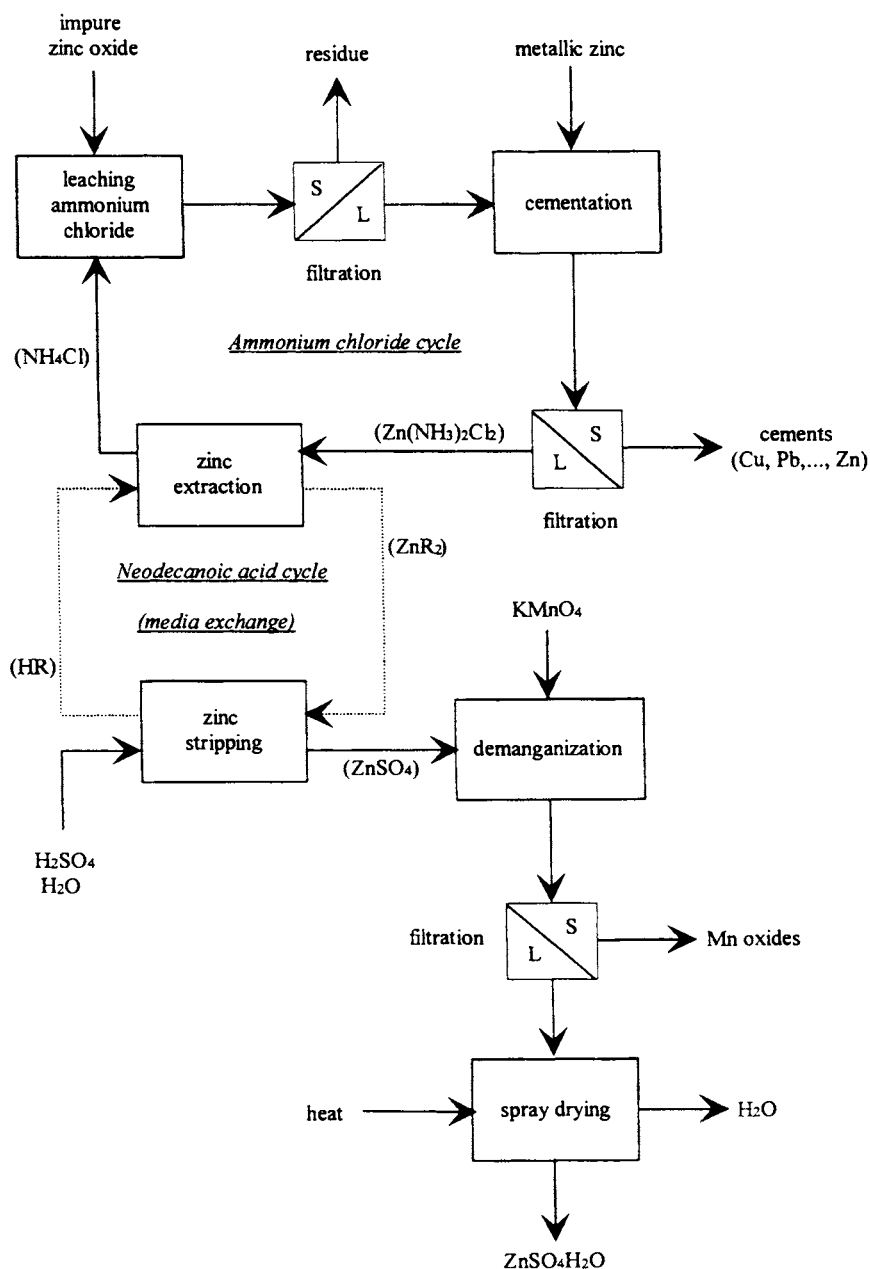
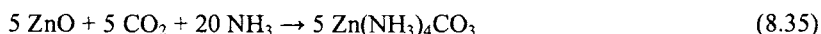


Figure 8.16. Flow sheet of the process for recovering copper and zinc by ammonium chloride leaching process (Ducați *et al.*, 1998)

Zinc is recovered by electrolysis in a cell with titanium cathodes and graphite anodes.

8.2.1.4.4. Ammonia-Ammonium Carbonate (AAC) Leaching Process

When zinc oxide is leached in ammonium carbonate, it is solubilized producing zinc ammonium carbonate in solution. In place of ammonium carbonate stoichiometric combination of ammonia and carbon dioxide may be used, leading to the reaction:



Zinc oxide is produced by calcining the zinc ammonium carbonate complex. At high temperature the compound is decomposed with carbon dioxide and ammonia released in the gaseous phase, basically reversal of the chemical process of Equation 8.28.

Other metals occurring in the residues, copper, nickel, cadmium, cobalt, manganese and ferrous iron also produce soluble amines. (Ferric iron precipitates as insoluble ferric hydroxide). These metal amines are reduced to the metallic form and rendered insoluble at the right redox potential by metallic zinc.

This is called AAC process and has been applied to recover zinc oxide from different kinds of metallurgical residues including those occurring in automobile scrap recycling (Prado *et al.*, 1985), zinc ashes and drosses and furnace dust (Prado, 1990).

8.2.1.4.5. INTECT (Integrated, Cost Effective, Clean Treatment) Process

Recently described by an international team (Kanari *et al.*, 2002), this is also essentially a hydrometallurgical process, but with a few additional interesting features. Before leaching the EAF goes through a step of electrodialysis, which enables to hydrochloric acid and alkali metal hydroxides from the alkali metal chlorides in the EAF dust.

Electrodialysis is a membrane separation process used in wastewater treatment; details are described in Chapter 11. The zinc oxide is then leached in hydrochloric acid. The zinc ferrite fraction is not leached. It is pelletized and recycled. To the liquid fraction zinc dust is added to displace lead, cadmium and other metals by cementation reaction. Zinc is then precipitated as basic zinc carbonate by sodium carbonate. This is thermally decomposed to produce high purity zinc oxide. The process is illustrated in Figure 8.17.

8.2.1.5. Physical Separation Methods

Some flue dust fines are found to contain metallic phases, principally nickel and metal droplets consisting of iron, chromium and nickel (Geldenhuis (2002)). As the densities of pure nickel and metal droplets are approximately 8.9 and 7.9 g/cm³, respectively, compared to that of oxides, which is less than 5 g/cm³, the metallic particles could be separated from the oxides by gravity separation. An alternative route is to take advantage of the magnetic properties of nickel to recover it by magnetic separation. Such an approach has been investigated on flu dust fines by Geldenhuis (2002).

Gravity separation was conducted on a shaking table in a ratio of approximately 100 L water to 1 kg dust. A substantial increase in the nickel grade is obtained, from 1.66% Ni in the feed to 7.06% in the stream of concentrate 1, with a nickel recovery of 39.9%. The nickel grades of the concentrate 2, middling and tailing streams are 1.41 %, 0.94% and 0.93% respectively.

Magnetic separation was done with a wet low intensity magnetic separator (LIMS) drum. The dust and water were simultaneously fed to the magnetic separator drum in a ratio, dust to water of approximately 5 L water to 1 kg fines. At a field strength of 600 G

50.6% nickel is recovered with a grade of 8.3% Ni, considered to be acceptable. (For a description of shaking table, and magnetic separators, see Chapter 3).

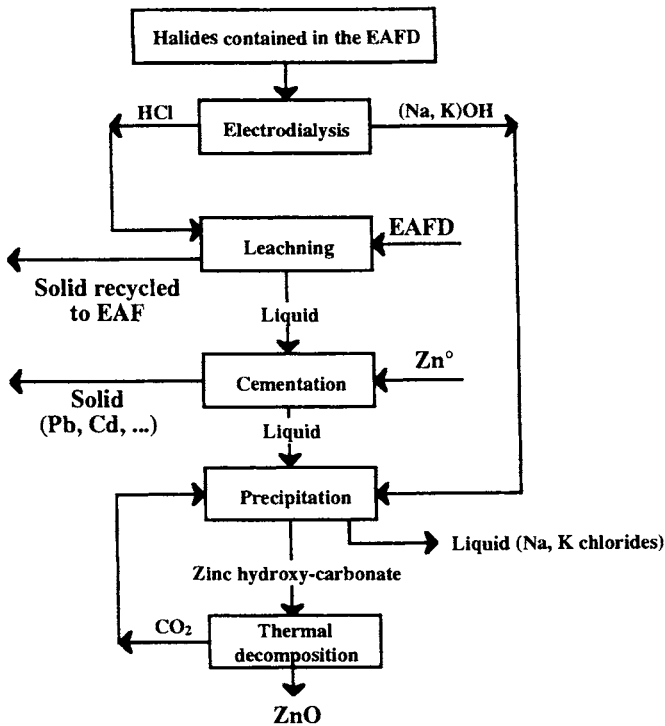


Figure 8.17. Schematic representation of EAF dust treatment by INTECT process (Kanari *et al.*, 2002)

8.2.1.6. Direct Reduction of EAF Dust to Produce Steel

A patented process to convert iron bearing metallurgical wastes, for example, EAF dust, into steel products has been described by Kotraba and Bottinelli (1994). It is based on the reduction of the metallic oxides in the dust by a solid carbon reductant. Pulverized coal is used as a carbon source and is intimately mixed with the EAF dust prior to agglomeration as pellets. The reactions occur within the pellets leading to the formation of iron, zinc, lead and cadmium. The zinc, lead and cadmium vapors are condensed in a splash condenser and the residue, mainly iron, is sent for pelletization. The flowsheet is shown in Figure 8.18.

8.2.1.7. PRIMUS Process of Direct Reduction of EAF Dust

This relatively new process is based on direct reduction of iron oxides to pig iron by coal fines in a multiple hearth furnace and recycling the EAF dust enriched with zinc. Oxide (Hansmann *et al.*, 2002). The basic process flow sheet is shown in Figure 8.19.

The multiple hearth process is the core equipment of the process. The EAF dust or any zinc-bearing metallurgical residues are pelletized and charged on the top-level and coal on one or several lower levels. The furnace temperature is about 1100 °C. The iron

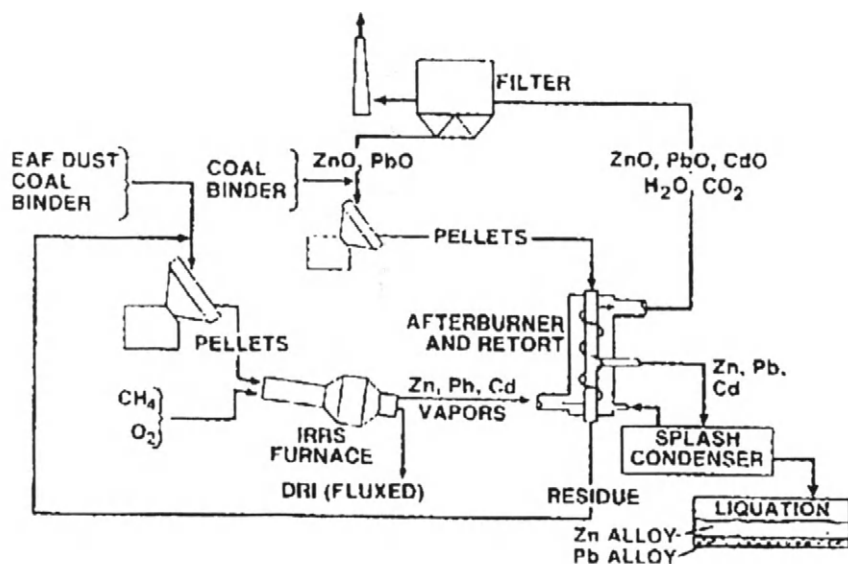


Figure 8.18. Flow diagram of direct reduction of oxides in EAF dust (Kotraba and Bottinelli, 1994)

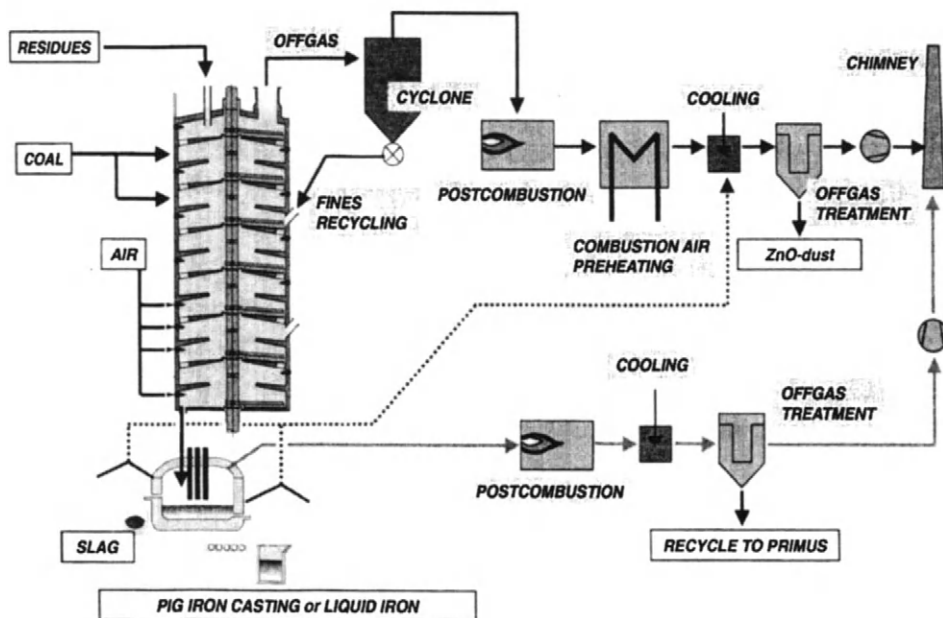


Figure 8.19. Flow sheet for the treatment of EAF dust by PRIMUS process (Hansmann *et al.*, 2002)

produced by the reduction of iron oxides is discharged and directly fed into a melting furnace. The off gases rising at the top pass through a cyclone, which filters out entrained

solid, which is returned to the furnace. The volatile metals (lead, cadmium) evaporate and are conveyed to a second off gas cleaning. After cooling this fraction is separated as dust in a bag house filter. The pig iron produced is tapped into a ladle and transported to a melt shop.

The process has been applied to EAF dust, BF (blast furnace) and BOF (basic oxygen furnace) sludge and other zinc-bearing metallurgical residues. More than 90% of zinc and other volatile metals are removed. The filter dust consists of 60-65% zinc as zinc oxide with 6-9% lead, 2-3% sodium, and potassium and less than 0.5% iron. The pig iron produced is blast furnace quality.

Environmental factors connected with the process have not been fully discussed. In particular, the quantity of zinc and lead in the off gases is of special concern. The gas cleaning unit has to be adapted to meet the environmental requirements.

8.2.1.8. Combined Pyro- and Hydro Metallurgical Process

An industrial method, which combines pyro- and hydrometallurgical steps leading to the production iron and zinc has been described by Cernak and Maselli (2000). In the pyrometallurgical step, the EAF dust is treated with coal fines in a rotary hearth furnace (RHF). The feed material comprising EAF dust, and coal fines is passed through a mixer, briquetter and fed into the RHF. Many constituents of the EAF dust are vaporized and a high quality iron remains in the hearth. This is sold to a steel manufacturer. The zinc oxide is recovered from the off gases by passing through a baghouse filtration system. It is purified by hydrometallurgical step, treating with ammonium chloride (see section 8.2.1.4.3). Other metal contaminants (lead, cadmium, copper, silver) are separated by cementation with zinc dust. The zinc oxide is precipitated by dilution through a series of cascading tanks. The zinc ammonium chloride is hydrolyzed (reversal of the reaction of zinc oxide with ammonium chloride) and high grade (minimum 99.8 %) zinc oxide is produced.

It should be noted, in conclusion, some of the methods described are currently dormant due to unresolved economic and marketing issues., but they are available for further developments. Zunkel (2000) has presented a technology status report of recovering zinc and lead from EAF dust. Liebman (2000) has reviewed the current status of EAF dust recycling in North America.

8.2.1.9. Processing by DC Arc Furnace

Processing of EAF dust by a DC arc furnace has been described by Ye (2000). EAF dust with coke is introduced into the furnace through a hollow electrode and they enter the hot plasma where melting and reduction (of iron) takes place simultaneously. Direct exposure of the dust to the very high temperature of the plasma ensures high recoveries of zinc (> 99 %) and lead (> 99.99 %). Zinc and lead oxides are collected in a gas cleaning system. The product carries only about 1 % iron.

An additional feature of the process described by Ye is that it also includes a step to remove the halogens, which are often present in the EAF dust, originating from metal halides, mostly chloride and fluoride, in the dust. The halide concentration is reduced down to 200 ppm chloride and fluoride. Further reduction can be done by sulfation, that is, reaction with sulfur dioxide and oxygen, whereby halides are converted to sulfate:



Conversion of halides to sulfate is environmentally desirable.

8.2.2. Blast Furnace Dust

The off gases produced in a blast furnace (BF) carry dust containing iron and zinc oxides. Until about 20 years ago, the scrubbing system used sea water for disposal. This has led to serious environmental problems as the accumulated solids elevates the sea bed and has to be dredged to maintain sufficient depth required for navigation and marine life. This led to exploring methods of processing BF dust. In some places, in particular, in the Netherlands (Honin^g *et al.*, 2000), the dust is presently recovered as a dewatered sludge and stored in a controlled storage site with a plastic liner. It is then separated by a hydrocyclone into a zinc-rich and zinc-poor fractions.

BF dust contains enough carbon (40-50%) to reduce the iron content (20-30%) and recover zinc and lead contents at high enough temperature. This has been done by feeding through a hollow electrode from where it passes through plasma or arc of electrode furnace. As the BF sludge contains more than the required amount of carbon to reduce iron, the excess carbon is consumed by adding BOF (basic oxygen furnace) sludge with lime, which is another waste material. A mixture of white powder, mainly calcium oxide, forms on the iron phase. A liquid slag is created by adding sand. Zinc and lead are effectively removed as oxides in the vapor phase.

Another method investigated by Honin^g and coworkers (2000) is based on pyrohydrolysis in a chloride medium, whereby the metals are converted to chlorides, which are then condensed from the gas stream. Zinc and lead are precipitated as hydroxides by superheated steam.

8.2.2.1. Recovery of Zinc and Magnetite by Jarosite (Hydrometallurgical) Process

Blast furnace dust produced in steel-making contains significant percent (10-15) zinc along with iron (often exceeding 50%) and smaller percentages of lead, manganese and copper. Both zinc and iron are recovered as their compounds by hydrometallurgical treatment. In a laboratory study described Jandova and coworkers (2002), steel-making baghouse dust is leached with 3 M sulfuric acid at 80 °C maintaining liquid to solid ratio 10:1. The leach residue is recycled back to a second batch of dust. The filtrate more dust is added and the sulfuric acid concentration maintained by mixing the required amount of concentrated sulfuric acid. The leach extract is treated to produce jarosite. Sodium hydroxide and sodium sulfate are added, pH maintained at 2 and the mixture heated at 95 °C for 5-8 h. Sodium jarosite formed is filtered and converted to magnetite. This is done by mixing sodium or ammonium hydroxide. The following reaction occurs:



(Conversion of jarosite to hematite is also applied for processing iron-containing effluents. It will be described in Chapter 10; see Section 10.3).

The filtrate after the separation of sodium jarosite is processed to recover zinc. Residual iron is precipitated at pH 4. Other metals are removed by cementation by zinc dust at 60 °C. The filtrate is a concentrated solution of zinc sulfate from which the metal is extracted by electrolysis. The flowsheet of the process is shown Figure 8.20.

Zinc may also be extracted by solvent extraction using LIX reagents and recovered by stripping with hydrochloric acid (Zeyabadi *et al.*, 1997).

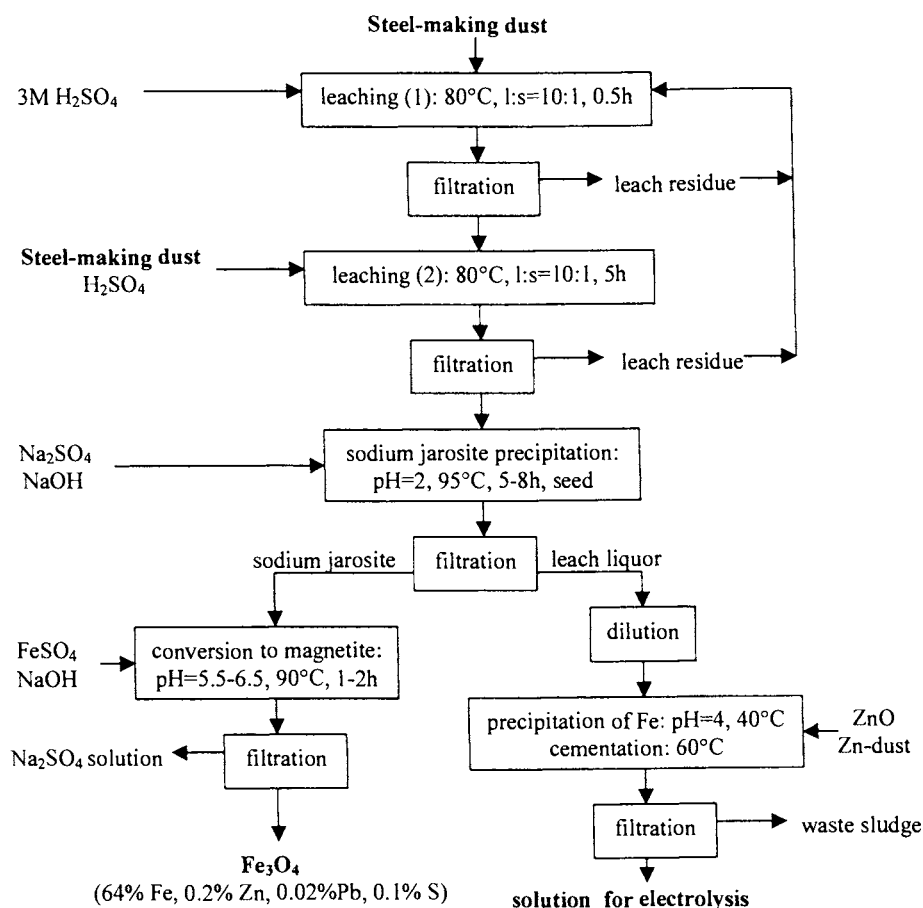


Figure 8.20. Flowsheet of processing steel-making dust (Jandova *et al.*, 2002)

8.2.3. Secondary Smelter Dust

The dust is generated in the secondary smelting operations contain volatilizable components such as zinc, lead, cadmium, tin and alkali chlorides, as well as a variety of entrained particulates (Fe, Cu, Ca, Si, Al). Some of the values, metals like zinc and copper can be recovered and the balance disposed off as an environmentally safe disposable slag.

A hydrometallurgical process, based on the leaching of oxides by ammonia-ammonium carbonate (AAC) aqueous solutions has been used for the extraction and recovery of zinc, copper and cadmium (Prado and Prado, 1995). By this reagent, the metals, which form ammonia complexes are solubilized. They include copper, zinc and cadmium. When ammonia is stripped from the leaching liquor, these metals are rendered insoluble and precipitate as carbonates or basic carbonates. Lead carbonate is dissolved by ammonium acetate at 80 °C forming lead acetate.

A 2-stage process has been developed by Prado and Prado (1995). In the first stage, AAC leach removes and recovers zinc, copper, and cadmium, as basic carbonate (basic zinc carbonate, BZC) or zinc oxide, and a cement containing copper and cadmium. The residue is a lead (or lead-tin) concentrate. In the second stage lead is dissolved in ammonium acetate solution, and recovered as carbonate. The second residue may be a tin concentrate (stannic oxide). Figures 8.21 and 8.22 show schematic representation of the 2-stage process.

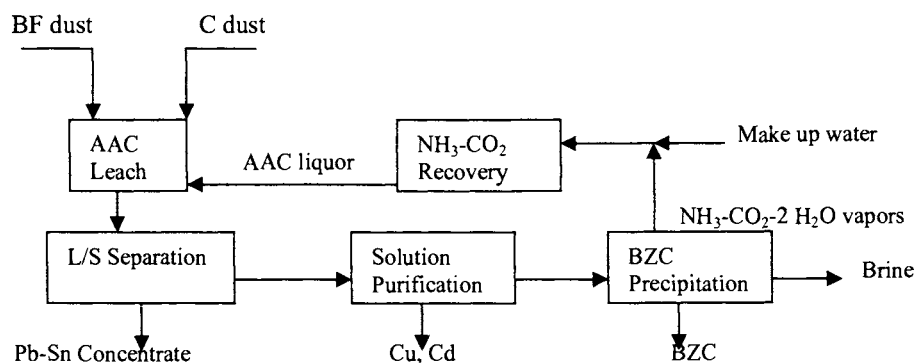


Figure 8.21 Ammonia-Ammonium carbonate circuit to solubilize metal oxides from secondary dust (Prado and Prado, 1995)

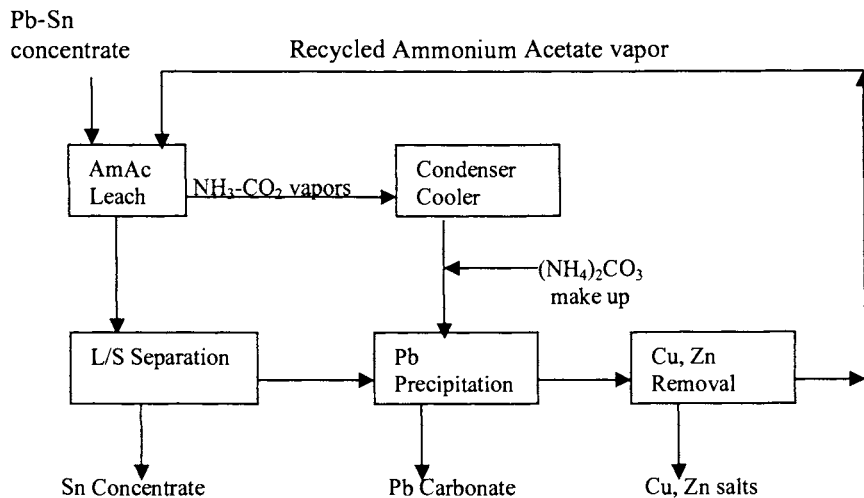


Figure 8.22. Ammonium acetate circuit for the recovery of lead (Prado and Prado, 1995)

Zinc, copper and cadmium are recovered as concentrates in solution. Lead carbonate free of impurities is precipitated. After the removal of these metals the residue can be used as a tin concentrate and may be recycled for enrichment.

8.2.4. Flue Dust from Chimney

Large amounts of zinc ash flue dust containing more than 80 % zinc are accumulated during galvanization processes at the surface of the molten bath and in the chimney. The dust consists of mainly zinc oxide and zinc metal. Recovery of zinc from a chimney dust by thermal treatment at 550 °C has been described by Barakat (2000). Addition of ammonium chloride as flux is found to enhance recovery. Up to 70 % of the zinc, purity 99.2 % is recovered with 20 % ammonium chloride at optimum temperature of 600 °C for 30 minutes. The ammonium chloride improves the recovery efficiency by minimizing the oxidation of zinc metal at elevated temperature by atmospheric oxygen. The oxide film produced separates the individual droplets of molten metal particles from one another, and prevents them from coalescing together to form ingots. The ammonium chloride forms a coating on the molten surface and prevents it from oxidation. Ammonium chloride begins to sublime at 340 °C and equal volumes of ammonia and hydrogen chloride are evaporated. The vapors form an insulation film around the molten zinc and prevent any further oxidation. Also, the reaction between the hydrogen chloride and zinc oxide layer to form molten zinc chloride layer helps coalescing of zinc droplets to collect together forming ingots, leading to higher recovery efficiency of zinc.

8.2.5. In-Plant Recycling of Metallurgical Dust

A new technological process has been recently described, which is applied to recycle metallurgical dust and sludges. It is called oxyfines and is based on oxyfuel technology (von Scheele and Johansson, 2002). It provides an efficient internal recycling of dust and sludge, which (the sludge) is recycled without a drying stage. The technology can be applied on-site to existing processes, to handle dust treatment and recycling problems in the metallurgical industry. The technology is based on the 'waste' materials having known compositions. They are thus used as raw materials in the existing processes that often generated them. The particles are agglomerated into solid-state aggregates of a suitable size, which removes harmful elements.

The technology uses a special oxyfuel burner to inject the dust into the furnace. The kind of oxyfuel burner can also handle sludge containing up to 65% water. The sludge is atomized, splitting it into very small droplets. The technology has been successfully applied for recycling of a wide range of metallurgical dusts and slag (von Scheele, 2004). Two examples will be described.

The first example is of iron powder dust. Large quantities of very fine filter dust from iron powder production, containing almost pure iron, have been recycled into the EAF. At a feeding rate of up to 3.5 ton/ hour, over 95 % of the injected dust is used in the molten bath giving an iron recovery of approximately 98 %. The recycled dust is well suited for use as a substitute for raw materials such as scrap and alloys. There is no burning of the iron dust above the bath surface.

The second example is of ferrochromium dust generated in the crushing operation of ferrochrome ore. At a feeding rate of 300 kg/h, 95 % yield (product/feed dust) is obtained, which is mainly FeCr with very low level of oxide. The operating practice and the carbon content of the feed is believed to have beneficial role in maintaining a reducing atmosphere leading to low oxide formation.

In another process developed in Sweden, flue dust is recycled to the blast furnace in the form of a cold-bonded briquette (see Chapter 6, Section 6.3.8 for description of briquette). The blend of by-products for briquette production consists of blast furnace

flue dust, filter dust from environmental filters, briquette fines and a scrap mixture consisting of coarse particles of BOF sludge and fines of steel and desulfurized scrap. Excess flue dust could have a negative effect on the strength of the briquette, which is attributed to the coke content of the particles. On the other hand, the carbon content in the flue dust serves to lower the quantity of reducing agent used in the blast furnace. Replacing flue dust by screened-off fines from the blast furnace (BOF slag, lime stone and manganese slag), desulfurized scrap, or mill scale sludge leads to increased strength (Sikstrom and Okvist, 2002). The dust is conveyed via a screw conveyor to an extruder. In a homogenizing and heating section inside the extruder, the dust is heated by external heating to 100-200 °C. The optimum temperature depends upon the composition of the dust and binding agent. Bitumen, 7-10% is found to be suitable binding agent to produce agglomerate of excellent stability and shear strength. It is added in melted state in the mixing and homogenizing section of the extruder. Best results are obtained by monitoring the process parameters, including amount of binding agent and dust added, power input, rotational speed and temperature. In the cooling section of the extruder, the temperature is lowered until the rigidity and strength is high enough to push the material through a forming plate and cut it into desired length. The forming plate may be heated to create a very smooth and rigid surface of the product. The flow diagram is shown in Figure 8.23.

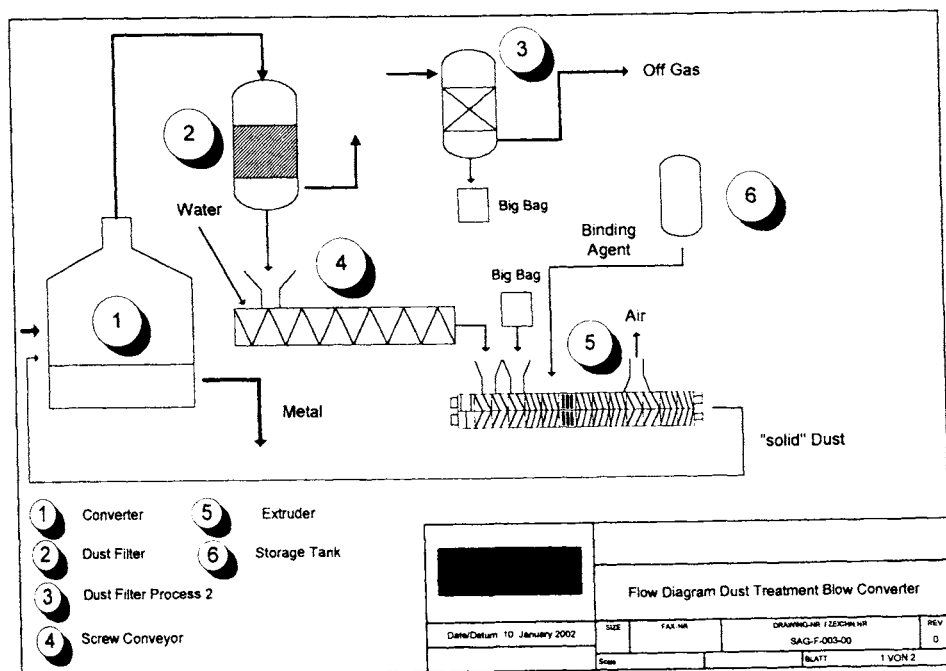


Figure 8.23. Flow diagram for treating converter dust (Rieke, 2002)

8.2.6. Processing of Steelmaking Residues

Iron-containing residues generated in steel plants contain several toxic elements and require further processing. In an integrated process described by Eetu-Pekka and coworkers (2005) the residues go through a magnetic separation step. In the second stage

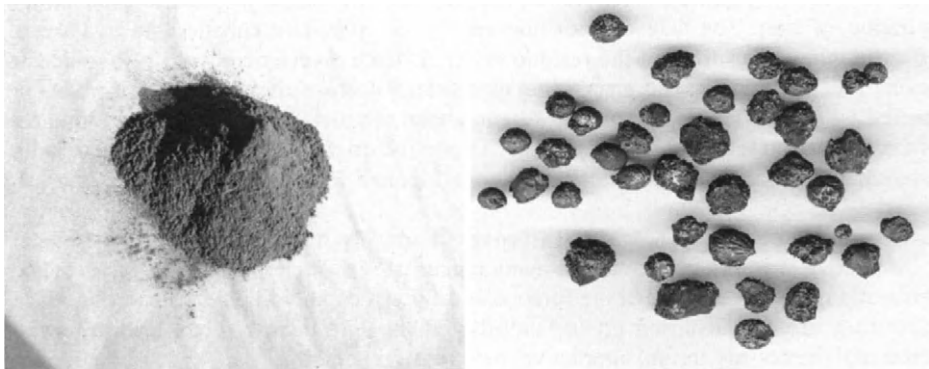


Figure 8.24. Ferrochromium dust of <0.1 mm (left) is recycled and converted into virtually all metallic agglomerates (von Scheele, 2004)

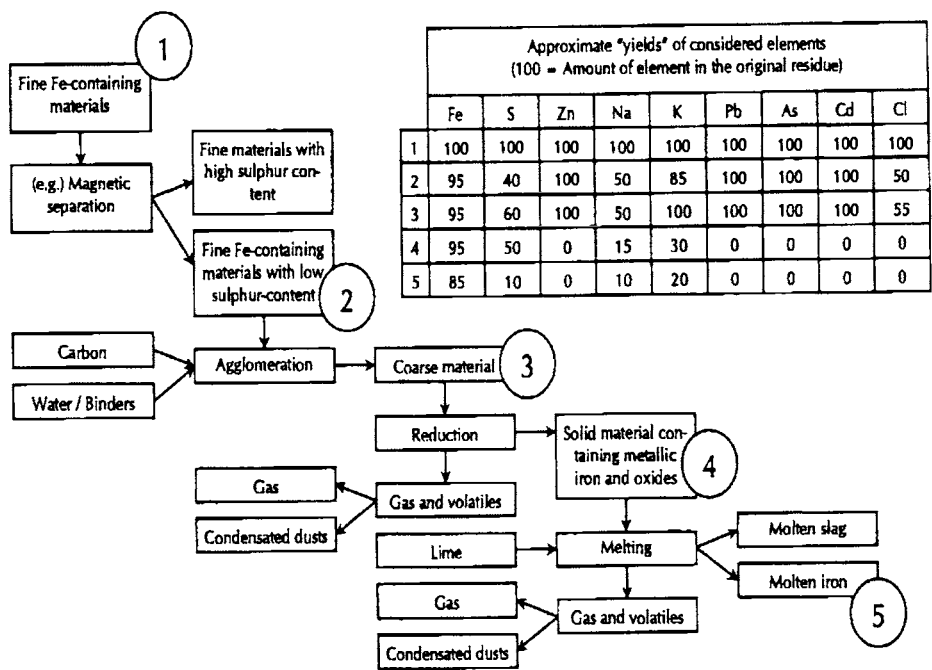


Figure 8.25. Processing of fine iron-containing residues (Eetu-Pekka *et al.*, 2005)I

they are agglomerated, before the reduction of iron oxides. The element, which is most problematic is sulfur. Some of it is transferred in to the gas phase during reduction as hydrogen sulfide and carbonyl sulfide (COS). There would still be a large amount of sulfur in the residue after the reduction phase. One way to decrease the amount of sulfur is to separate the residues with high sulfur content before the processing and leave them outside of recycling. Other possible methods suggested are to enhance the transfer of

sulfur into the slag phase by controlling the slag composition or by ensuring the carbon saturation of iron. The slag composition can be controlled to enhance the transfer of sulfur by addition of lime to the residue material. Excessive lime should be avoided to prevent precipitation of solid phases like dicalcium silicate. Sulfur content of iron can be lowered by increasing the carbon and silicon content in metal, by adding carbon into the residue material. Optimum quantity depends upon the original composition of the residue material. The process is schematically shown in Figure 8.25.

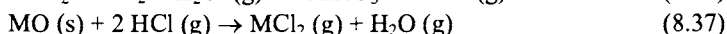
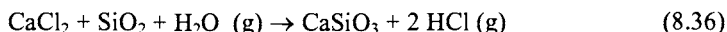
8.3. Metal Recovery from Fly Ash

Municipal waste is incinerated in many countries. Two types of ash are generated by incineration: bottom ash left in the furnace and fly ash captured by bag houses. In many places they are still disposed off in landfills. As they are getting filled, it is becoming increasingly necessary to find alternative methods of processing.

Fly ash contains many heavy metals, especially zinc, lead and copper. There is potential to recover them and reuse as resource materials. Several techniques have been investigated to achieve this goal.

8.3.1. Separation by Segregation Reaction

In the segregation process investigated by Abe and coworkers (2001), fly ash is directly heated in a controlled inert atmosphere, using nitrogen gas and then chlorinated by hydrogen chloride gas, which is generated by the action of steam on calcium chloride. The metal chlorides formed are reduced by hydrogen, which is produced by reacting carbon with water. The reactions are as follows:



The metals deposit on the surface of carbon and are recovered by separating carbon froth flotation (taking advantage of the natural hydrophobicity of carbon; see Chapter 3, for details on the flotation technique)

The waste gas is quenched to suppress the generation of dioxin, a toxic organic compound contained in the fly ash.

A flow sheet of treatment of fly ash is shown in Figure 8.26. Details of the segregation roasting equipment is shown in Figure 8.27. Fly ash mixed with 20 % carbon by weight (active carbon or oil-coke fly ash) and water (30 % by weight) is fed into a rotary kiln and roasted in a controlled nitrogen atmosphere of nitrogen at 800-900 °C. The roasted fly ash is mixed with water to produce a slurry and carbon is recovered by flotation. Recoveries ranging from 60 % of copper and 40 % zinc and lead have been achieved. (Abe *et al.*, 2001).

8.3.2. Metal Recoveries from Secondary Fly Ash

Secondary fly ash is generated from the melting of primary fly ash. The composition varies widely as it is derived from municipal waste, the composition of which varies with local conditions. Percent zinc, for example, varies from 2.2 % to 20.7 % in the secondary

fly ash generated by treating municipal waste from Japanese cities (Yoshida and Nagasaki, 2001).

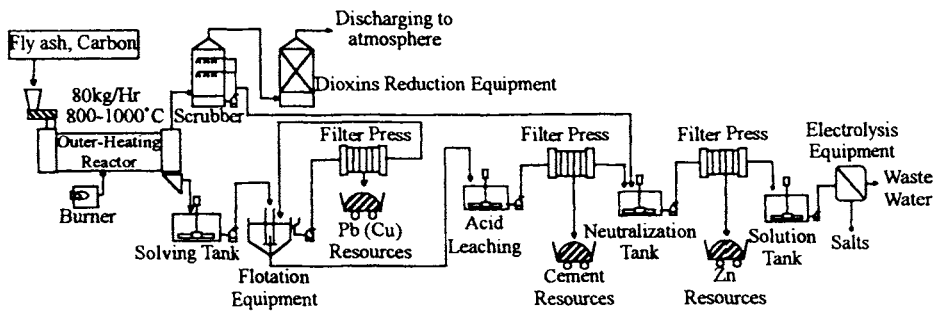


Figure 8.26. Flow sheet of treatment of fly ash (Abe *et al.*, 2001)

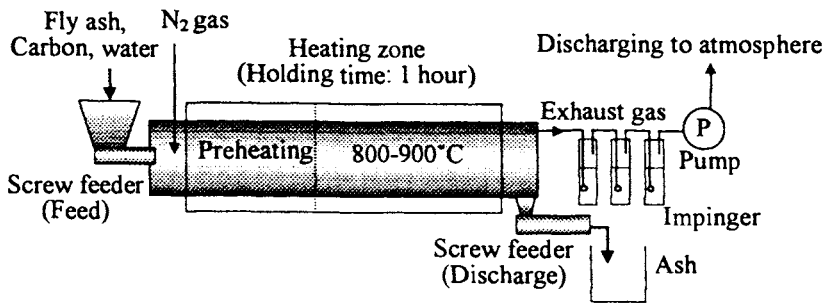


Figure 8.27. Segregation roasting equipment (Abe *et al.*, 2001)

Processing of secondary fly ash to recover zinc and lead has been done by pyrometallurgical operation using Mitsui furnace system (described in Chapter 3). Zinc present as ferrite (ZnFe_2O_4) is reduced to zinc vapor and then oxidized by excess oxygen to produce zinc oxide. Lead is similarly recovered.

8.4. Processing of Shredder Dust

Considerable quantities of dust is generated in the shredding of discarded automobiles, scrapped home electric appliances and similar other items. This dust carries both metallic as well as non-metallic components. Composition of one such material from Japan is shown in Table 8.20.

The occurrence of both organic and metallic components makes this a potential secondary source of metals and non-metallic products. Japanese researchers have described a "Total System Process" to achieve this objective. By this they have shown the possibility to recover metals and convert the organic matter into fuel oil. The process comprises several stages, as shown in the flow diagram of Figure 8.28.

The first stage is pyrolysis of the shredder dust. This is done in a rotary kiln, which serves as pyrolysis cell in furnace. The cell is heated to 550 °C which decomposes the

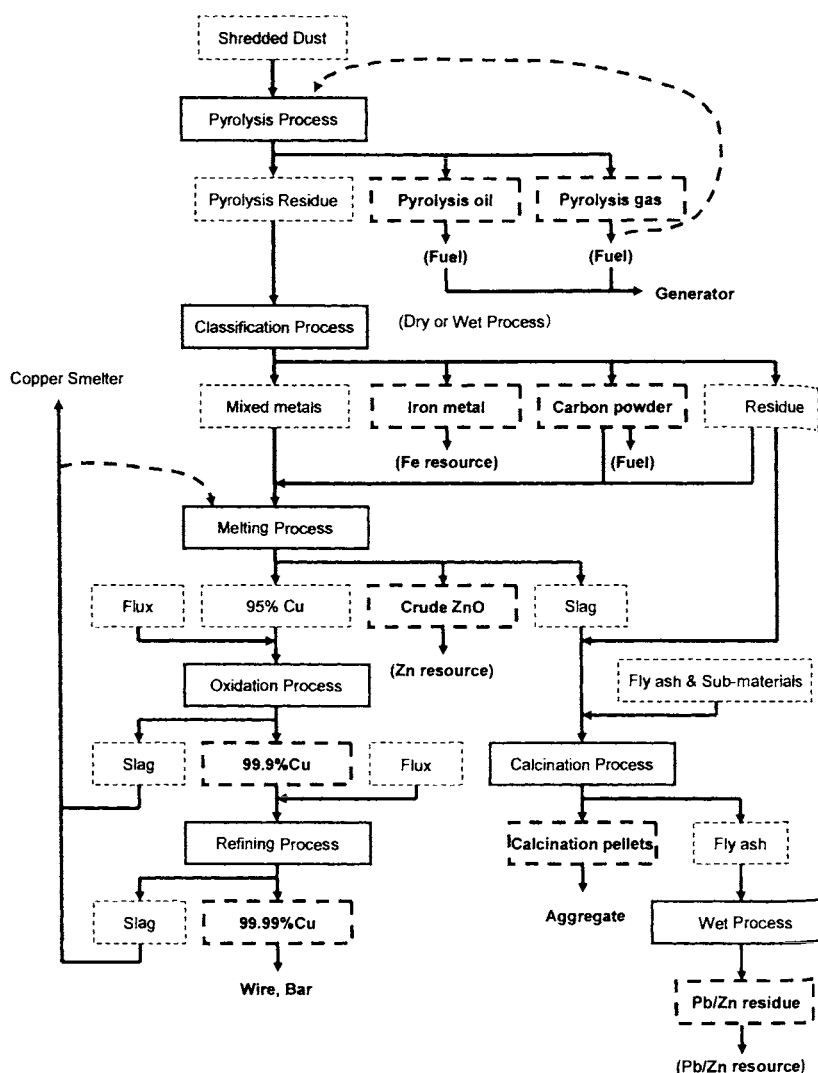


Figure 8.28. Material flow in resource recovery from shredder dust in Total System process (Sekiguchi *et al.*, 2002)

dust and generates hydrocarbon vapors. The vaporized hydrocarbon is recovered as pyrolysis oil and gas used as fuel. The metals and carbon remain as residue. Approximately 6% of it is copper. By a classification process (air classifier using high velocity stream of dry air or wet classifier if the residue contains chlorine compounds; see Chapter 3 more details of classifier equipment). The metal fraction thus separated is charged in a reduction furnace with coal at 1400 °C the molten metal is then refined to produce 99.9% copper by air oxidation. It is further refined to 99.99% copper by pyro-smelting.

Table 8.20. Composition of a Shredder Dust processed in Japan (Sekiguchi et al., 2002)

Bulk density (g/cm ³)		0.3
Low heat capacity (Kcal/kg)		4500
Humidity (%)		5-15
Flammable Content (%)		62
Ash content (%)		38
Analytical data on Elements (Weight %)		
Volatile elements	C	45.0
	H	5.7
	N	1.4
	O	5.3
	Total S	1.6
	Cl	3.0
	Sub-total	62.0
Metals and Non-metals	Total Fe	5.6
	Pb	0.3
	Cu	3.0
	Ni	0.03
	Mg	0.9
	Al	2.7
	SiO ₂	10.3
	Al ₂ O ₃	0.7
	CaO	3.6
	Sub-total	27.43

The slag produced in the process is mixed with classified waste residue like fly ash and calcined in a furnace to form an aggregate, which is used as concrete material.

8.5. Metal Recovery from Pickling Sludge by Smelting Reduction

Pickling sludge generated in steel industry (see Chapter 7, Section 7.2) contains chromium, nickel and molybdenum besides iron. It also contains 35-40% lime, 21% fluorine (as calcium fluoride), 3% sulfur (as calcium sulfate and elemental sulfur) and small quantity of magnesia. Laboratory investigations (Ma *et al.*, 2002) have shown the potential for recovering the metals by direct smelting reduction. The experimental set up is shown in Figure 8.29.

The pickling sludge powder is uniformly mixed with coke powder and put in a graphite crucible placed in a furnace with nitrogen gas protection at room temperature. The furnace is first manually heated up to 600 °C and then the temperature is automatically controlled with a heating rate of 6 °C/min. the sample is held at 1400-1430 °C for 1-2.5 hours and then the furnace is cooled to room temperature with nitrogen gas protection. The investigators obtained up to 90% metal recovery, but not all tests showed the same results, indicating the work to be done to optimize the experimental conditions for the process to be applied on a large scale. The metal phase contains 65% iron, 12-15% chromium, 11-12% nickel and about 1% molybdenum. The slag produced consists mainly of calcium fluoride (70-75%) and calcium sulfide in smaller proportion (10-15%).

The presence of calcium sulfide makes it unsuitable to be used as a flux material unless it is first desulfurized.

The off gases in the process are found to contain (by analysis by the mass spectrometer in the set up) mainly carbon monoxide, carbon dioxide and water; and hydrogen fluoride, nitric oxide, sulfur dioxide, carbonyl sulfide (COS) and fluorine in low concentrations.. The following reduction reactions are proposed to explain the product composition:

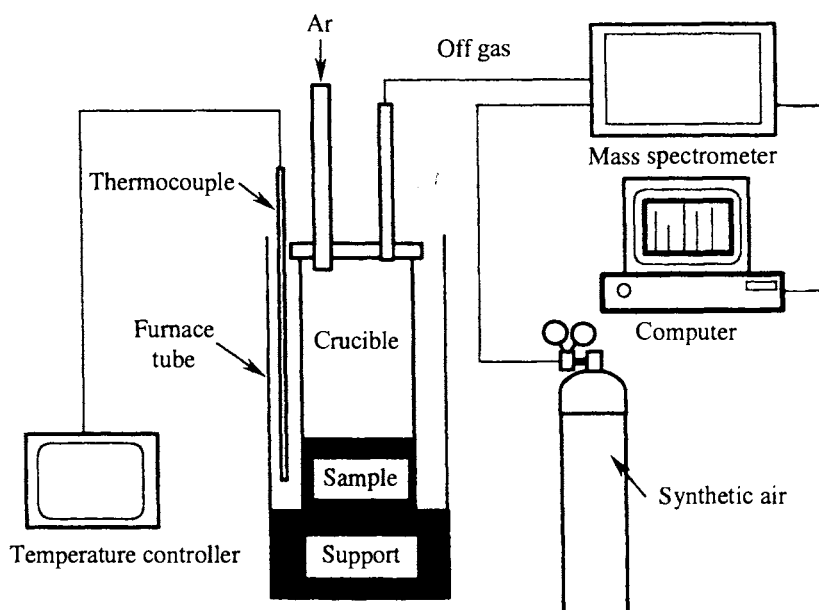
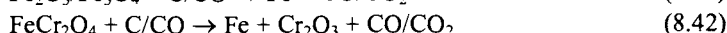


Figure 8.29. Schematic illustration of smelting reduction set-up with unit for off gas analysis (Ma *et al.*, 2002)

Nitric oxide is formed, possibly due to decomposition of nitrates at 400-800 °C. Hydrogen fluoride is produced by the hydrolytic decomposition of metal fluorides while the thermal decomposition of calcium sulfate produces sulfur dioxide. Sulfur dioxide is also produced along with calcium sulfide by the action of sulfur on lime. Carbonyl sulfide detected in the range 750-1100 °C is produced probably by the direct combination of carbon monoxide and sulfur. At higher temperature, it is mostly decomposed. The reactions are as follows:





Selected Readings

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- Southwick, L. M., 2004. Reversing philosopher's stone: recovering iron and other metals from slags and other residues, *Waste Processing and Recycling in Mineral and Metallurgical Industries V*, 699-722. Eds. S. R. Rao, F. W. Harrison, J. A. Kozinski, L. M. Amaratunga, T. C. Cheng, G. G. Richards. Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada.

Chapter 9

BY-PRODUCT PROCESSING AND UTILIZATION

Many mineral and metallurgical processes generate secondary products, which are not usually sought after. Until recently, they were either stock piled or disposed off as 'wastes'. Interestingly, many of these secondary or 'waste' products contain valuable material, which can be recovered through new technologies (discussed in Chapter 8) or they can be directly used for specific industrial, construction or agricultural purposes, sometimes after appropriate treatment. Conversion of such materials to valuable, marketable products could lead to development of secondary or 'spin off' industries and they can be useful by-products of the original process. Some examples of such by-product processing and utilization of those products will be discussed in the present Chapter.

9.1. Processing and Utilization of Slag

Slag is the molten byproduct or coproduct of many metallurgical and special (coal fired thermal plants for instance) operations, that is subsequently cooled (air, pelletized, foamed or granulated) for use, or, unfortunately in too many cases, disposal. Ferrous (iron and steel) and nonferrous (copper and nickel for instance) metals are the most commonly used, world-wide, structural and functional materials. The resulting large quantities of slags produced and their potential impact on the environment have prompted material scientists and civil engineers to explore the technically-sound, cost-effective and environmentally-acceptable use of a wide range of slags in construction. There is a full range of proven construction uses - from aggregate to cementitious materials - for copper, nickel and phosphorus nonferrous slag.

9.1.1. Iron Blast Furnace Slag

The use of iron blast furnace slag as a cement supplement is one of the big successes in the field of by-product recycling industry. Previously a waste product with limited use as a base aggregate for roads and ballast for railways, it is now much in demand as a valuable supplement for Portland cement as a result of the discovery that rapidly iron cooled blast furnace possessed the properties of hydraulic cement when finely ground. The quantity of slag produced per ton of pig iron is relatively small (~250 kg) but the global production of pig iron is around 500 million tons per year and thus the amount of iron blast slag produced is around 100 million tons per year (about 10% wt of the global production of Portland cement).

Water granulation and air-cooling are techniques (see, Production of Granulated Slag in Chapter 8) used to prepare iron blast furnace slag for use as a cement supplement.. These can either be ground for cement or used 'as is' for light weight aggregate. The blast furnace slag contains a high proportion of the principle mineral component of Portland cement, tricalcium silicate.

Steel slag contains less lime than blast furnace slag and forms mainly dicalcium silicate that does not have the same hydraulic properties as iron blast furnace slag. There is some indication that the dicalcium silicate undergoes a spontaneous crystal change leading to spontaneous disintegration of slag aggregate. The conversion from open hearth steel-making to ladle metallurgy greatly speeded up the steel making process. A downside of this faster rate is that the dolomite or olivine used as a flux is not always completely digested resulting in a slag containing free magnesium oxide (periclase). The periclase tends to hydrate over time again leading to disintegration of steel slag aggregate. The industry response to these difficulties has been to stockpile the slag for six months to stabilize before screening for aggregate use. Another approach has been to crush and magnetically separate the slag to remove metallic iron inclusions and then blend the product as cement kiln feed. The use of steel slag as a component of cement kiln feed has been shown to increase the kiln capacity and reduce the energy requirement per ton of Portland cement clinker produced. Table 9.1 compares the composition and mineralogy of typical iron and steel slags with that type typical clinker: Further discussion on incorporating slag in cement will be in Section 9.1.5.1.

Table 9.1. Chemical Composition and Mineralogy of Slags Compared with that of Clinker ((Geiseler, 2000)

Mineral %	BF slag %	BOF slag %	EHF slag %	Typical clinker %
SiO ₂	35-59	11-18	8-18	18-25
Al ₂ O ₃	8-12	1-4	3-10	3-8
Fe total	<1	14-19	20-30	2-6
CaO	36-42	48-54	25-35	60-67
MgO	4-12	1-4	3-9	0-6
SO ₃	2-3	<0.5	<0.5	1.5-4
P ₂ O ₅	0.00	0.00	0.00	0.21
TiO ₂	0.00	0.00	0.00	0.21
Na ₂ O	0.32	0.12	<0.1	0.19
K ₂ O	0.57	0.02	<0.1	0.50
Mineralogy				
C ₃ S (3CaO.SiO ₂)				40-70
C ₂ S (2CaO.SiO ₂)		40		20-40
C ₃ A (3CaO.Al ₂ O ₃)		7		3-17
C ₄ AF		34		5-15
4CaO.Al ₂ O ₃ .Fe ₂ O ₃)				

Many uses for steel slag have been found as indicated in Figure 9.1. The limitation on sales is primarily the cost of transportation that limits most low value added uses to a radius of about 80 km from the point of production.

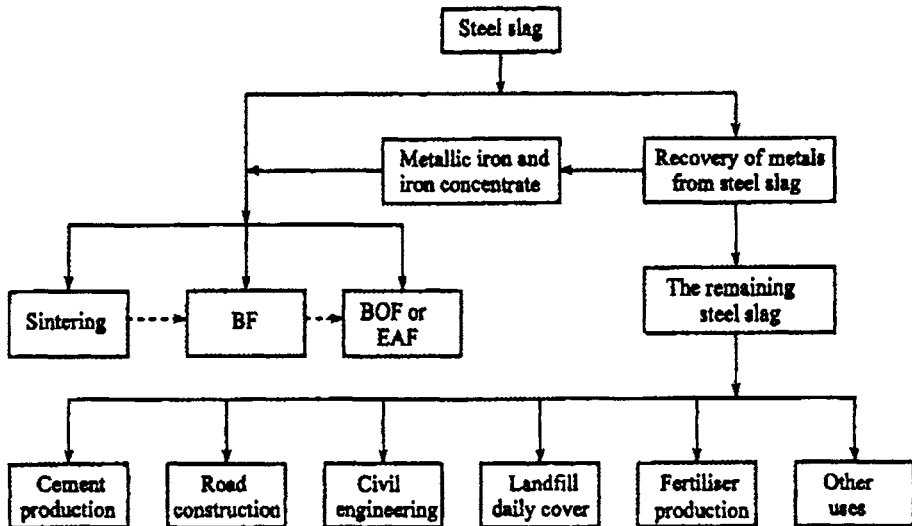


Figure 9.1. Utilization of steel slag (Shen and Forsberg, 2003)

9.1.2. Utilization of Slag in Construction Industry

There are three main points fundamental to conducting the effective study of a specific slag, which forms the basis for uses in construction, listed by Wong and Emery (2004)

- First, there must be a sound understanding of the overall compositional and physical properties of the specific slag being investigated, especially any potentially negative characteristics (volume expansivity related to hydratable oxides, particularly CaO and/or MgO, for instance). The slag properties to be considered are chemistry (typically as oxides), composition (mineralogy), physical and mechanical, including a comparison of these properties with those of other slags and related materials which may be replaced by the specific slag, or used in conjunction with the slag.
- Second, in order to achieve appropriate and optimum utilization of a specific slag, it is essential to have a comprehensive understanding of the production, properties, design methods, construction uses and specifications of the conventional material(s) that the slag may replace or incorporate the slag. The conventional materials could be bulk (aggregate for instance) or cementitious (portland cement for instance). The relationship of the processing methods and properties between conventional material(s) and slag(s) must be understood and investigated so that any potential use of the specific slag in construction can be thoroughly exploited.
- Third, it must be recognized that slags are distinct, rather unique materials, and generally different from any natural mineral materials. Like any other byproduct or coproduct (or waste unfortunately too often), slag is a type of special raw material with its own characteristics that must generally have

additional processing for uses in construction. It is important, therefore, that material and construction specifications based on conventional mineral resources and materials do not preclude the use of suitable quality slags with demonstrated satisfactory performance for the intended purpose. The importance of proper slag processing, with quality control, for approved construction uses cannot be over emphasized.

Each specific slag, in terms of type, process and source, should be fully evaluated for each proposed use, given the significant differences in properties that can be involved and the specific performance requirements for bulk and cementitious uses.

Slag utilization in construction is an overall process, which includes several stages from slag production to end uses. Successful utilization is generally based on several stages or links. The overall general process consists of seven links, as shown in Figure 9.2 for highway construction, any one of which might affect the final use of the specific slag. These links include: pre- or post-treatment of slag; chemical and physical (particularly potential expansion and deleterious components) properties and the factors which affect them; and the evaluation of potential field performance for the intended uses. Comprehensive slag utilization studies consist of three main stages: treating and processing; intrinsic properties; and properties of end products (uses). The slag uses shown in Figure 9.2 are divided into three broad areas: use as granular material or aggregate (there is often a wide range of aggregate uses; from granular material to special applications such as filter media); use as portland cement concrete aggregate; and use in cementitious applications (cement manufacture and/or slag cements).

There are three relationships to be considered for slag utilization, as shown in Figures 9.3 and 9.4: (i) the relationship between chemical and mineral composition and any potentially 'negative' properties; (ii) the relationship between any negative slag properties and the performance requirements and properties of the end products (uses); and (iii) the rational use of slags with different properties to ensure optimum use of the specific slag. For example, volume expansion is the main factor likely to affect the successful use of a specific steel slag as a highway construction aggregate; volume expansion is dependent on the chemical and mineral composition of the specific slag and thus critically affects the evaluation of the slag and its quality control.

To effectively use a slag, it is necessary to know how its chemistry and mineral composition affect any potential negative properties (volume expansion of steel slag for instance) (Relationship 1), and how the negative properties can affect the performance of the end products (uses) (Relationship 2). Relationship 3 is dependent on Relationships 1 and 2. Relationship 1 determines the necessary treatment modification of the properties of the specific slag and related quality control. Relationship 2 is essential to enable the slag, with known or modified properties, to be put into use in construction. Once Relationship 2 is known quantitatively and demonstrated, the use becomes viable. Once Relationship 1 is known, suitable Relationship 2 treatment methods, if necessary, can be chosen and then Relationship 3 for optimal end uses established. It is imperative that all potential negative behavior and/or deleterious components are thoroughly checked and evaluated for a specific slag in terms of the intended and optimal use requirements (Figure 9.4). Slag is actually an energy-containing material, particularly when rapidly solidified (pelletized or granulated) from the molten state to a vitrified form (process energy locked in - 'latent energy'). In determining the uses of a specific slag, proper

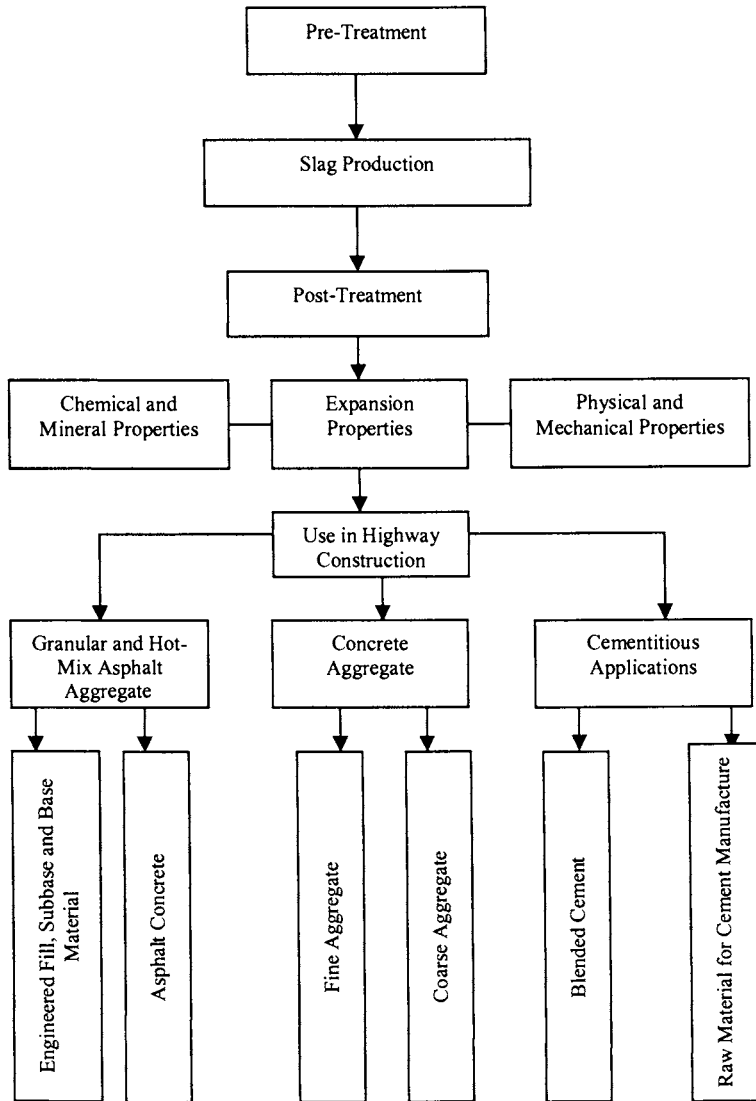


Figure 9.2 - Overall Process of Slag Utilization in Highway Construction (Wang and Emery, 2004)

attention should be paid to the optimum use of this energy potential. This is one of the three objectives of byproduct and coproduct (or waste) utilization: protection of the environment; full use as a bulk and/or energy resource; and technical beneficiation for value-added uses. The term “slag utilization” can be defined as the effective use of a specific slag to achieve these objectives. Under this definition, landfill is clearly not utilization and does not contribute to a sustainable society. On the other hand, any cementitious use of a slag could be considered as energy recovery and the highest value

added. For example, the use of slag as a skid-resistant aggregate takes advantage of its surface characteristics such as hardness, where hardness is strength related property with little energy recovery. On the other hand, use as a cementitious material in blended cement essentially recovers the latent (invested) energy. It is very important to focus on cementitious (energy) uses of slags where possible, rather than just aggregate (bulk) uses. More quantitative assessment is generally needed for higher end uses of a slag. This is shown in Figure 9.4, where from left to right, increasing potential invested (process) energy is 'recovered', necessitating a higher degree of stability and more rigorous quantitative work to quantify slag performance properties.

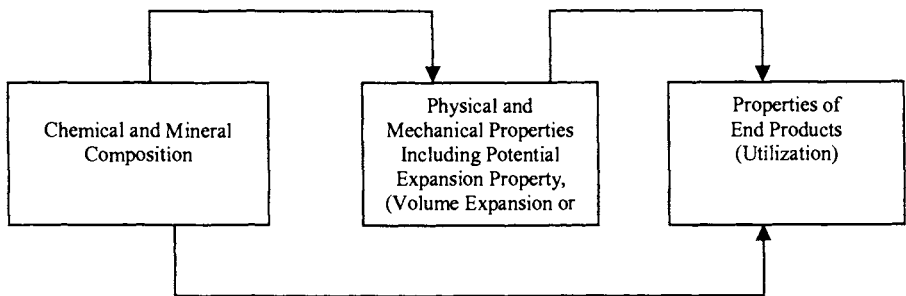
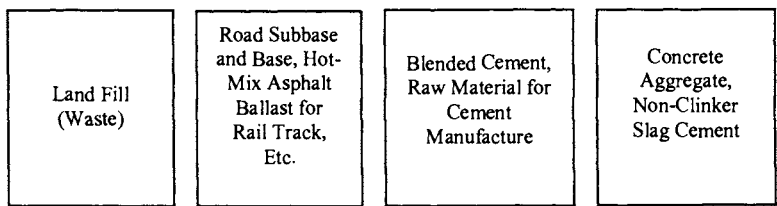


Figure 9.3 – Relationships for Slag Utilization in Construction (Wang and Emery, 2004)



The requirement for stability of slag in use (from lenient to rigorous) →
The degree of use of latent (chemical) energy in slag (from none to full) →

Figure 9.4. Typical Grades of Slag Utilization in Construction (Wang and Emery, 2004)

9.1.3. Quantification in Slag Utilization

The reason for a specific slag not currently being fully utilized is often due to a general lack of quantification work on the properties of the slag (expansion potential for instance) and the performance requirements of the end products (uses). A technical opinion unsupported by thorough characterization and performance testing is not sufficient to encourage the use of a slag in the construction industry without misgivings or concerns. As Wang and Emery (2004) have stated, the impact of past utilization mistakes is very difficult to overcome even for proven uses. Usability criteria and properties of composites made from a specific slag can be determined from a study of the basic properties of the slag and the specific application specifications for a use, particularly stability and deleterious materials control requirements.

The relevant, necessary slag quantification work for engineered fill, rail ballast, sub-base/base material, erosion control material and hot-mix asphalt aggregates includes: laboratory testing (volume expansion characterization for instance); evaluation; establishing processing requirements; establishing specification requirements and quality control procedures; and combining this technical suitability with a check of environmental factors and cost-effectiveness. For slag use as portland cement concrete aggregate the quantification requirements are more detailed given the importance of long-term durability and stability in a wide range of environments and structures. For slag use in blended cement, in addition to the quantification of hydraulic properties, stability and durability for various substitution ratios, the grindability (cost) of the slag is very important. Wang and Emery (2004) have established some useful criteria for slag utilization. It should be noted, however, that each specific slag must be fully quantified and checked for each specific use as these are only general guidelines.

9.1.3.1. Prediction of Volume Expansion – Criterion for Slag Use as a Granular Material

For steel slag use as a granular material (aggregate) in unconfined applications such as granular base and hot-mix asphalt aggregate, volume expansion (stability) is still of major concern (Wang, 1992). (A detailed quantification for confined applications such as structural fill or concrete aggregate is imperative and these uses must always be viewed with great care as only special quality steel slags will demonstrate the required volumetric stability (Wang and Montgomery, 1992). A usability criterion for unconfined applications has been developed based on the physical properties of a given slag:

$$F \leq k \frac{(\gamma_s - \gamma_o)}{\gamma_s^2} \times 100\% \quad (9.1)$$

where F is the hydratable oxide content (CaO and/or MgO) of a given slag; γ_s is the specific gravity of the slag; γ_o is the bulk relative density of the slag; and k is a constant related to the slag's physical properties. When the hydratable oxide content of a given steel slag is less than the right hand term, the slag will not expand macroscopically when used as a granular material. This must then be confirmed through standard slag expansivity testing (Farrand and Emery, 1995).

9.1.3.2. Volumetric Stress – Criterion for Use in Rigid Applications

For slag used in a rigid matrix (portland cement concrete for instance), the resulting integrity and volume stability are basically controlled by the minimum allowable stress of the matrix material and the maximum volumetric stress (expansion stress) of the slag used in the matrix. A criterion for this has been developed as follows (Wang and Emery, 2004):

$$\sigma_d = k \frac{\pi d \sigma_e}{R \phi} \leq \sigma \quad (9.2)$$

where σ_d is the 'dangerous' stress level of the slag aggregate (N/m^2); k is a factor of safety larger than 1; d is the particle size of the slag aggregate; R is the particle cracking ratio; σ_e is the volumetric expansive stress of a compacted mass of the slag on a unit area

at unit height (N/m^3) which is obtained from a laboratory accelerated autoclave testing for a given slag; and ϕ is a filling factor for the slag aggregate. When the maximum tension stress of a given slag is less than the allowable stress σ , the entire product will not fail or lose strength owing to the fact that the matrix strength is sufficiently high to constrain the expansion stress generated from the slag particles. Once again, it is necessary to confirm this through detailed durability testing of the concrete incorporating the specific slag. It is imperative that only special quality steel slags, of clearly proven suitability, are considered for concrete aggregate, cementitious and confined application uses (Wang and Montgomery, 1992).

9.1.4. Applications in Road Construction

Steelmaking slags have been used as asphalt constituent, after coating with a bituminous binder (Wachsmuth *et al.*, 1981). When thus treated, the products possess some properties, which make them superior to natural stone. They include absence of clay and silt, cubicle shape, rough surface texture with good frictional properties and adhesion to bituminous binders, low coefficient of thermal expansion, good skid and wear resistance, high stability and resistance to rutting, due to their high specific gravity (Emery, 1977; Geiseler, 1994). These properties have led to the use of slags as an asphalt constituent in road construction (Wachsmuth *et al.*, 1981; Emery, 1992). Table 9.2 shows a comparison between typical road building materials and slag materials. It is clear that BOF and EAF slags can be processed to give an aggregate with high strength and high resistance to weathering.

Table 9.2. Technical Properties of Steel Slags (Geiseler *et al.*, 1994)

Characteristics	Aggregate Type			
	BOF Slag	EAF Slag	Basalt	Granite
Bulk Density (g/cm^3)	3.1 - 3.7	3.2 - 3.8	2.8 - 3.1	2.6 - 2.8
Resistance to Impact determined on crushed (wt%) aggregates (size 8 - 12 mm)	10 - 26	10 - 26	9 - 20	12 - 27
Resistance to Weathering Absorption of water (wt%)	0.2 - 1.0	0.2 - 1.0	< 0.5	0.3 - 1.2
Freeze / Thaw resistance particles < 5 mm (wt%)	< 1.0	< 1.0	< 1.0	0.8 - 2.0
Los Angeles Test test aggregates 8-12 mm particles < 5 mm	9-18	8-15	-	15-20
Polished Stone Value - PSV	54 - 57	58 - 63	45 - 55	45 - 55
Compressive Strength (N/mm^2)	> 100	>100	>250	>120

There are, however, several problems to be tackled before this potential can be applied in practice. Usually there is a wide variation in the composition of steel slags, even when they are produced in the same plant and furnace. This is due to the batch mode of production and the large number of different steels produced, causing inconsistency in the performance of slags. Transportation of slag, except when it is used locally, will make it less economical. Another major problem is the presence of high volumes of free lime and periclase (MgO) (Geiseler, 1994). These two oxides may not completely dissolve due

Table 9.3. Possible Applications of Granulated Slag. Key Features and Competitive Materials (Sudbury and Kemp, 2006)

	Median, Range or Characteristic Size Tyler Mesh or as indicated	Pertinent Properties (Illustrative)	Competitive Materials
Abrasive grit	10	Good cutting power	Coal slag, garnet, specular hematite
Shingle grit	10	Ultra violet opacity	Trap rock crushed and dyed
Shingle backing	100	Asphalt adhesion	Crusher dust
Asphalt aggregate	10 – 100	Asphalt adhesion/cubicity	Sand
Winter sand	10	Skid resistance, absorbtivity	Sand
Highway surfacing	10	Skid resistance	Sand
Cement aggregate	10 – 30	Compatibility	Sand, gravel
Cement supplement	3500 cm ² /gm	Strength development	Fly ash, blast furnace slag
Cement alternative	3500 cm ² /gm	Strength development	Mortar
Water filtration	10	High Permeability & SG	Sand
Foundry sand	10	Thermal stability	Natural olivine
Steel plant flux	4 mesh	Chemistry	Dolomite
Backfill mix	10	Packing density	Very finely crushed rock
Nursery mulch	30	Protective qualities	Organic mulch
Marine defenses	10 – 30	High sg	Gravel
Gabion filler	Not applicable	Too fine	Pit cooled slag
Ballast systems	10-100	Heavy/handle able	Sand and gravel
Slope stabilization	10	High specific gravity and permeability	Sand and gravel
Highway	10 – 100	High specific gravity, permeability, colour	Sand and gravel
Spawning beds	10 – 100	Permeable/Fungal resistance	River gravel
Silicon fertilizer	10	Silica solubility	Wollastonite
Gas storage	10 mesh	High internal porosity	Zeolites

to the short processing time in the furnace and also they can precipitate during cooling of the solidified slag. As a result, free lime may be present in amounts up to 7 % by weight and periclase to a lesser extent. Hydration of these minerals results in a large volume expansion, which destroys the integrity of any structure built from this material. Free lime hydrates quickly causing volume expansion in a short period of time; whereas periclase hydrates slowly, over a period of several years, resulting in long-term expansive behavior.

Another serious problem in the application of slag is leaching of metals, in particular, chromium and vanadium, both toxic metals, which can be environmentally harmful, when slag interacts with natural water. It is largely governed by particle size and permeability of the material. A recent study by Borell (2005) describes the use of granulated slag (called Iron Sand; see Section 8.1.5.2) in road construction. It is used as an insulating and draining material in the sub-base course. It shows very low leachability and is considered to be environmentally inert. Many other possible uses of granulated slag are listed in Table 9.3.

9.1.4.1. Nickel Slag Use in Highway Construction

There is a full range of proven highway construction applications for suitable quality nickel, copper and phosphorus slags. An example is illustrated by a recent positive development in the use of large quantities of air-cooled nickel slag in the reconstruction and widening of a highway in the Dominican Republic (Emery, 1999). The specific nickel slag is a coproduct of ferronickel production by the smelting of laterite ore. Large quantities of nickel slag stock piled in the disposal area of the Falcondo ferronickel smelter has proven to be a convenient material source. Due to the thermal shock of air-cooling, the molten nickel slag is 'fragmented' to a convenient size for engineering fill and granular sub-base use. Unlike steel slag, which typically exhibits volumetric stability problems as discussed before, nickel slag does not cause this problem. Table 9.4 summarizes the testing results for nickel slag aggregates used in the highway construction. In addition, the material also passed aggregate disruption and aggregate expansion tests. Based on considerable practical positive international experience, satisfactory local use for several years, leachate characterization, mineralogical evaluations and the favorable comprehensive accelerated stability/durability testing (Table 9.4), the nickel slag has been approved to be suitable material for engineered fill, granular sub-base and hot-mix asphalt aggregate use. Several million cubic meters of the nickel slag have been used for highway construction, thus replacing a substantial amount of river gravels and making a very positive contribution to the environment. Additionally the regular construction industry use of the nickel slag (called Falcondo aggregate) is now being established for domestic and export markets (Wang and Emery, 2004).

The work and analysis of Wang and Emery (2004) provides a guiding outline for slag utilization, with an example based on the application of an air-cooled nickel slag as engineered fill, granular sub-base, and hot-mix asphalt aggregate in highway construction. This takes advantage of the potentially useful properties of the slag, in particular, cementitious property. This makes a significant contribution to sustainable development. As nickel extraction has been increasing steadily in recent years, with the growing demand for the metal, the slag generated is a valuable source available for utilization and can, at least in part, meet the demand for construction material.

Table 9.4 – Summary of Test Results of Nickel Slag Aggregates Used in Highway Construction (Air-Cooled Nickel Slag Aggregates) (Wong and Emery, 2004).

TEST	SAMPLE DESCRIPTION		
	Nominal 25 mm Minus Sample #1	Nominal 25 mm Minus Sample #2	Nominal Retained 25 mm Sample
1.18 to 2.36 mm	50/0/0 (Good/Fair/Poor Particles)	50/0/0 (Good/Fair/Poor Particles)	-
2.36 to 4.75 mm	50/0/0	49/1/0	-
4.75 to 6.7 mm	50/0/0	50/0/0	-
6.7 to 9.5 mm	50/0/0	50/0/0	-
9.5 to 13.2 mm	50/0/0	50/0/0	-
>25 mm	-	-	12/0/0
	Pass	Pass	Pass
Autoclave disruption testing was also completed for two particles of nickel slag which exhibited cracking attributed to thermal shock. Both particles passed the autoclave disruption test (remained sound and did not exhibit any additional cracking).			
A 1700 g sample of the nominal 25 mm minus nickel slag (passing 25 mm retained 4.75 mm) was examined by a petrographer. The sample was found to consist solely of hard nickel slag. Occasional cracked particles were identified (thermal cracking) as well as some very vesicular particles, but no deleterious or non-slag particles were identified. One particle of nickel slag appeared to have some cemented sand attached to it, but the particle itself was hard.			
Percent			
Expansion, 7 days at 60°C	0.06 (negligible)	0.04 (negligible)	Not Tested

9.1.5. Uses of Metallurgical Slag in Cement Industry

Steelmaking slag has some compositional similarities to Portland cement as may be seen from a comparative percent composition in Table 9.5. Portland cement (PC) is essentially a quaternary blend of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$. The chemical similarities of steel slag and PC can be compared as follows: (Montgomery and Wang, 1991):

1. Aluminum oxide in steel slag exists in solid solution. In PC, aluminum oxide forms C_3A , and C_4AF .
2. The iron oxide in the slag exists mainly as FeO with small amount of ferric oxide.
3. While there is great similarity in compositions, it should be noted that because of composition fluctuations, the slag may become unstable due to excess free lime. Steel slag containing excess lime could be an activator. These are essential parameters for using steel slag as a component material for cement manufacture and have been extensively examined.
4. CaO in steel slag mainly forms C_2S , C_3S and merwinite (C_3MS_2), while in PC clinker, it forms C_3S , C_2S , C_3A and C_4AF . (C stands for Ca, A for Al, F for Fe).

Table 9.5. Chemical Compositions of Steel Slag and Portland Cement

Element	Steel slag	Portland cement
FeO	5-30	-
Fe ₂ O ₃	7-9	3
SiO ₂	10-18	22
Al ₂ O ₃	3.3-3.6	5.5
CaO	35-37	64.1
MgO	7-11.5	1.4
MnO	4-6.5	-
V ₂ O ₅	0.87	-
TiO ₂	0.76	-
P ₂ O ₅	1.78	-
SO ₃	-	2.1

9.1.5.1. Incorporation of Steel Slag in Cement

There are two methods for incorporating steel slag in cement manufacture. In the first, the steel slag is calcined in the kiln together with the other raw materials. The steel slag is used as a substitute for lime stone (Kondo *et al.*, 1974). Slag additions of up to 10 % of the raw materials is effective without any detrimental effect on the technical properties of the resultant cement (Sersale *et al.*, 1980).

The second is a non-calcining process. Generally, this is preferred for incorporating steelmaking slag. Steel slag, ground blast furnace slag, PC clinker (OPC) and gypsum are mixed and ground together. An activator like caustic soda, calcium chloride, calcium hydroxide may be added to stimulate slag activity. The materials are ground to a fineness greater than 3500 cm²/g (Idemista *et al.*, 1981). The additions of steel slag are usually in the range of 10 to 55 % by weight of the total materials, with ground blast furnace, ordinary PC clinker and gypsum constituting the remainder (Montgomery and Wang, 1991). The strength of steel slag blended cement may be similar to that of OPC when the incorporated amount of steel slag is lower than 35 % and the content of OPC clinker is greater than 55 % by weight of the constituent materials. If the content of the OPC clinker is lower than 55 %, the strength of steel slag blended cement decreases by 5 % for each 10 % reduction in the amount of OPC clinker (Idemista *et al.*, 1981).

The problem of dimensional instability of the steel-making slag due to the high and variable lime content in BOF slag and their lack of hydraulic activity have been overcome by the use of a new slag forming agent (Conjeaud *et al.*, 1981). This is a synthetic material combining CaO, MgO, Al₂O₃ and Fe₂O₃, abbreviated to C, A, M, F, and thus the name CAMFlux is given to this new material. When this is added to the converter during refining it produces slags with low free lime content and useful hydraulic properties without any detrimental effect on the conversion of iron into steel. In the slag thus produced, the amount of alumina (Al₂O₃) is increased and the amounts of iron (Fe²⁺) and free lime have decreased.

A process to add air cooled blast furnace and steel slags directly to the cement kilns has been described. Called CemStarSM process, it is claimed to have several benefits over addition of slag to the raw mill or addition of granulated slag to the finish mill (Perkins, 2000). The slag needs to be crushed only to 100% passing a 20 mm screen, which makes it less energy intensive. A further benefit of adding crushed air cooled slag to the cement

kiln is that the slag has been calcined in the blast furnace or steel furnace. This results in lower carbon dioxide emission

9.1.5.2. Instant-Chilled Slag

Instant chilling process is a physical method, which modifies the properties of steel-making slag for utilization in the cement industry (Montgomery and Wang, 1991, 1992). It is done in four stages. The first is air cooling where the molten slag is placed on shallow plates to a bed thickness of approximately 100 mm and air cooled for 4 minutes. This is followed by an initial water cooling cycle during which the slag bed is continuously water sprayed for about 20 minutes to produce an end temperature of 500 °C. After water cooling the slag is loaded into slag carts and transported to a spraying station for further spraying for 4 minutes to reach an end temperature of 200 °C. Finally, the slag is placed in a water pool and cooled to around 60 °C to complete the process and it is sent for magnetic screening to separate the iron fraction. The slag is treated in a batch process with a total treatment time of 1.5 to 2.5 hours. This is an environmentally friendly process, producing slag of particle size 30-50 µm with <4 % free lime content. Magnesium oxide occurs as mixed crystals in the solid solution phase. The composition is not deleterious to the volume stability (Montgomery and Wang, 1991, 1992). Considerable benefits have been reported from the use of instant chilled slag as coarse aggregates in concrete. They include increased strength of the concrete, an increase in the modulus of elasticity, a reduction in the brittleness and an increase in the fracture toughness (Montgomery and Wang, 1991, 1992).

9.1.5.3. Oxidation of Slag

Cementitious nature of the steel slag can be enhanced by oxidizing the iron in the slag to the trivalent state, and by quenching the slag to form a partial glass (Murphy *et al.*, 1995; Meadowcroft *et al.*, 1996). The effect of oxidation of iron is the elimination of wustite (see Table 8.3) which deteriorates the cementitious properties of the slag, lowering of melting point, and decrease in alkalinity. Four types of oxidizing slag have been identified (Morino and Iwatsuki, 1999). They are described in Table 9.6.

9.1.5.4. Stabilizing Steel Slag

Stainless steel slags can be stabilized by adding "Carbonated-Aluminated Salts" (CAS), which are cement-based stabilizers containing lime, aluminum sulfate and sodium carbonate. The composition on dry weight basis is PC 50 %, Ca(OH)_2 30 %, $\text{Al}_2(\text{SO}_4)_3$ 15 % and Na_2CO_3 5 %.

The main minerals in stainless steel slag are merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_3$), dipside ($\text{CaMg}(\text{SiO}_3)_2$), magnesium aluminum oxide ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) and magnesium silicate ($\beta\text{-2MgO} \cdot \text{SiO}_2$). The slag has latent hydraulic properties. Mixing CAS with the slag accelerates the formation of $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$. These hydrates are considered to be contributing to the development of strength of stainless steel slag mixtures, thus arresting deterioration of strength due to the expansion of the conventional stainless steel slags (Kamon *et al.*, 1993). Durability of the slag mixture can be enhanced by the addition of a fine grain material, a clay mineral like kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), which increase the density of mixtures (Kamon *et al.*, 1993). Stainless steel slag thus has a potential use as a sub-base coarse material when it is treated with CAS and kaolinite.

Table 9.6. Types of Electric Furnace Oxidizing Slag Aggregates Made by Different Cooling Processes (Morino and Iwatsuki, 1999).

Type of oxidizing slag	Method of cooling processing	Types of aggregates Abbreviation	Abbreviation
Air-granulated slag	Rapidly cooled slag, cooled rapidly from the melting slag to about 200 °C	Only fine aggregate	AGSF
Water-granulated slag	Semi-rapidly cooled slag, by spraying water on 800°C red melting slag	Fine aggregate coarse aggregate	WGSF WGSC
Acid-cooled slag	Slowly cooled slag (at the natural speed)	Fine aggregate Coarse aggregate	ACSF ACSC
Improved slag	Semi-rapidly cooled slag and slowly cooled slag, improved by removing the iron. I	Fine aggregate Coarse aggregate	IWGSF IWGSC

Table 9.7. Mineral Composition of EF Oxidizing Slag Aggregates

Type of slag	Major mineral composition	Minor mineral composition
Air-granulated slag	Wustite (FeC) Magnetite (Fe ₃ O ₄) Iron chromite (FeCr ₂ O ₄) Silicate glass	Magnesioferrite (MgFe ₂ O ₄) Rankinite (Ca ₃ Si ₂ O ₇) Gehlenite (Ca ₂ Al ₂ SiO ₇)
Water granulated slag	Wustite (FeO) Gehlenite (Ca ₂ Al ₂ SiO ₇) Calcium silicate (B-Ca ₂ SiO ₄)	Magnesio-iron-aluminum-oxide (MgFeAlO ₄) Calcium magnesium silicate (Ca,Mg)SiO ₄
Air cooled slag	Wustite (FeO) Calcium silicate (B-Ca ₂ SiO ₄) Gehlenite (Ca ₂ Al ₂ SiO ₇)	Magnetite (Fe ₃ O ₄) Iron chromite (FeCr ₂ O ₄) Wollastonite (CaSiO ₃)
Improved slag	Wustite (FeO) Gehlenite (Ca ₂ Al ₂ SiO ₇) Calcium silicate (B-Ca ₂ SiO ₄) Kirschsteinite (CaFeSiO ₄)	Magnesium-iron-aluminum-oxide (MgFeAlO ₄) Manganese-chromium-silicate (Mn ₃ Cr ₂ Si ₃ O ₁₂)

9.1.6. Uses in Fertilizer

The oxygen refining of high phosphorus pig iron (1.6-1.8 % P) results in a slag rich in phosphorus (see Table 8.3), which is readily assimilated by plants and can therefore be potentially used as a fertilizer supplement when the P₂O₅ content of the slag exceeds 12 %. Phosphorus percentage is usually high in the first slag and it can be used in agriculture. In the final slag, however, phosphorus content is less and it may be

advantageous to recycle. A basic slag also contains trace elements beneficial to vegetable growth such as Mn (2-4 %), Zn (25-80 ppm), Cu (13-60 ppm), Co (2-5 ppm) (Geiseler, 1994). However, the solubility of the phosphate content of the basic slag is negligible, which makes it ineffective as fertilizer. In order to increase the release of P_2O_5 coal and potassium permanganate are mixed with the slag. It is suggested that oxidizing action of permanganate produces soluble organic acids by the degradation of coal. These acids solubilize the phosphate (Singh and Chattopadhyay, 1995).

Sulfur in slag is another important constituent of agricultural use as it is recognized as a nutrient needed in fertilizers. The sulfur concentration of slags is many times greater than that in conventional sources (like ammonium sulfate). Few studies have been conducted on the role of sulfur in plant responses to treatment by slag material. In a study cited by Levonmaki and Hartikainen (2002), the improved availability of sulfur is found to increase the percentage of raw protein in barley grain.

Silicon in slag also influences the growth and health of plants. Silicon is considered to be one of the micronutrients of plants. Normally, plants assimilate silicon in the form of silicic acid, $Si(OH)_4$, which is the dominating species at $pH < 9$. Silicon is also an important microconstituent in human nutrition ((Levonmaki and Hartikainen, 2002).

9.1.7. Application in Soil Conditioning

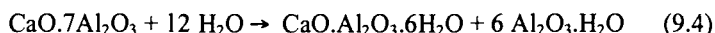
Many types of slag, which absorb phosphate or form insoluble compounds with phosphate have been investigated to suppress the liberation of phosphate from sediment (Yamada *et al.*, 1986, 1987). Adsorption of phosphate on the slag surface and re-dissolution of the adsorbed phosphate from the slag surface depends on the pH of the solution. A suppression mechanism for the liberation of phosphate is based on the following three effects:

1. Effect of materials such as glass beads on the surface of the sediment. The liberation of phosphate from the sediment is considerably suppressed by simply covering the surface of the sediment.
2. Chemical effect of hydrogen sulfide generation in an anaerobic state. The precipitated phosphate of trivalent iron, $Fe(PO_4)$ in sediment is reduced to divalent iron (ferrous) phosphate, $Fe_3(PO_4)_2$ in an anaerobic state and sulfates are reduced to sulfide by bacteria (see Chapter 5 for a discussion of sulfate reducing bacteria.) The sulfide ions generated react with ferrous phosphate and the phosphate ion produced is liberated into the sea water. As the sea sand and slag cover the surface of the sediment, the sulfide ion reacts with the metals (Fe, Mn) on the surface of sea sand and slag, and metal sulfides (FeS , MnS) precipitate on it. The reaction of the sulfide ion with ferrous phosphate on the surface of the sediment does not occur, leading to the suppression of phosphate liberation (Yamada *et al.*, 1987).
3. Adsorption effect due to slag. The granulated slag adsorbs a large amount of orthophosphate, and the adsorption of orthophosphate is related to the surface characteristics of the slag such as porosity.

9.1.8. Acid Neutralization by Steel Slag

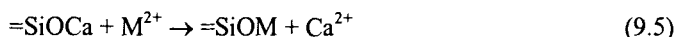
Steel slags have the capacity to neutralize acid and can be used as neutralizers of acidic soils and other wastes, which require to be neutralized before they are disposed off. The neutralizing process is affected by mineralogical composition, in particular, by the hydration of the mineral phases. The main reactions of hydration for calcium silicates and

calcium aluminate lead to the formation of calcium hydroxide and aluminum oxide respectively, which have stronger neutralizing capacity than the silicates and aluminosilicates.



As a result, the acid neutralizing capacity increases with time. Some of the neutralizing reactions may also be controlled by kinetic factors (Yan *et al.*, 2000).

Besides neutralization, slag also has the potential to adsorb some of the heavy metals of acid rock drainage by exchange interaction of the calcium silicate:



In a laboratory study Feng and coworkers (2004) have demonstrated the sorption of toxic metals by slag and separation of the loaded slag by flotation. The slag is flocculated using a polyamine flocculant and floated by sodium dodecyl sulfate.

9.1.9. Production of Fiber and Permeable Blocks from Slag

Fiber, a synthetic mineral wool, has been produced from various types of slag by passing through a fiberizing equipment. Molten slag is dropped onto a spinning wheel. For standard mineral wool, the slag temperature is 1260 to 1650 °C. The synthetic wool and can have iron oxide added to the charge to produce a fiber with better coverage. A pure white fiber is produced by using more carbon in the charge to draw all iron into a silvery pig product. A slag must contain calcium oxide, silica, and certain quantities of slag modifiers like alumina and titanium dioxide. Magnesium oxide and copper oxide are undesirable compounds, the less of either of these metals in a slag, the better quality wool is produced (Philippe and Bennett, 1995).

Fiber is found to leach less than water-cooled slag of the same composition. The reduction in leachability is due to the fact that when a slag cools slowly, the basic calcium aluminosilicate bonds are more perfectly completed and other metals are excluded from this bond. The bonds are now hard to break, but the metals excluded from that bond are easily extracted. Rapid cooling makes the slag much less leachable.

Permeable blocks and pavement bricks have been made from Molten Slag (Nishigaki, 2000). The ash that is produced by incinerating municipal waste is melted at a high temperature and converted into a slag. The slag is passed through mesh of 5 mm. The iron content of the slag, which would cause bubbling is removed by a magnetic separator. Two kinds of blocks are made, one with a single layer of slag, and another with two layers. The base layer consists of slag and sintering accelerator that sinters the slag at temperatures below the melting point of the slag, at the ratio 91:9. An organic binder, carboxy methyl cellulose (a polymeric compound) is added for molding.

For the production of pavement brick, after removing the ferrous metals by magnetic separator, the slag is crushed and passed through 1.0 mm sieve. The slag is then mixed with grog, ceramic gravel and clay in the ratio 20:35:25:20. To this mixture, 2 % of pigment is added. It is then kneaded and blended by a mixer and molded by a 200 ton

friction press. The bricks are then dried for about 48 h at 80-150 °C and sintered in a tunnel kiln for about 80 h at 1200-1230 °C.

9.1.10. Use of Steel Converter Slag as Nickel Adsorber (Ortiz *et al.*, 2001).

The iron oxide, principally magnetite (Fe_3O_4), in steel converter slag has adsorbing properties. At $\text{pH} > 6.5$ it adsorbs several heavy metal ions as they bind with the OH groups at the iron oxide surface. The adsorption studies on nickel have shown that 1 g of converter slag used as adsorbent material can reduce the nickel concentration from 20 to 1.57 mg/L. The low pH adsorption system and increase in temperature, however, lower the adsorption efficiency.

9.1.11. Production of Porous Slag Blocks by Carbonation

As the slag contains calcium oxide as one of the principal components, it reacts with carbon dioxide and the reaction leads to the formation of hardened blocks with some

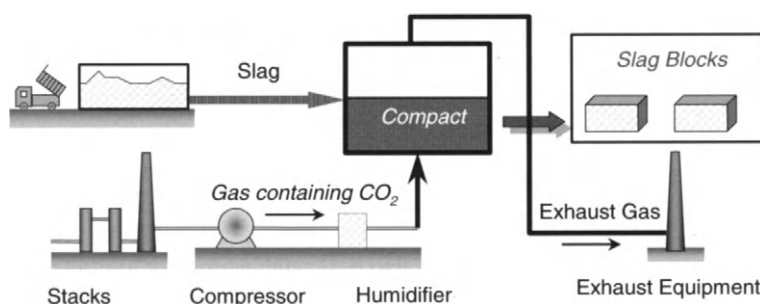


Figure 9.5. Schematic diagram of experimental apparatus for producing carbonated slag block (Miyata *et al.*, 2004)

desirable properties. The process is called carbonation. Investigators in Japan have developed a process to produce large steelmaking slag blocks, which can be used as artificial fish reefs and seaweed cultivation beds (Miyata *et al.*, 2004).

The slag, produced in the dephosphorizing process, is ground to recover metallic iron and sieved to obtain particles < 3 mm diameter. Carbonation is done in an apparatus shown schematically in Figure 9.5.

A mold with dimensions 1.0 x 1.0 x 1.2 m is used to produce 1.0 x 1.0 x 0.5 m blocks. Exhaust gas comprising 20 % carbon dioxide, saturated with water vapor is introduced into the mold through the holes at the bottom of the mold at a pressure of 0.106 Mpa at rate of 0.1 m³/mm for 5.5 days. After carbonation, cylindrical samples are taken from the block using a core boring machine to measure compressive strength and porosity.

The main carbonation product is calcite (CaCO_3). Miyata and coworkers (2004) have found that the carbonated blocks do not show cracks even after they are placed on the sea bottom at depth up to 1.5 m. They are superior to concrete blocks when used as the base material for coral reefs.

9.1.12. Nickel and Copper Slag as Secondary Raw Material in Carbon Steel Making

Production of copper and nickel by pyrometallurgical treatment of their sulfide minerals generate iron containing slag, the iron derived from chalcopryrite (CuFeS_2) or

pentlandite (NiFeS). The quantity of slag thus produced is approximately twice as much as the quantity of produced copper and nickel (Sanchez *et al.*, 2004). After enrichment by pyrometallurgical treatment, the slag would contain about 42% iron as a silicate ($2\text{FeO} \cdot \text{SiO}_2$). Using calcium carbide as reducing agent, the slag is treated in an electric arc furnace to produce iron (Eetu-Pekka *et al.*, 2005). One major problem for this process is likely to be the contamination of steel by copper. It could be solved by developing methods to extract the copper (and any other metal) from liquid steel (Emi, 2004).

9.1.13. Other Potential Uses of Slag

The properties of slag can be taken advantage of in applications where chemically inert material with characteristics of cement are desired. Potential use of steel industry slag to construct landfill covers has recently been described (Herrmann *et al.*, 2005). It serves to form protective layer of the cover. An important requirement for such application is that the material must pass leachability test (see Chapter 2). Some of the EAF slags tested show high mobility of molybdenum and are not suitable. Ladle slag is also problematic as hardens rapidly. This can be decelerated by mixing EAF slag (free from molybdenum).

9.2. Processing of Dross

Another byproduct in many metallurgical operations is called dross. (See Chapter 6). It is a byproduct of metal industry, but it could contain up to 70 % valuable metal. The dross could be an environmental hazard if it is disposed of in landfills. When it gets wet, reaction with water produces hydrogen, ammonia, methane and ethylene and causes copper to leach out. The treatment and disposal methods practiced until recently are often inefficient and not environmentally friendly as considerable amount of metal is lost to the surroundings. Technologies to reclaim the metal contents of the dross are required.

9.2.1. Treatment of Dross in Aluminum Industry

It is estimated, for every 1,000 tons of aluminum scrap processed, 760 tons of secondary aluminum, 240 tons of dross residues and 3 tons of bag-house dust are produced. As aluminum is easily oxidized, a barrier of the metal oxide quickly forms on all new surfaces of aluminum because the spacing in oxide and substrate are the same. This same aluminum oxide can equally well form on the surface of molten aluminum if not protected by slag or covers of flux. As the oxide layer gets thicker in the presence of heated air, it is important to submerge scrap with large areas as quickly as possible in order to minimize oxidation. Reverberatory furnaces do not process scrap with surfaces which are too dirty. Even with this protection, however, aluminum oxidation occurs to some extent, and both aluminum metal and its oxide are absorbed by the slag and the flux covers to form "dross".

The oxide formation could be reduced using a flux that is molten at the furnace temperature and would float on the molten aluminum. This flux acts as a barrier between the metal and atmospheric oxygen, thus reducing oxide formation and lowering the production of dross and increasing aluminum recovery. Salt and potash are widely used for this purpose, but they lead to environmental consequences, as will be discussed further.

Three types of dross are identified by the aluminum industry:

White dross - produced by the primary industry, metal smelters, extruding plants, sheet

mills, foundries, die casters. The furnaces at these operations are run without fluxing, and the dross skimmed from the furnace is grey or metallic white. It contains approximately 80 % aluminum, primarily as oxide. However, oxidation (referred to as "thermiting") will occur rapidly at the high temperature and the absence of the flux. If not controlled, all of the metal could convert to oxide. It can be controlled by an oxygen-free environment.

Black dross is generated by secondary aluminum smelters using open hearth reverberatory furnaces for melting old castings, clippings, turnings and used cans. A salt potash flux is used in the open hearth to reduce the amount of oxidation on the exposed metal. At the high molten temperatures, the flux melts and acquires dark color, hence the name "black dross". The flux minimizes thermiting; however, it dilutes the dross and the metal recovery is only 12-18%. It contains 20-50 % oxide, and 40-55 % chloride fluxes.

Salt cake. Recovery of aluminum from white and black dross is done in molten salt rotary furnaces. A salt flux, commonly mixtures of sodium and potassium chlorides, with a small amount of cryolite (a sodium-aluminum fluoride) is used in the furnace to maximize the recovery of the metal, and the spent flux is discharged from the furnace. This residue, containing 3-5% metal, 15-30 % oxide, and 50-75 % chloride is referred to as salt cake and is normally disposed off in landfills. - produced by the rotary furnace and contains 3-5 % aluminum metal, fluxes, which are.

9.2.1.1. White Dross Treatment

Two principal methods are physical separation of aluminum from dross residue in hammer mills; and melting in rotary salt furnaces. The recovery of other products from dross is a natural extension of the crude process involving size reduction, washing, and screening. The process has taken several forms, all essentially the same in principal and differing only in the design of selected unit operations.

Arc Plasma Process. In this process, the plasma consists of nitrogen or other gas heated to temperatures approaching 5,000° C while passing between the poles of an electric arc. (See Chapter Section 3.4, Chapter 3 for details of Plasma Process). Both air plasma and nitrogen plasma have been used. The heated gas transfers heat to the charge in the rotary furnace. The non-metallic fraction resulting from the treatment process, primarily aluminum oxide and magnesium oxide, and aluminum nitride (produced with nitrogen plasma) is non-toxic. The principal advantage of the plasma process is that it does not require salt to be present as flux and therefore, a clean product, not requiring further processing is obtained (Lavoie *et al.*, 1990).

The process is used for large scale treatment of dross. About 18,000 tons of dross, mainly white dross, are treated per year in a plant of Alcan in Quebec, Canada. The system is easy to use with minimum maintenance requirement and electricity consumption of approximately 250-300 kWh/tons of dross (Breault *et al.*, 2000). Black dross has been processed on a small scale only. As the aluminum content of black dross is generally low, it has to be milled and screened before charging to concentrate aluminum (Lavoie and Lachance, 1995).

The arc plasma process recovers 65 % of aluminum metal in the dross. The remaining is distributed in the non-metallic phase (NMP), which contains 12 % metallic aluminum, 52 % alumina, 20 % aluminum nitride. The total alumina equivalent amounts to 99 %. This is taken advantage of to produce calcium aluminate, a useful industrial product. It is obtained by sintering NMP with limestone at a maximum temperature of 1300 °C. Water is added before the material enters the kiln to hydrolyze aluminum nitride to oxide.

Calcium oxide and aluminum oxide react producing calcium aluminate, CaAl_2O_4 . This is used in the ladle treatment of steel, where it serves as heat barrier and slag conditioner. It is also used for sulfur removal from molten iron.

Rotary Arc Furnace Process. Another pyrometallurgical process developed by Hydro-Quebec in Canada, known as DROSCAR process (Drouet *et al.*, 1995) uses a direct current electric arc instead of a plasma torch, fuel or gas burner; Figure 9.6.

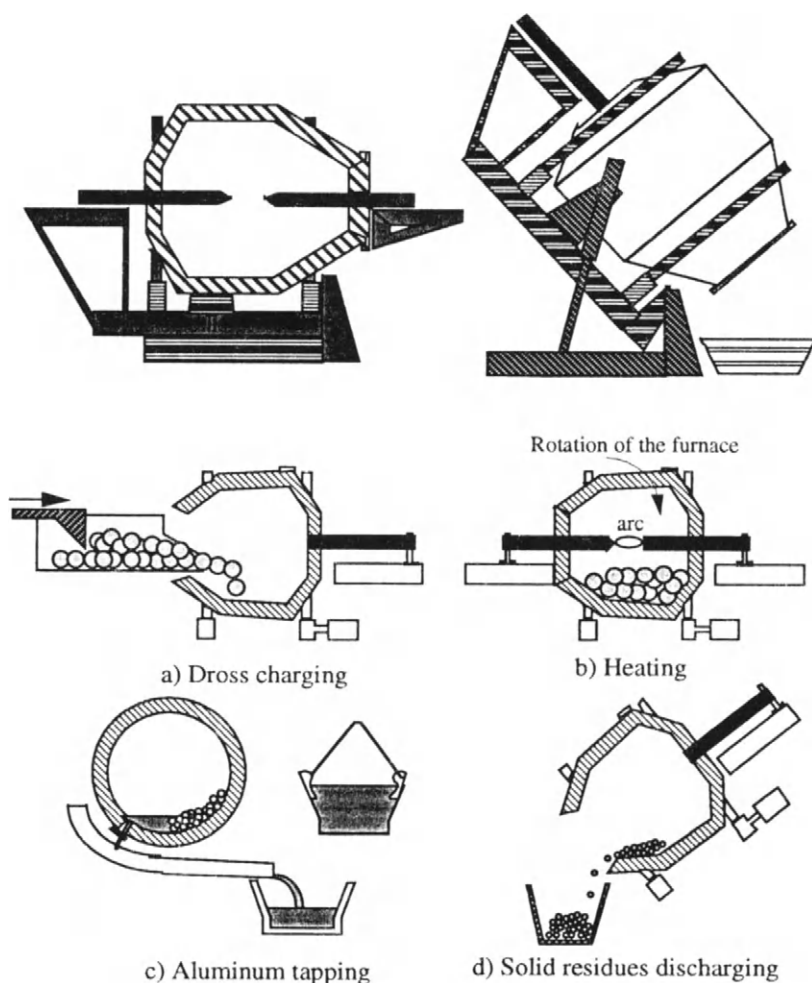


Figure 9.6. Air rotary arc process. A. Tilting rotary arc furnace. C. Phases of the treatment process. (Drouet *et al.*, 1995)

A dc electric arc stretched and maintained between the two graphite electrodes is used to heat the charge above the melting point of aluminum. The furnace rotates during heating of the dross to provide mechanical stirring, which breaks the oxide film on the droplets of aluminum present in the dross, and promotes agglomeration of the molten metal. It also prevents the formation of hot spots on the charge or refractories, and improves energy

transfer. When heating is completed, the metal is tapped from the furnace through a hole on the side. The solid residues remaining in the furnace from a greyish powder removed by tilting the furnace forward while slowly rotating it.

Up to 94 % aluminum is recovered by this process. It also has several other advantages including greater energy efficiency, reduced gaseous and particulate emissions (3 m³ per ton of dross treated as compared to 30 m³/ton for the air plasma process). No salt is added to improve recovery. As the process use a graphite arc, there is no water-cooled part in the furnace, thus potential hazard by any possible water leaks is eliminated. The solid residues are less contaminated than those produced by an air plasma torch. The residues could contain heavy metals such as lead, cadmium, chromium, depending upon the metal being melted, ingot or scrap.

Other Pyrometallurgical Processes. Several modified rotary barrel processes have been developed, which avoid the use of salt flux to prevent oxidation of aluminum. In one process described by Geus and coworkers (1995), when the oxidation rate tends to increase at the point of incipient melting of aluminum, the burner is turned off, and a mixture of argon and oxidizing gas is fed into the furnace. The proportions of the gases and the rate at which they are fed into the furnace are controlled to give a desired temperature for the best agglomeration of the metal in the charge. When the maximum amount of metal has been agglomerated, the furnace is tilted forward to decant the liquid metal.

In another process, known as ALUREC (Gripenberg *et al.*, 1995), oxidation of the metal is prevented by atmosphere control, thus eliminating the use of salt flux. Instead of an air-fuel burner, an oxy-fuel burner is used. This produces a higher temperature (2700 °C as compared to 1900 °C with air-fuel burner.) This results in a smaller flame and direct contact with the charge is avoided. Also, there is less convection and less mass transfer between oxy-fuel flame and the charge. These features keep the oxidation of aluminum under control. Other advantages of the process are higher thermal efficiency and the absence of nitrogen in the exhaust gases, which can potentially produce some aluminum nitride, affecting the recovery of aluminum.

An electric energy based process to recover metal will be described in Section 9.2.2.

9.2.1.2. Black Dross and Salt Cake Treatment

Several methods have been used for the treatment of black dross and salt cake, leading to the recovery of by-products. They include physical separation methods (see Chapter 3), hydrometallurgical methods, pyrometallurgical methods and solar ponds.

Physical Separation. Aluminum dross is crushed, ground, and physically separated into non-metallic and metallic fractions, either by dry or wet screening. The undersized, non-metallic fraction is disposed of in landfills, the intermediate sized particles are sold as exothermic hot topping to foundries, and the coarse fraction is remelted.

Hydrometallurgical Processing. The dross is crushed and screened into three fractions. The coarse fraction is sent back to the crushing and screening circuits. The fines contain virtually no aluminum and are sent to a leaching plant for brine extraction and recovery of aluminum oxide by filtration. The brine, containing sodium and potassium chlorides in solution, is purified to recover ammonia, calcium sulfate, and magnesium chloride. It is then dewatered in a flash evaporator/crystallizer to produce salt crystals used as flux in melting furnaces.

Pyrometallurgical Processing. This process employs a rotary slag furnace (directly

fired rotary-reverberatory furnace) to remelt salt slag (partially concentrated by crushing and screening). It is called Rotary Salt Furnace (RSF) process. The furnace consists of a horizontal, refractory-lined cylinder, which is rotated during the process. The energy is supplied by an air-fuel flame entering at one end. The exhaust gases leave through a duct at the opposite end of the furnace. Large volume of the flame leads to contact between the flame and the charge and to mass transfer between the flame flue gases and the charge. This could cause oxidation of aluminum. A salt flux, a mixture of sodium and potassium chlorides is added to control the oxidation. The salt mixture is at near the eutectic point to provide low temperature melting. The flux covers the metal and prevents oxidation and also dissolves or suspends the oxides in the dross. The amount of flux added depends upon the oxide content of the dross. As an example, 500 kg flux is added to 1000 kg of dross containing 50 % aluminum metal (Gripenberg *et al.*, 1995). At the end of the process, the separated molten metal remains at the bottom of the furnace and the liquid non-metallic product (NMP) mix of salts and oxides floats at the top. The aluminum and NMP are removed from the furnace through separate tap holes.

A major drawback of this process is the non-metallic byproduct, referred to as salt cake, mainly a mixture of oxides, aluminum nitride and metal salts. The salt cake is a growing environmental problem. The costs of disposal keep increasing and in some countries the disposal is prohibited. Methods for the processing of the salt cake product by separating the components in it has been recently developed; see Section 9.2.3. New salt-free methods have been developed in recent years.

9.2.1.3. Salt-Free Processing of Hot Aluminum Dross

This innovative process, described by Drouet and coworkers (2000) makes possible in-plant recovery of aluminum. It is named DROSRITE process, in which hot dross is charged to a refractory-lined rotary furnace, immediately after skimming from the aluminum holding furnace. The furnace is sealed and maintained under an argon atmosphere. The furnace is heated by the controlled reaction of oxygen with residual aluminum contained in the dross residue, after the recoverable metal is tapped. The process operates in five steps: charging, processing, metal tapping, furnace heating and discharging the residues. In the charging step, the furnace, preheated between 800 and 900 °C is flushed with argon. The door of the furnace is opened and the dross discharged. The door is then closed. In the processing step, the furnace cavity is purged with argon. The furnace is rotated as necessary to gently tumble the charge, for approximately 15 to 430 minutes. By this tumbling energy from the refractory walls of the furnace is transferred to the charge. In the third stage, the tap hole is opened, and the metal is poured into the receiving vessel or ladle. In the fourth stage, a controlled amount of oxygen is injected into the furnace cavity, which burns some of the non-recoverable aluminum contained in the residue. When the temperature reaches 800 to 900 °C oxygen injection is stopped. This converts the aluminum in the dross to aluminum oxide, the reaction generating a large quantity of heat, 1,700 kJ/mole, which amounts to 8.7 kWh per kg of aluminum reacted or 9.8 kWh per g of oxygen. This serves to heat 7.7 kg of residue and the refractory wall of the crucible. In the last stage, purging with argon is repeated, the door of the furnace is opened and the residue is discharged. The furnace is ready for the next cycle.

An industrial unit of the process is typically installed in close proximity to the casting department of an aluminum plant. In addition to efficient use of the reaction heat

generated, the DROSRITE process yields high metal recovery, does not require addition of a salt and does not produce salt cake requiring disposal. Other environmental benefits are no production of carbon dioxide, nitrogen oxides and nitrides. The process has little off-gas. The principal product is suitable for the production of calcium aluminate (CaAl_2O_4) or for other value-added use.

9.2.1.4. Aluminum Dross for Aluminum Sulfate

Primary aluminum dross containing aluminum oxide is a potential inexpensive raw material to manufacture aluminum sulfate, a useful industrial compound. The oxide is separated from the metal fraction and reacted with sulfuric acid to produce aluminum sulfate, from which alum, which is a double salt of potassium and aluminum sulfates, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ is manufactured.

Aluminum metal separation from salt cake has been described by Shen and Forssberg (2003). The first step is a dry separation of metallic aluminum from oxides and salts. Aluminum is ductile, but oxide and salt aggregates are brittle. This difference is used to separate the metal from oxides and salts by multi-stage crushing and screening; see Figure 9.7. By this separation, clean aluminum metal pieces with approximately 7 % yield can be obtained. The oxide and salt powder from the first step are then leached with water. The oxides are not soluble while the salts dissolve. The solid-liquid mixture is pumped into a thickener. The underflow is filtered and washed with recycled water. The clean oxides are recovered. The overflow and the filtrate are salt-rich solution, which is sent to evaporation and crystallization to recover a salt product.

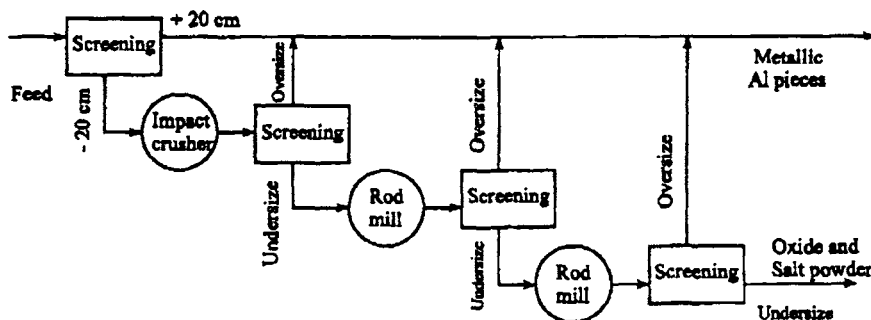


Figure 9.7. Separation of aluminum from salt cake ((Shen and Forssberg, 2003)

9.2.1.5. Aluminum Recovery from Dross by Flotation

A laboratory study by Soto and Toguri (1986) has shown the potential to recover aluminum metal from dross by floating the metal using potassium amyl xanthate as collector. Aluminum metal is not floatable by xanthate, but if the surface is coated with a film of copper it becomes floatable as xanthate is adsorbed at the copper surface making it hydrophobic. The copper film on aluminum is created by cementation reaction, treating the dross with cupric sulfate solution, whereby cupric ions are reduced to copper metal by aluminum: $3 \text{Cu}^{2+} + 2 \text{Al}^0 \rightarrow 3 \text{Cu}^0 + 2 \text{Al}^{3+}$

Using 600 g/ton copper (from cupric sulfate solution), 100 g/ton amyl xanthate and 100 g/ton frother up to 80 % aluminum could be recovered with a grade of about 70 % metal. Prior to the addition of cupric sulfate, the dross is scrubbed for dispersion of the

aluminum oxide in the dross.

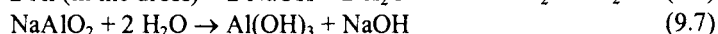
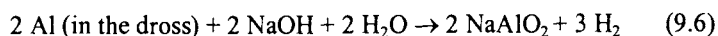
9.2.2. Potential Applications of Slag and Dross from Aluminum Industry

A novel potential application of aluminum dross in steel-making industry has been investigated by Yang and coworkers (2004). It makes use of calcium aluminate (CaAlO_2) produced from the dross as fluxing material in place of lime-calcium fluoride (CaO-CaF_2) which is commonly used in current practice.

In the first stage, the dross is treated by an electric energy-based process to recover aluminum. Electric energy is converted to heat by plasma torch or graphite electrodes. This is claimed to be more efficient than using plasma with the advantages of not requiring water cooling, not producing nitride in the secondary dross, and the arc system is said to require less specialized personnel for operation and maintenance. The process is also more energy efficient and yields high metal recovery. The non-metallic solid product occurring at the end of the process is discharged by mechanical scraping. This secondary dross is used for making calcium aluminate by sintering with limestone (CaCO_3) in a rotary kiln. Tests conducted by Yang and coworkers (2004) have shown that the calcium aluminate flux thus produced has high melting rate and good desulfurization capacity. It could well replace calcium fluoride as flux in steel production. This would have dual benefit. In addition to more complete use of the dross produced in aluminum industry, the replacement of calcium fluoride will achieve a desirable environmental objective of reducing the use of a fluorine compound, which has potentially adverse effect on environment.

Potential uses of the non-metallic portion (NMP; see Section 9.2.1.2) of the dross have been investigated by Tougo and coworkers (2000). The NMP is heated at about $1,400^\circ\text{C}$ in a rotary calcining furnace. High temperature treatment leads to the formation of change in the crystal form of alumina. The new material contains 75 % α -alumina and 20 % spinel. This composition imparts high degree of hardness and abrasion to the material and it can be used as a road aggregate.

Another potential use is in castable refractories. This is described in a laboratory study by Park and coworkers (2002) with black dross with low sodium and potassium content (as only a small amount of salt flux was used in the melting of the scrap). The aluminum in the dross is first recovered as aluminum hydroxide by leaching with 10% sodium hydroxide and hydrolyzing the sodium aluminate with the addition of aluminum hydroxide fines as seed material. The reactions are as follows:



There is potential to recover the hydrogen gas generated in the leaching process. The sodium hydroxide is recycled.

The residue from the leaching step is roasted in a rotary kiln at 900°C to convert the residual metal component into the oxide. The roasted residue is mixed with several types of aggregates and alumina cement to make it into castable refractory.

Other potential applications of aluminum dross are shown in Figure 9.8.

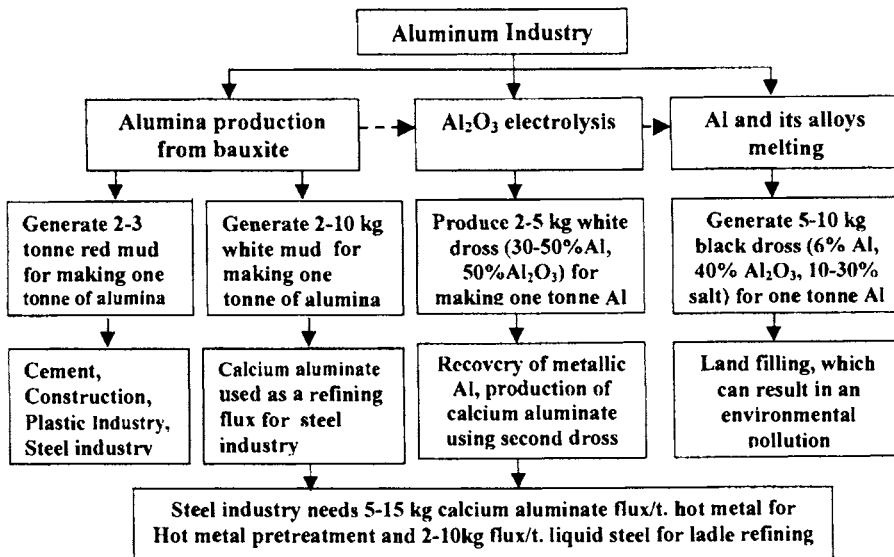


Figure 9.8. Sources of slag and dross from aluminum industry and their potential applications (Yang *et al.*, 2004)

9.2.3. Recovery of Salt Flux from Salt Slag

The salt flux used in the dross treatment processes generates a salt slag, which, if not processed, would be an additional waste, with potential environmental liability connected with land filling. It is very desirable to develop methods to reclaim the salt from the slag waste to reduce environmental consequence. One approach, developed in Tennessee is to recover salt by leaching in water and evaporating (Russell and Sweeney, 2000).

A process flow sheet is shown in Figure 9.9. and one for the treatment of slag in Figure 9.10. Milled residue is leached in a rotary mixer with water. The mixing process generates heat (to a temperature of about 63 °C, which facilitates dissolution of the salt. Minimum amount of water is used to produce brine concentration of approximately 25 %. The leaching process continues for an established period of time that varies with the material being processed, after which the leach slurry is fed to a centrifuge to concentrate the brine. In the centrifuge, the oxide materials may be washed to lower the non-metal product (NMP) cake salt content to approximately 2 % by weight chlorides to nearly 0.5 %. The salt containing wash water is captured and provides make-up water for subsequent leaching steps. After the brine and wash water are removed, the NMP is dewatered to approximately 15 % moisture by spinning the cake at higher speed. The dewatered cake is then peeled out of the centrifuge and on to a conveyor for subsequent use or disposal. Concentrated brine from the centrifuge next passes to a clarifier thickener to remove the fines present in the centrifuged solution. The solution has a pH of 10 due to the presence of ammonia. Polyelectrolyte flocculants suitable for high ionic strength and high pH are used to facilitate clarification. Sludge is pumped from the bottom of the clarifier and is dewatered by a rotary vacuum filter to aid disposal. Clarified brine is pumped into storage tanks and processed by the evaporation plant. This separates the two

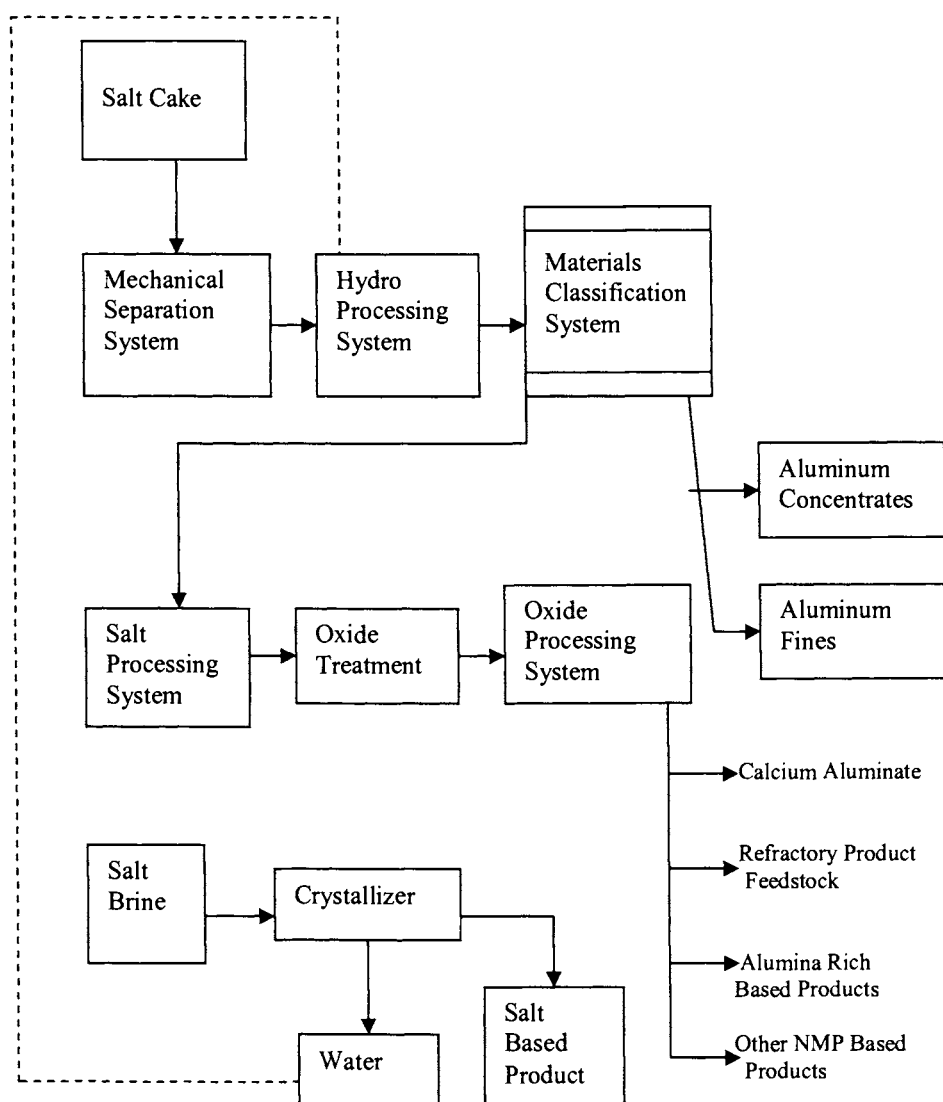
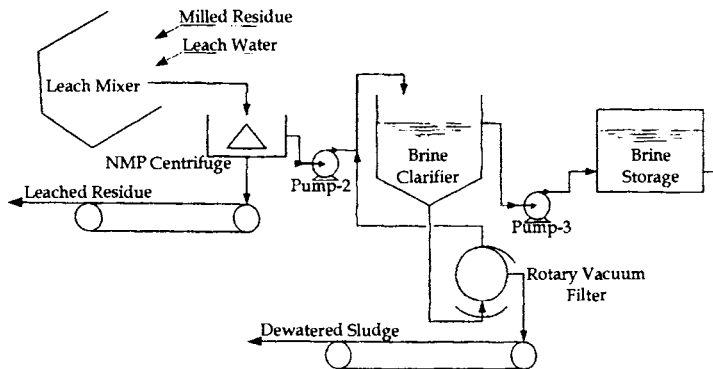


Figure 9.9 Generalized flow diagram for the processing of salt cake produced in the treatment of aluminum dross (Pickens 2000)

processes (leaching and evaporation) allowing for more flexible operating schedules. Clarified brine is next pumped into a submerged combustion evaporator. Excess combustion air is used. The evaporator operates at 99 °C. Salt precipitated is removed by constant circulation through crystallizer tanks, which provides cooling and lower velocities to allow the salt formed to accumulate in their conical bottoms. The salt slurry is then sent to a centrifuge for dewatering and recovery. The dewatered salt retains approximately 165 % moisture. It is mixed with potassium chloride (about 10 % of the

recycled salt weight) to produce a desired mixture and then dried to a moisture content of approximately 5 %. This material is suitable for re-use in the furnaces. It is estimated that approximately 65 % of the salt present in the residue is recovered, giving a produce containing 68 % sodium chloride and 30 % potassium chloride and 2 % trace components including sulfates, and salts of barium, strontium, magnesium, copper, iron, lead, manganese and zinc.

Leach Plant



Evaporation Plant

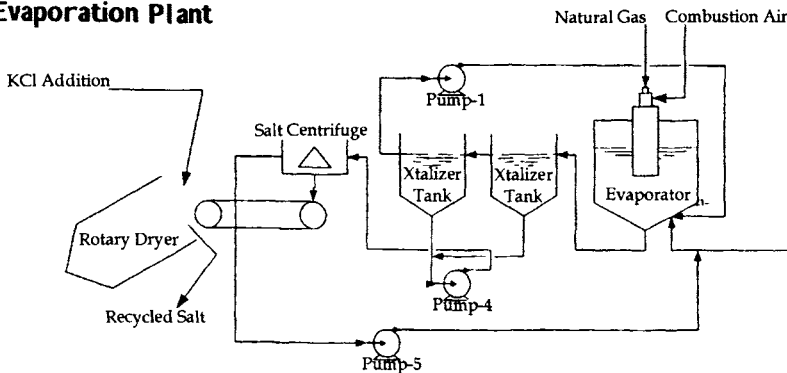


Figure 9.10. Flow diagram of process for recovering salt flux from aluminum salt slag (Russell and Sweeney, 2000)

9.2.3.1. Recovery of Salts from Zinc Solder Dross

Zinc solder dross contains tin and lead, about 15 % each, about 0.4 % aluminum in addition to about 65 % zinc. There is significant potential for reclaiming the metals as their salts by acid leaching. A process with two stage sulfuric and hydrochloric acid leaching followed by selective separation/precipitation of the salts has been described by Barakat (1997). A flow chart of the steps is shown in Figure 9.11.

The dross is leached in 3 % sulfuric acid with acid to solid ratio of 20 mL/g at 45° C for 1 hour. This leaches all zinc as sulfate. The leach residue containing lead and tin is filtered and leached with 5 M HCl containing a small quantity of nitric acid as an oxidant with acid to solid ratio of 10 mL/g at 80° C for about 1 1/2 hour. Aluminum is recovered

from the first leachate as calcium aluminum carbonate by treating the treating the sulfate leachate with limestone at pH 4.8. Zinc is recovered as zinc sulfate crystals. It may also be precipitated as zinc carbonate by mixing with sodium carbonate. The hydroxides of lead and tin are leached with 5 M hot hydrochloric acid. About 73 % of lead is recovered as lead chloride by cooling the leach products down to room temperature. The remaining lead is recovered as lead hydroxide at pH 9.5. Tin is recovered as hydrated yin oxide by treatment with caustic soda. By this process, over 99 % of each of the metals are recovered as their compounds.

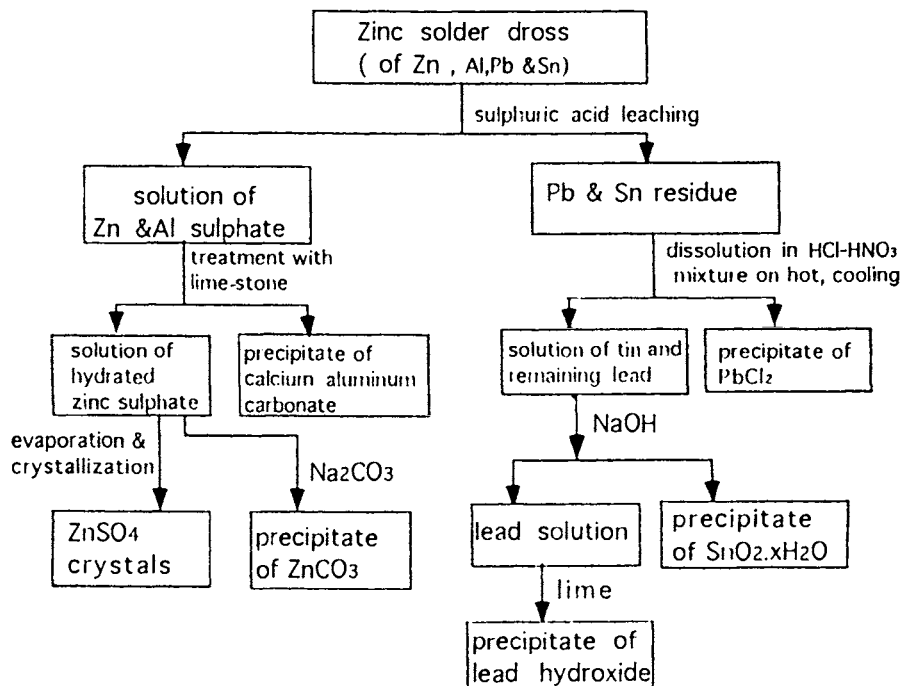


Figure 9.11. Flow chart for the recovery of salts of zinc, aluminum, lead and tin from zinc solder dross (Barakat, 1998).

Similar leaching methods for the recovery of zinc as chloride, sulfate or acetate from fine fraction of zinc dross have been described (Rabah and El Sayed, 1995). The optimum conditions are in the range of 1.1 - 1.3 times (on stoichiometric basis) acid, a solid to liquid ratio of 1:6-1:7 at a temperature in the range 60°-80° C and leaching time of 30-60 minutes. Zinc extraction up to 99 % has been achieved.

9.3. Processing of Fly Ash

Fly ash is generated in a number of incineration processes, where industrial or domestic (municipal) wastes are incinerated to reduce the volume by about 90 %. It also reduces the chemical reactivity of hazardous organic compounds and produces energy, typically in the form of steam, which is marketable. The incineration processes, however, generate two main environmental problems; it generates solid and gaseous reaction

products. The primary problems associated with toxic gases like sulfur dioxide, nitrogen oxides and dust removal are well controlled, but the treatment of heavy metals require application of techniques of metal recycling.

Fly ash produced in the combustion of lignite is composed of predominantly silt-sized, spherical, amorphous ferro-aluminosilicate minerals (Adriano *et al.*, 1980) and is characterized as having low permeability, low bulk density and high specific area. Two major classes of fly ash are specified on the basis of their chemical composition resulting from the type of coal burned. These are designated Class F and Class C. Class F is fly ash normally produced from the combustion of anthracite or bituminous coal. It contains silica, alumina and ferric oxide making a total of 70 %. Class C is produced from sub-bituminous coal and lignite, and also from bio-fuel combustion in metallurgical furnace and contains silica, alumina and ferric oxide to a total of 50 %. Class C fly ash has cementitious properties, whereas Class F is rarely cementitious when mixed with water alone.

9.3.1. Use of Fly Ash to Control Acid Generation from Sulfidic Wastes

Due to its high calcium content, mainly as oxide, hydroxide and carbonate the class C fly ash has significant neutralization capacity, and is therefore a potential inexpensive neutralizer. This has been investigated for counteracting the acid generating potential of mine waste, producing acid rock drainage (Mylona *et al.*, 2002; Xenidis *et al.*, 2002) (Occurrence of acid rock drainage will be discussed in Chapter 10). Experiments were conducted in columns filled with tailing material and fly ash. Deionized water was passed through the column and the leachate collected over a period of time. The addition of lignite fly ash to sulfidic tailings from a source in Greece at a low amount (10 % w/w) is found to increase the pH of leachate to 9.6-9.0. In a control run, with no fly ash, the pH is 4.5. The higher pH resulting from treatment of the tailings with fly ash effectively inhibits the dissolution of zinc and manganese. Calcium and sulfate are the major ionic species in the drainage of fly ash treated tailings.

A similar application of fly ash generated from bio-fuel combustion to form a dry cover on mine tailings has been investigated Isaksson and Lindgren (2005). It serves to minimize oxygen diffusion into the tailings thus preventing the formation of acid rock drainage. The fly ash used for this application should, however, pass environmental leachability test (Chapter 2) and should not generate toxic metal ions. It is mixed with other components, sewage sludge and bark waste to increase alkalinity and provide nutrient for the growth of vegetation on the cover. This application is specially useful in the reclamation of abandoned mine sites.

9.3.2. Metal Recovery from Fly Ash

Incineration process produces two waste products: bottom ash and primary fly ash (PFA). Bottom ash is seldom classified as hazardous and is disposed without further treatment in a sanitary landfill. On the other hand, fly ash, collected by electrostatic precipitators or bag filters, is often hazardous due to high content of zinc and lead (Warren *et al.*, 1993).

One of the methods of treating fly ash, which makes it a useful by-produce is melting at high temperatures in a furnace to convert most of the ash into slag consisting of silica, aluminum, iron and calcium and immobilize small portions of the heavy metals. The slag is used in road construction (see Section 9.1.4). During the melting process, the majority

of the heavy metals are vaporized as volatile metal chlorides and concentrated in newly formed fly ash from the furnace, called secondary fly ash, SFA. This method is now used in Japan on a large scale (Nagib and Inoue, 2000). As some of the metals, especially zinc and lead are present in SFA in concentrations sufficient for economic recovery, SFA could be considered as an "artificial ore" and is used as feed material to some smelters to produce lead and zinc. However, if the concentration of chloride ion is high, the SFA is not acceptable for smelting processes. In such cases, acid or alkaline leaching followed by solvent extraction is an alternative recovery process. The leach residue could be processed into a bound road construction material.

Table 9.8 shows typical chemical compositions of PFA and SFA. X-ray diffraction analysis suggests that majority of zinc occurs as amorphous compounds (since no characteristic peak of any known zinc compound is detected) while lead occurs as lead chloride and sulfate.

Table 9.8. Chemical Analysis of Primary, Secondary Fly Ash (Nagib and Inoues, 2000).

Element	Zn	Fe	Pb	Mg	Al	Na	K	Ca
PFA	0.805	1.37	0.12	1.64	3.92	5.97	4.90	42.11
SFA	40.18	2.12	9.7	0.06	1.85	11.48	7.95	0.23

9.3.2.1. Recovery of Vanadium and Nickel

Power generation industry where heavy oil is used produces fly ash as a solid residue. It contains vanadium oxide (typically 3 % V_2O_5) and nickel oxide (about 1 % NiO). The residual carbon level in the fly ash is very high, about 80 %. Studies conducted Abdelatif (2002) have shown significant potential to recover the two metals by pyrometallurgical treatment of the fly ash.

The fly ash is dried, decarburized and desulfurized in a large muffle furnace for about 16 hours at 1000 °C. About 150 kg of this pretreated fly ash is then screened to -1mm to remove alumina and silica. Next, it is mixed with ferrosilicon or aluminum as reducing agent and lime as flux. Test results suggest aluminum to be a better choice as it leads to lesser energy losses, higher metal extraction and better quality of alloys, ferrovanadium and ferronickel.

Reduction of the metal oxides in fly ash to produce ferro-vanadium and ferro-nickel has been described by Pickles and Alcock (1983). The operation was carried out in an extended arc flash reactor, which generates a large volume of hot plasma. Fly ash with carbonaceous reductant is heated to 800 °C in 3 minutes. Nickel oxide and ferrous oxide are partially reduced by the counter current flow of reducing gases within the lower hearth zone. On passing through plasma zone at temperature exceeding 2000 °C, the charge is melted and the reaction proceeds at extremely fast rates. Metal and slag phases collect in the hearth where reactions are completed. Reduction mainly occurs in the slag phase. The slag and metal are tapped through a hole into a cast iron mold. Ferro-nickel is produced at 15 kW and ferro-vanadium at 25 kW.

9.3.2.2. Metal Recovery from Secondary Fly Ash

A typical primary fly ash, PFA and secondary fly ash, SFA, from a source in Japan have been processed by leaching to recover the metals (Nagib and Inoue, 2000). Acid leaching (HCl) is found to be more effective than alkaline leaching. By leaching in 10 %

hydrochloric acid, 62.5 % Zn and 39.5 % Pb from PFA and 94 % Zn and 77 % Pb from SFA are leached. By 20 % acetic acid 62 % Zn and 94 % Pb from PFA and 97 % Zn and 98 % Pb from SFA are leached. But, acetic acid also dissolves some impurities such as iron, magnesium and aluminum. Alkaline leaching has the advantage that it dissolves only Pb and Zn from the fly ash leaving all other impurities in the solid residue. Alkaline leaching of SFA with 3 N sodium hydroxide followed by washing of the residue using 5 % hydrochloric acid dissolves 98 % lead, and 69.6 %. In place of the acid when washing is done by water 81.4 % lead and 35.3 % zinc are dissolved from SFA. Figure 9.12.

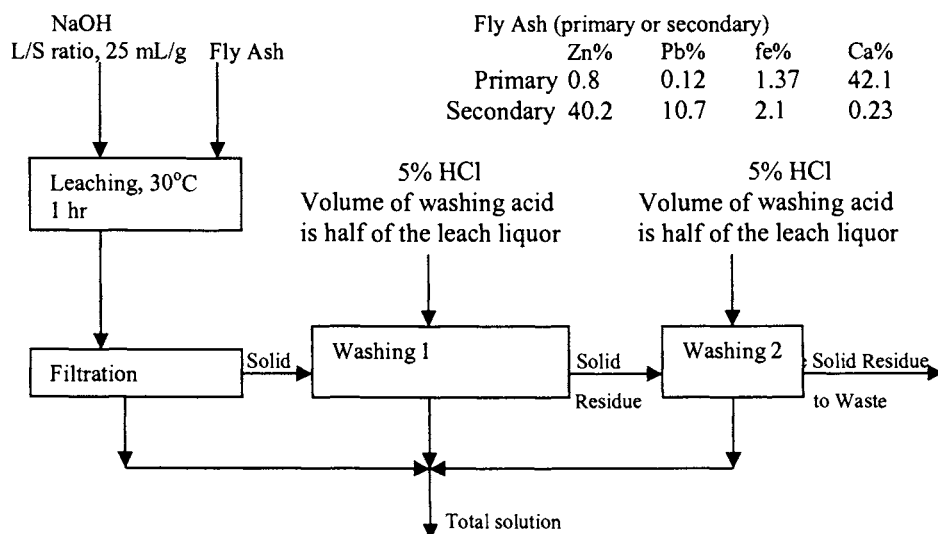


Figure 9.12. Flow sheet of alkaline leaching of fly ash using sodium hydroxide solution (Nagib and Inoue, 2000).

9.3.2.3. Metal Recovery from Oil Sands Fly Ash

In the oil sands operations of Alberta, Canada, bitumen locked in the sands is extracted. The bitumen is then converted to synthetic crude by thermal treatment. Fly ash is produced in the process. This carries several metals, most notably zirconium and vanadium, and in smaller quantity, molybdenum. Table 9.9 shows composition of fly ash from one source (Holloway and Etsell, 2004).

Table 9.9. Analysis of Decarbonized Suncor 1986 Fly Ash, wt %

V	Al	Ca	Fe	Mo	Ni	Si	Ti	L.O.I.
2.81	13.1	1.18	5.65	0.18	1.01	26.4	1.46	26.7

Extraction of vanadium and other metals from oil sands fly ash has been investigated for the potential value of these metals. Mineralogically, the fly ash is a poorly crystallizable, glassy amorphous mixture with clay and sand. Vanadium is associated

with this complex silicate phase in solid solution (Holloway and Etsell, 2004). In order to increase the solubility of vanadium, the fly ash is roasted at 950 °C with sodium or potassium chloride. The alkali metal promotes the formation of a different set of crystalline minerals, albitic feldspar ($\text{NaAlSi}_3\text{O}_8$), noselite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}$). The solubility of vanadium from the resultant mineral assemblage is much higher, 75-85%. Up to 90 % vanadium is extracted by sodium or potassium chloride leaching. Vanadium solubility is higher with potassium than with sodium chloride as shown by Holloway and Etsell (2004). Based on this knowledge, a process has been proposed for the total utilization of oil sands fly ash, which involves recovering various metals of value and other by-products (Holloway and Etsell, 2006). The flowsheet is shown in Figure 9.13.

The first step in the process is decarbonization. Carbon present in the fly ash is burnt at 500-600 °C. This has been found necessary as vanadium recovery is drastically reduced with salt roasting if greater than 15% carbon occurs in the fly ash. The heat generated in the combustion of carbon allows the operation to be heated autogenously. Following decarbonization, the fly ash is salt roasted with sodium chloride in rotary kilns. The optimum roasting conditions for fly ash from one source are, roasting for 3 h at 850-950 °C with sodium chloride additions of 20-30%. By hot water leaching of the calcine vanadium extraction of 75-85% has been achieved. Quenching the roasted ash provides enough energy to heat the leach solution leading to concentrating of the final extract to between 27 and 42 g/L V.

A desilication step is included in the flowsheet to minimize silicon contamination (caused by the small quantities of silicates derived from the fly ash. This solution pH is raised to 10-11 adding sodium hydroxide and aluminum sulfate at a Al:Si ratio between 2:1 and 3:1. Digestion of the precipitate for 30-60 minutes at 95-97 °C produces a filterable sludge containing over 90% of the silicon and most of the metals (Cu, Fe, Ni, Ti, Zn) precipitated from the solution. Vanadium is precipitated as ammonium metavanadate (NH_4VO_3) by adding ammonium chloride. Vanadium is recovered as pentoxide by calcining the metavanadate.

In addition to vanadium, it is possible to recover molybdenum as 30-40% of this metal is leached. It is not precipitated with ammonium vanadate and builds up in the evaporation/salt recovery circuit. By adding ammonium sulfide, molybdenum can be selectively precipitated as sulfide while other metals remain in solution. This is a very valuable by-product as it is free from other contaminant metals, which were precipitated in the desilication step.

The sodium chloride used in the process leads to the formation of hydrogen chloride, which is given out in the roaster off-gas. This is scrubbed, dissolved in water and used to produce ammonium chloride by neutralizing with ammonia. The leached calcine consists of aluminosilicate species. As the toxic metals are removed, it can be safely disposed off. It could also have potential applications in as fine aggregate for road construction or concrete manufacture in the same way as metallurgical slag described in Section 9.1.

Steady depletion of conventional petroleum sources has given major impetus to oil sands development. Oil sands are a major source of oil from Canada and supplying a significant portion of energy needs of the U.S.A. Synthetic crude produced from bitumen extracted from oil sands will be one of the major energy sources for the world. Treatment methods leading to the utilization of the components of the fly ash as the one developed by Holloway and Etsell are of great promise in achieving the objectives of clean environment and sustainable development.

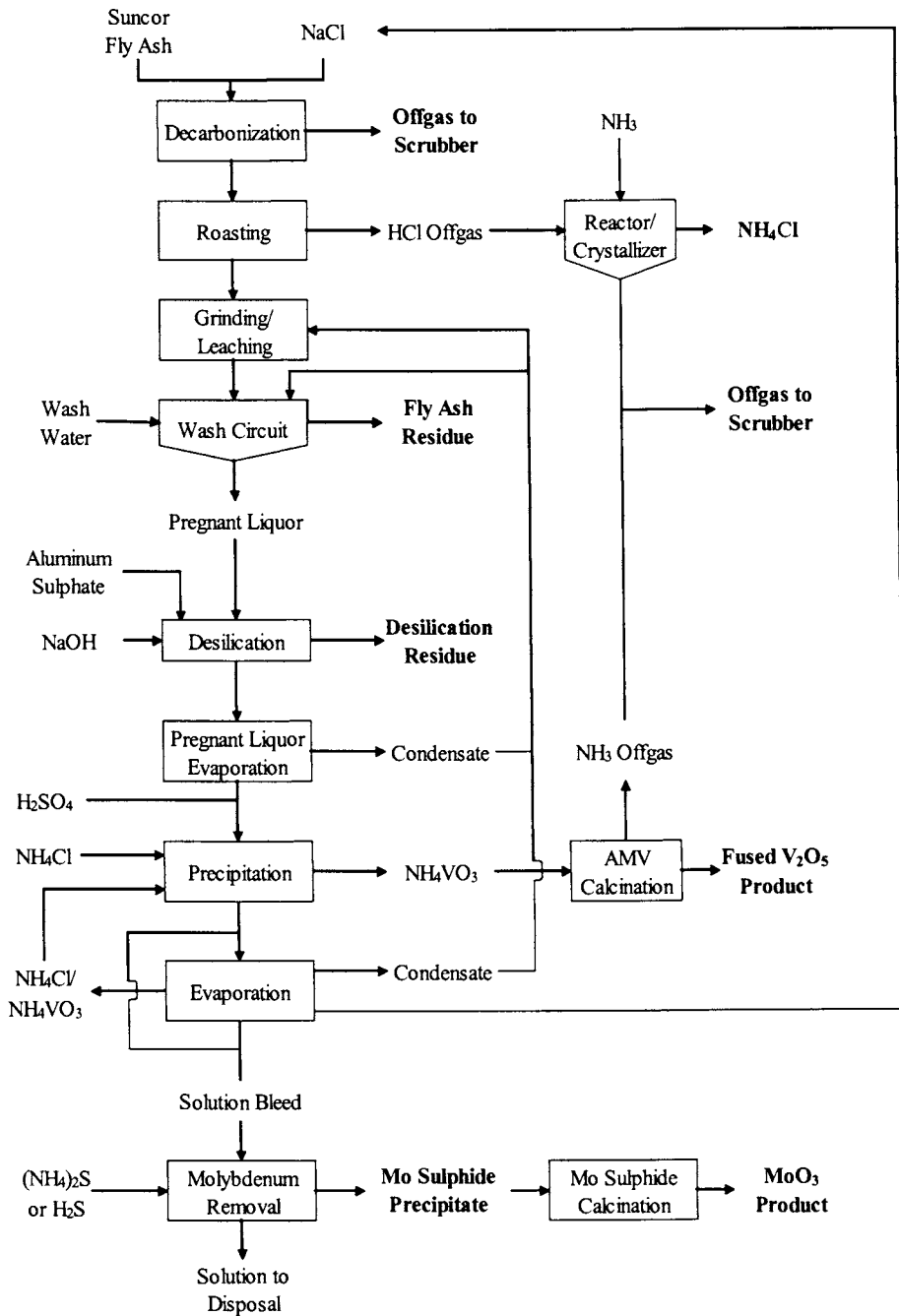


Figure 9.13. Proposed flowsheet for the total utilization of oil sands (Holloway and Etsell, 2006)

9.3.2.4. Metal Recovery from Fly Ash from Municipal Solid Waste

Enormous quantities of municipal solid waste (household waste) are often incinerated to decrease their volume and to ensure sanitary atmosphere. As a result, fly ashes are discharged from the incinerators. The fly ash contains toxic metals like lead and cadmium, and polychlorinated dibenzodioxins (PCDDs), potential carcinogen, which present environmental and health problems. Safe removal of metals and decomposition of PCDDs is necessary before disposing off the fly ash.

A recycling process to treat fly ashes has been developed by Japanese industry (Takahashi *et al.*, 2001). In this process heavy metals are volatilized and PCDDs are decomposed by roasting at high temperature. The ash is made into nontoxic pellets and the heavy metals are recycled as smelting resources. The basic process consists of (1) blending bentonite and silica sand with fly ashes, (2) grinding and forming it to pellets and (3) roasting them dry to decompose PCDDs and vaporize heavy metals. The nontoxic pellets are usable as construction materials. The flow sheet is shown in Figure 9.14.

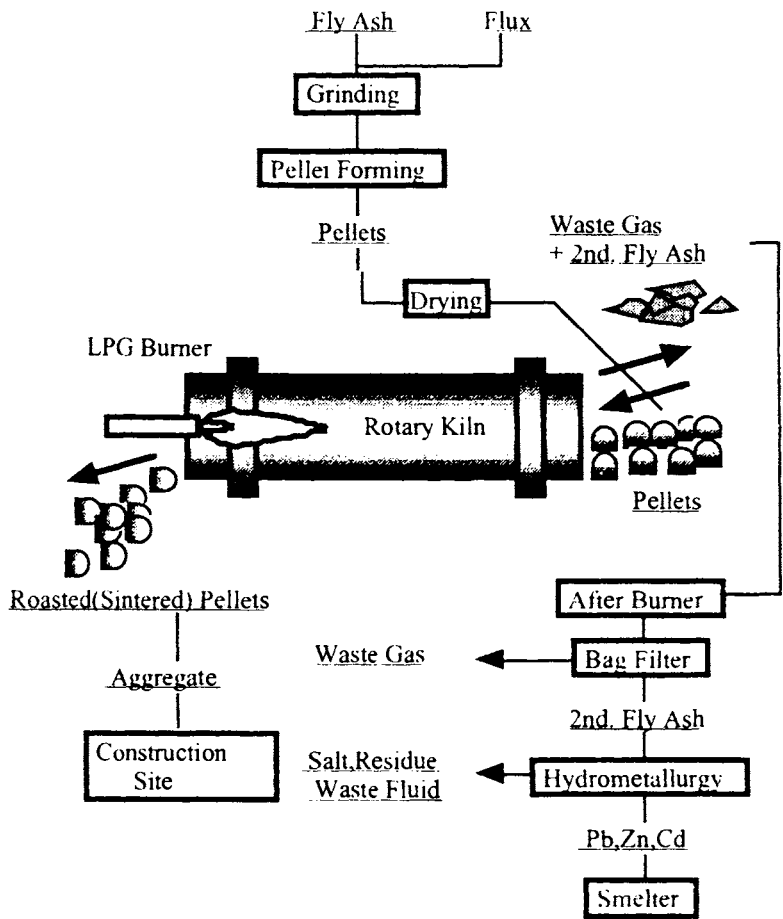
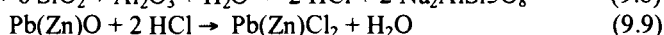
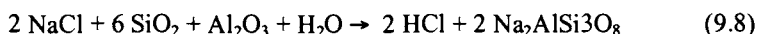


Figure 9.14. Flow sheet of the fly ash treatment process. (Takahashi *et al.*, 2001)

The roasted pellets are sintered and their diameter is reduced to 8 mm. The pellets thus produced contain mostly silica, alumina and lime while most of the heavy metals and salts (NaCl, KCl) are volatilized. The heavy metals are released as oxide and then converted into chlorides by reaction with the hydrogen chloride produced. The alkali metal chlorides react with silica and alumina in the additives and generate hydrogen chloride gas by the reaction:



The volatile components are passed through a secondary furnace to ensure almost complete (> 99.5 %) decomposition of PCDDs.

The process generates secondary fly ashes. The metals, Zn, Pb, Cu, etc., present in them are recovered by acid leaching.

9.3.3. Production of Zeolites from Fly Ash

Zeolites comprise a large group of microporous, crystalline solids with well-defined structures containing mainly aluminum, silicon and oxygen as well as cations and water in the pores (Weitkamp and Puppe, 1999). Natural zeolites are mined in many parts of the world, but most of the zeolites used in industry, are synthesized in alkaline media with different sources of silicon and aluminum components. Both natural and synthetic zeolites are known for their ability to act as catalysts, to adsorb liquids and gases and to exchange ions. As such, they find many applications in areas related to pollution control, radioactive waste management, petroleum refining, purification of gases, and as will be discussed in Chapter 11, in wastewater treatment to remove toxic metal ions in order to recycle water.

As the main components (about 80 %) of the fly ash are amorphous aluminosilicate glasses, which have great similarities with the raw materials used in the manufacture of zeolites (Janssen *et al.*, 1999), the potential use of fly ash to produce zeolites has attracted serious attention. Two alternative methods to treat pulverized fly ash (PFA) to produce zeolite have been explored, fusion method and hydrothermal method (Molina and Poole, 2004). In both methods the fly ash is first pre-concentrated by magnetic separation to remove iron oxides.

The fusion method comprises two stages. In the first, fly ash is mixed and ground with sodium hydroxide to obtain a homogeneous mixture and heated in a nickel crucible in air at 550 °C for 1 hour. A ratio 1.2 of NaOH/PFA is found to give a product with maximum cation exchange capacity (CEC), 250 milliequivalent/100 g. The fusion product is ground and dissolved distilled water, followed by an ageing process with vigorous agitation in a shaking water bath at room temperature for a period of 24 hours. The mix is then crystallized at 90 °C. The solid is then separated by filtration, washed and dried at 105 °C.

In hydrothermal method the fly ash is mixed with sodium hydroxide solution and the rest of the procedure is the same as before, except the temperature, which is 90 °C where the product is found to have maximum CEC (120 meq/100 g).

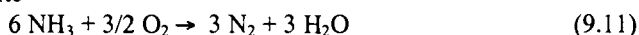
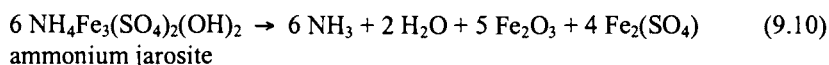
Fly ash is produced in many industrial processes carried out by incineration. The composition varies and has to be determined individually, by chemical and mineralogical analysis. The presence of toxic metals makes it a constant environmental hazard.

Treatment methods leading to the recovery of metals and other useful products are required to ensure environmental acceptability and sustainable development.

9.4. Glass and Ceramic Materials from Hydrometallurgical Jarosite Waste

Hydrometallurgical operations producing zinc metal generate jarosite and goethite as rich hazardous wastes. (See Chapter 8, 8.2.2.1) Mixing such residues with granites and heating to 800 °C leads to the formation of glass type materials. Several glass-compositions can be prepared by varying the compositions (Pelino *et al.*, 1999; Pelino, 2000). The principal reactions are the following:

In the 2500 - 550° C range:



In the 560° - 700° C range the ferric sulfate decomposes to ferrous sulfate. Above 700 °C the sulfates decompose to oxides. The metal oxides are then combined with other wastes available near the zinc plant to obtain a glass with adequate properties and which could be crystallized by controlled thermal treatment. The scraps and mud generated by extraction, cutting and sawing of the granite blocks (GW) are useful additives especially as such material is available in large quantities, often near the zinc plant where the jarosite is generated. The iron particles in the granite mud, and arising from sawing the blocks to obtain slabs, are separated by a magnetic field of 0.5-1.0 tesla. Other locally available wastes such as glass-cullet, lead slag and limestone are added in proper proportion to define the final composition of the glass. The melting is done in the 1400° - 1450° C in alumina crucibles. The melt is quenched in water and the frit obtained is broken and sieved.

The vitrification process thus serves both to maximized the waste utilization as well as to reduce the volume to be disposed of. By properly selecting the composition, glassy products with useful properties can be obtained.

9.4.1. Construction Materials from Jarosite Waste

Another form of jarosite contains sodium in place of ammonium ion group. It is called sodium jarosite, $\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12}\text{Na}_2$. It contains approximately 50 % Fe, around 30 % SO_3 , 6-8 % K_2O and Na_2O and 1.7 % Al_2O_3 (as impurity). This has been used as raw material for producing construction materials (Mymrin and Vaamonde, 1999). The jarosite waste is mixed with ferrous slag and another industrial waste containing zinc, lead, iron, manganese, chromium, and copper in percentage range 0.5-1.6 and cadmium 0.13 %. The mixture is compressed at 10 Mpa for one minute, The compacted mixtures are then hardened at 98 % humidity for 60-90 days. The materials thus produced are useful construction materials for various applications, as bases or sub-bases of roads, airfields and dams. They can also be used to make bricks, tiles and similar items.

9.5. Metal Recovery from Beryllium-Containing By-Products

In the manufacture of beryllium metal, beryllium oxide ceramics and beryllium alloys, a number of beryllium-containing by-products are generated. They include spent

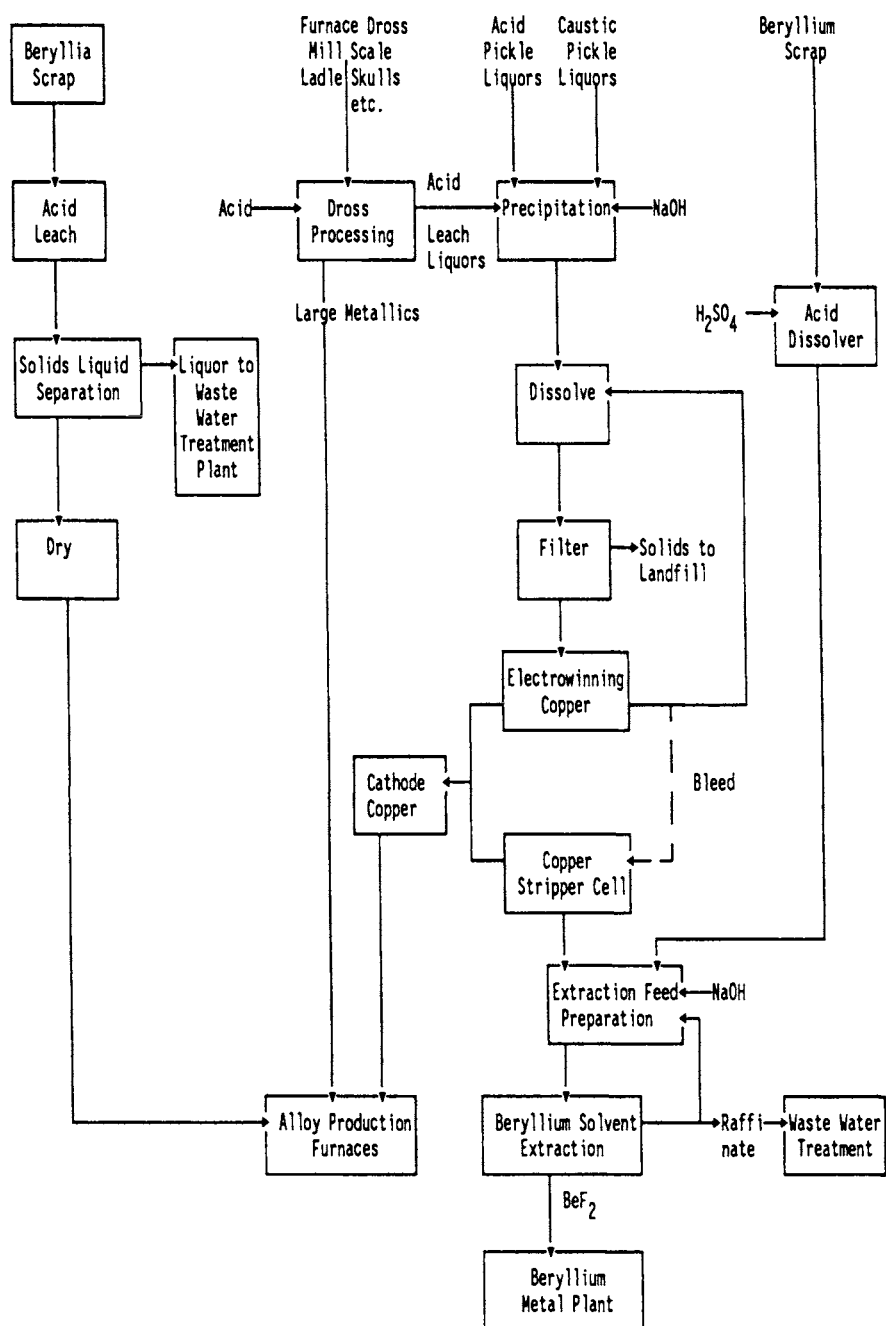


Figure 9.15. Integrated flow sheet for the processing of by-products of beryllium production (Kaczynski *et al.*, 1990)

molten alloy (prior to casting), mill scale (formed as a result of high-temperature treatment of beryllium copper alloys in an oxygen-containing atmosphere), alloy melting skulls (formed as a result of high-temperature treatment of beryllium copper alloys in an oxygen-containing atmosphere) and ventilation collector dusts. These materials contain significant amounts of beryllium and copper. Furnace dross, mill scale and skulls typically contain 80-88 % copper and 3-4 % beryllium, collector dusts contain 30-35 % copper and 10-12 % beryllium. The spent pickle liquor contains 51 % copper and < 1 % beryllium. Both copper and beryllium are recoverable from these by-products. An integrated processing scheme has been described by Kaczynski and coworkers (1990); see Figure 9.15. This integrates all beryllium-containing by-products and waste streams. It is largely self explanatory. It uses acid leaching to leach copper oxide and separate beryllium oxide, which is then used as feed stock for production of beryllium alloys. From acid pickle liquor copper is separated from beryllium by sodium hydroxide leaching (which dissolves beryllium oxide forming sodium beryllate). Cupric hydroxide is then dissolved in acid and copper recovered by electrodeposition. Beryllium is separated by solvent extraction.

9.6. Use of Mine and Mill Tailings as Backfill

In a mining area, after the ore is mined ground support has to be provided to reduce induced stresses caused by mining operations. This is often achieved by backfilling, that is, the filling of voids, which are left where the ore has been mined with either waste rock or waste materials from the mining and milling operations.

Mill tailings are the most commonly used as backfill materials as they are usually readily available at the mine site and can be readily integrated in the mining cycle at a minimum cost. It is estimated that each year 500 million tons of tailings and waste rock are produced in the Canadian mining industry (Amaratunga, 2001). However, only about 6 % (by weight) of this mine and mill waste is used for disposal as underground backfill. The main reason is that because of fine grinding, only a small percentage of mill tailings could be used for backfilling. In order to make a stable backfill, the material should be sufficiently coarse (Amaratunga and Annor, 1989).

Several techniques have been developed to make the finer fraction of tailings amenable as backfill material. The work of Amaratunga and coworkers at Laurentian University, Sudbury, Ontario is specially noteworthy in this area as it has significantly contributed for more productive use of mill tailings as backfill material (Amaratunga 2001).

The technique developed by Amaratunga is known as cold bond tailings agglomeration. The tailings are filtered to 90-92 % solids by weight and then mixed with Portland cement and fly ash as binders at preselected dosages (3-7 %) by weight. The material is then agglomerated in a balling drum. The pellets are then cured in a curing chamber for up to 32 days at 30°-40° C and 100 % humidity to develop their strength. For stabilization of reactive sulfide tailings pellets and to prevent acid generation, various chemical additives are encapsulated into the tailing pellets. The additives include a surfactant like sodium lauryl sulfate to serve as bactericide, sodium silicate as a neutralizer and Portland and gypsum as binders. The agglomerates produced are then mixed with the remaining portion of dewatered fines according to a predetermined ratio. At this stage, coarse tailings can also be incorporated into the backfill mixture design to produce a fill of high strength.

As alternative to Portland cement, calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) has been investigated and applied to produce backfill (Kuntze *et al.*, 1989). The hemihydrate can be produced from gypsum by calcining at atmospheric pressure in sulfuric acid solutions. By heating the hemihydrate to a temperature $> 350^\circ\text{C}$ and insoluble form of anhydrous calcium sulfate (called anhydrite) is produced. Calcination of hemihydrate at lower temperature produces soluble form of anhydrite, which is very hygroscopic. The insoluble form is more stable and does not absorb water unless it is exposed to it over a long period. It is suitable for backfill operation. Such gypsum based materials serve as a useful substitute for the more expensive Portland cement. The gypsum based backfills are able to achieve the required strength in the various environments typical of underground mines (Petroliro *et al.*, 2001).

9.7. Use of Tailings as Heavy Metal Adsorbent

An interesting application of silicate tailings is their use in environmental engineering (Schuiling, 1998). In a milled or finely crushed form they could be used in the treatment of polluted water and to stabilize heavy metals in waste deposits and contaminated sediments and to construct low-cost in-situ treatment solutions. One possible application

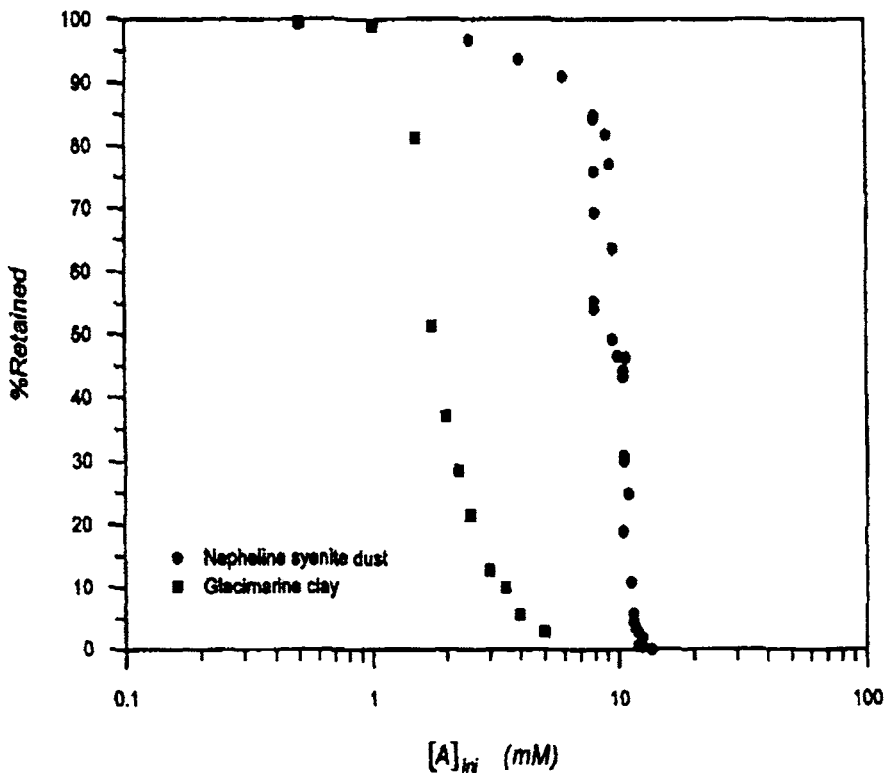


Figure 9.16. Adsorption isotherms at ionic strength $I = 0.05\text{ M}$ showing the percentage of copper retained as a function of the amount of acid added (the initial concentration) (Kleiv and Sandvik, 2000)

is the use of tailings as a geochemical barrier at the base of landfills and waste deposits, in addition to the traditional hydrological barriers. The probable mechanisms responsible for immobilizing heavy metals are adsorption at the particle surfaces and hydroxide precipitation. Both mechanisms are pH-dependent. It has been extensively studied on a wide range of hydrated oxides, oxyhydrates and aluminosilicates. Increase in adsorption from 10 % to 90 % usually take place in a limited pH interval of 1-2 pH units (Benjamin and Leckie, 1981). The pH dependence of heavy metal adsorption is due to competition for surface sites between heavy metal ions and hydrogen ions. When the initial conditions are sub-neutral or acidic, it is often necessary to raise the pH of the system for optimal adsorption.

Adsorption characteristics and buffering capacity of nepheline syenite (an aluminosilicate mineral) and glaucinite clay dust generated in the crushing and milling of the minerals have been described by Kleiv and Sandvik (2000). A set of results is shown in Figure 9.16. Both adsorbents remove close to 100 % of the copper initially in solution, but the adsorption takes place at different pH intervals. At an ionic strength of 0.05 M, the glaucinite clay adsorbs 50 % of the copper just below pH 5. The same percent adsorption on nepheline syenite dust occurs at pH 6. When the pH of the solution is sufficiently high, both adsorbents remove more copper from solution than can be achieved by precipitation alone.

The adsorption on the syenite dust is not significantly affected by the ionic strength of the system. This indicates chemisorption to be the principal mechanism. The combination of the ability to adsorb significant amounts of copper under sub-neutral conditions and the relatively large buffering capacity makes the nepheline syenite dust a potentially useful material from an inexpensive source to construct geochemical barriers.

9.8. Production of Ceramic Tiles from Iron Ore Tailings

Current practice of washing iron ore before it is processed for extractive metallurgical operation results in three products, coarse ore lumps with sizes in the range 10-80 mm, which are directly charged to a blast furnace, the classifier fines of size 150 μ m to 10 mm, which, with or without beneficiation are fed to sinter plants, and the tailings, below 150 μ m in size, which are discarded as waste. In India, where iron ore processing is one of the major industries, the generation of tailings is estimated to be 10-25 % of the total iron ore mined, amounting to 18 million tons per year (Das *et al.*, 2000). The tailings contain silica in high percentage (40-60 %, from various locations). This makes it a suitable raw material for the development of ceramic tile compositions.

In the process developed by Das and coworkers (2000), the tailings are mixed with clay and a fluxing material (40-50 % tailing, 30-50 % clay and 10-15 % fluxing material). The raw materials are wet milled for 10 h to obtain the desired fineness. The slurry obtained is screened, dried at 110 °C, powdered to break the agglomerate and granulated to small nodules for better compaction. The shaped particles are fired at 1060-1200 °C in air with a rate of heating 10 °C/min. Glazed tiles are produced from the material of this composition. The inventors claim that the tiles based on tailings are superior with respect to scratch hardness and strength while maintaining most of the other properties to meet standard specifications.

The use of iron ore tailings substitutes some of the expensive minerals used in commercial tile, thus lowering the cost. Further, as the tailings are already in powdered form and require no further grinding, which leads to energy cost saving.

9.9. Use of Bauxite Processing Residue (Red mud) for Fixation of Metals in Soil

A large proportion of contaminated sites contain trace elements (heavy metals and metalloids). Remediation of polluted soil has been a constant challenge in the use of land for constructing new homes or for recreational purposes. Current technologies used to remediate pollutes soil are generally too expensive. In addition, they may generate additional risks and produce secondary wastes and are often environmentally invasive. In situ technologies that require low inputs and are low cost are required for soil remediation.

Some of the metallurgical tailings with high alkaline content have been investigated as potential materials to reduce the metal content in contaminated soils. One of them is the residue produced in large quantities in the extraction of alumina from bauxite mineral. It is called red mud as it contains high proportion of ferric oxide from the bauxite ore. In a study by Lombi and coworkers (2002a) 2 % of this material is added to 1-kg soil. Over a period of time extending to a month, concentration of many of the toxic metals is significantly reduced. The effect, however, varies with metals and the nature of the soil. In the soils studied by Lombi and coworkers (2002a) cadmium and zinc in the soil pore water decreased respectively from 0.35 and 69 mg/L in the untreated soil to 0.016 and 1.5 mg/L as an average of the treated soils. The effect is, however, different for lead and copper. As the solubility of lead hydroxide is generally very low in non-acidic soils, the red mud treatment only slightly reduces its mobility. One way of reducing the mobility of lead is by the application of a phosphate, which produces insoluble pyrophosphate. In the case of copper, there is no significant change in the concentration in soil solution. Red mud treatment is thus effective to reduce metal ion concentration, but not all metals are removed to the same degree. The overall results, however, are generally satisfactory and serve the purpose of soil remediation. Oil seed rape, wheat, pea and lettuce grown in pots of treated soil show reduced plant toxicity by metals as compared to the produce grown in untreated soil. Optimum conditions for best possible remediation have to be determined for individual soils (Lombi *et al.*, 2002b).

9.10. “Zero Waste Process”

The ideal goal of any metallurgical process is “zero waste”, no waste generated in the process. That is possible when all reaction products are marketable. This will include the main product (a metal) and by-products. The process is designed in such a way that the reaction products, which would have been discarded as ‘waste’ are converted into useful by-products. Such an approach would be a valuable step towards the objective of sustainable development. Although such processes are not widely developed, there are a few examples, which are pointers in that direction.

Three examples, two from pyrometallurgical processing, and the second from hydrometallurgical processing will be discussed.

9.10.1. Total Utilization of Steel Processing Products

This innovative process developed by Fleischanderl coworkers (2004) aims towards total reclamation of byproducts converting them to usable products. It has been specially applied in processing several byproducts and wastes generated in steel industry and industries using steel as a major component of their processes or products. It is based on the smelting reduction of suitable blends of acid and basic by-products from carbon steel (CS) and stainless steel (StS) industry, such as basic steel-making slag and dust or acidic

scrap residues (SR) from scrap handling in EAF plants, and also complementary acid byproducts from other industrial sectors, such as fly ash from power plants, automotive shredder residues (ASR) or bottom ash from urban incinerators (BI ash). The principle is illustrated in Figure 9.17.

The main products are the refined slag or mineral product with a target chemical composition and hot metal or metallic product to be recycled for production of steel. Carbon-based reductant like coke, anthracite coal are added to the blend of by-products for smelting reduction. Depending on raw materials and target mineral product, small quantities of stronger reductant such as ferrosilicon or additives like lime or bauxite may also be used. The process employs an electrically heated ladle type furnace, with allowances for top charging into the foamy slag bath and coarse materials, and for deep pneumatic injection of powdery materials into the hot metal heel; see Figure 9.18. Additional features are bottom stirring and post-combustion in the upper part of the slag bath. The furnace is equipped with a water-cooled cover.

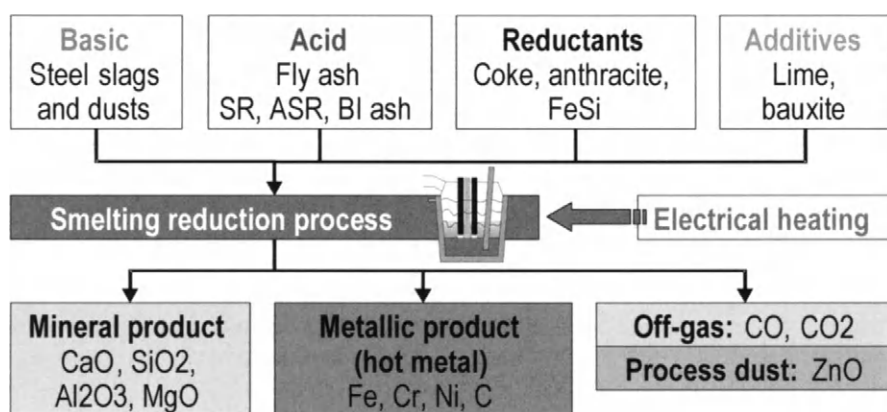


Figure 9.17. Principles of the “Zero Waste” process (Fleischanderl *et al.*, 2004)

An example of the application of this approach is in the recovery of chromium and nickel from stainless steel slag. The input material is slag and dust (EAF) and fly ash from power plant. The basic component of slag reacts with the acidic component of fly ash (mainly ferric oxide) producing chromium and nickel oxides and a slag, which has the properties of hydraulic binder. The nickel and chromium oxides are reduced by carbon from coal.

The inventors of the process have also analyzed off-gas resulting from the thermal reduction. Measurements have shown very low emissions of dust, carbon monoxide and volatile organic carbon even when scrap residues are charged in a test ladle. The process dust is also largely contained. It appears that the thick foamy slag bath effectively serves as filter to avoid carry-over dust leading to very low dust content in off-gas. A potentially valuable dust is produced by slag filter, with very high contents of zinc and lead (50-70% equivalent of ZnO), starting with feed in which these metal contents are low. The metals may be recovered by applying appropriate methods described for the treatment of electric arc furnace dust (see Chapter 8).

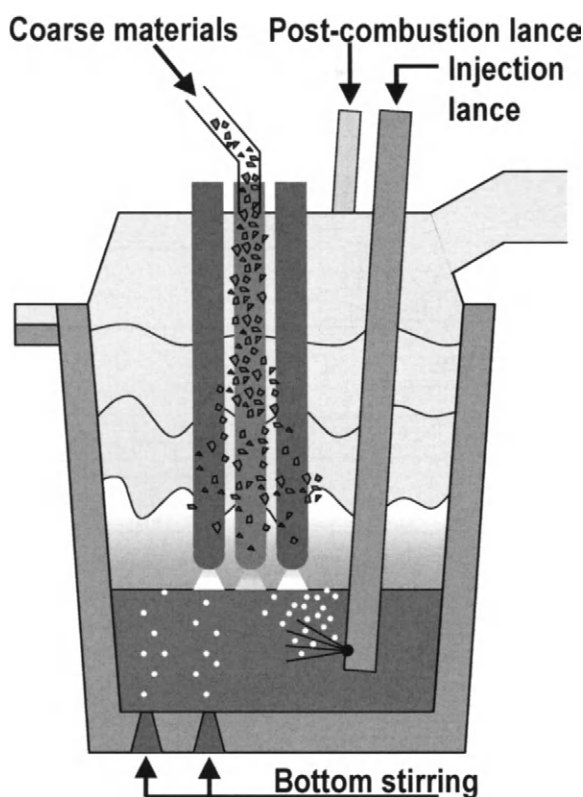


Figure 9.18. Schematic view of the ladle furnace used for “zero waste” process (Fleischanderl *et al.*, 2004)

The process described is still in the developmental stage, but it has great potential for converting the waste generated in metallurgical processes into useful products.

9.10.2. Waste Minimization in Smelter by By-product Processing

An excellent example of minimizing process waste by processing various byproducts has been described by Abe and coworkers (1996).

The main process is the treatment of a copper concentrate in a smelter to produce electrolytic copper and copper and nickel compounds. Some of the byproducts are treated inside the smelter and some are processed outside. The overall process flow is shown in Figure 9.19. The items of byproduct treatment are also shown

The heat of exhaust gas from the reverberatory furnaces is recovered in the waste heat boilers and used to generate the electric power. Sulfur dioxide in the exhaust gas is neutralized by calcium hydroxide to produce calcium sulfite, which is oxidized to make calcium sulfate (gypsum) for sale. Converter off gas consisting of sulfur dioxide is oxidized and sulfuric acid is produced. The waste brick rejected (72 % MgO , 10 % Cr_2O_3 , 9 % Al_2O_3 , 5 % Fe_2O_3 and 3 % SiO_2) from the converter is also processed and sold as cement material.

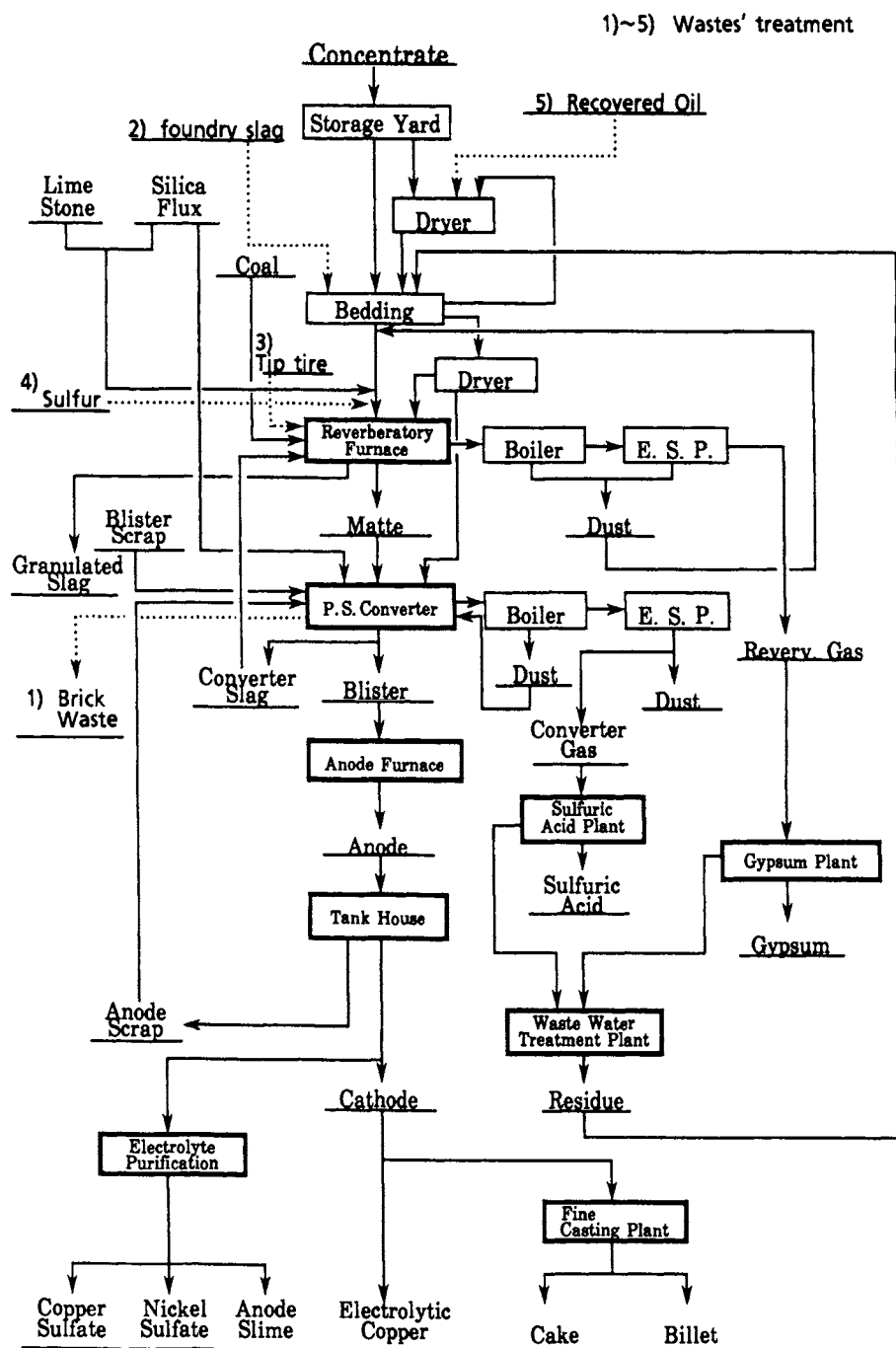


Figure 9.19. Process flowsheet to treat byproducts produced in a smelter operation to produce electrolytic copper and copper compounds (Abe *et al.*, 1996)

9.10.3. Sherritt Ammonia Leach Process to Recover Nickel and Cobalt

This process has been developed to separate and recover nickel and cobalt, from sulfide concentrates. The feed material consisting of the concentrates is leached in the presence of air under pressure in a solution buffered with ammonium sulfate and with concentrations of ammonia in excess of that required to form co-ordinate bond complexes of the metals. The excess ammonia is removed by adding sulfuric acid, to reduce the molar ratio of complexing ammonia to metal ions to 2:1. Copper is precipitated at the same time as cupric sulfide by hydrogen sulfide, or elemental sulfur plus sulfur dioxide. (Copper ammine complex is decomposed and the copper is precipitated as hydroxide, which is converted to oxide, while nickel and cobalt remain in solution as their amines are more stable and require lower pH for decomposition).

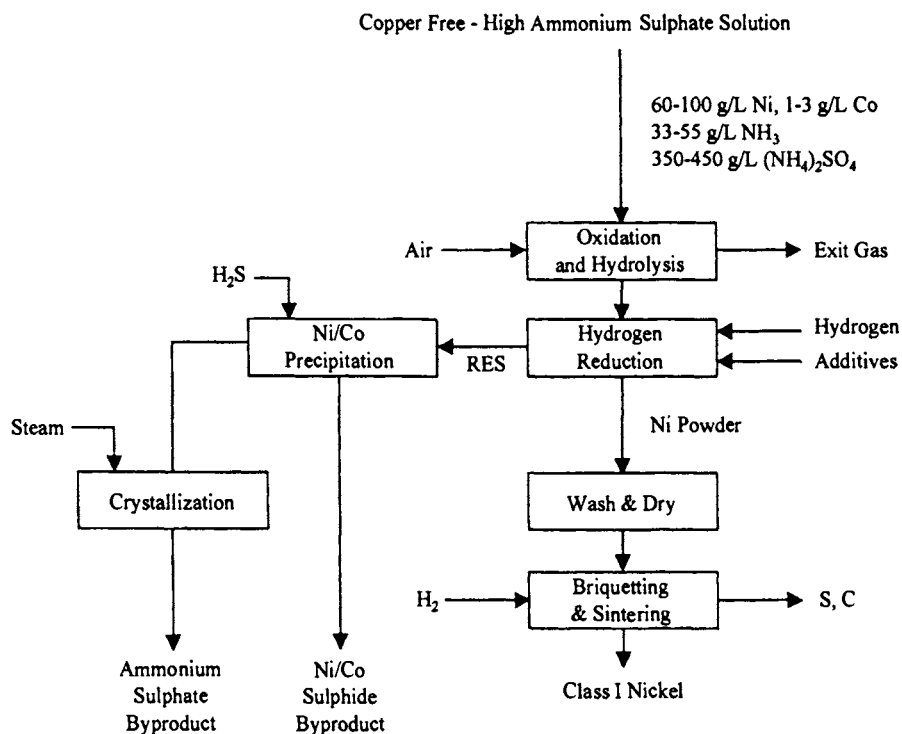
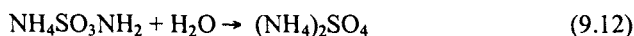


Figure 9.20. Simplified flow sheet of nickel, cobalt recovery by ammonia leach process (Campbell *et al.*, 2001)

The ammoniacal leach of the nickel and cobalt sulfide concentrates produces a highly buffered solution containing about 350 g/L ammonium sulfate and 50 g/L Ni and 1.5 g/L Co. While most of the sulfide sulfur is oxidized, a significant portion occurs as sulfur compounds in lower oxidation state, such as thiosulfate and sulfamate ($\text{NH}_4\text{SO}_3\text{NH}_2$). These are oxidized after separating copper sulfide at elevated temperature to fully oxidize the sulfur. The sulfamate is hydrolyzed to produce ammonium sulfate;



The high ammonium sulfate buffer helps to minimize the precipitation of nickel hydroxide

After the separation of copper, most of the nickel is recovered by reduction by hydrogen. The remaining solution still contains several grams per liter of nickel and cobalt, which are precipitated using hydrogen sulfide and the mixed sulfides sold as a cobalt concentrate product. It may also be recycled to the leaching step, where the sulfides are leached and the ammonia component is converted into ammonium sulfate. A simplified flowsheet of the process is shown in Figure 9.20. The process is a good example of using all input feed and converting it to metal products and a useful by-product, thus eliminating waste. It is practiced in Corefco refineries at Fort Saskatchewan, Alberta, Canada. Other examples are found in papers by Bolton and coworkers (1997) and Campbell and coworkers (2001).

Selected Readings

Rashid Khan, M., (editor), 1996. *Conversion and Utilization of Waste Materials*, Taylor & Francis, Washington, DC,

Chapter 10

RESOURCE RECOVERY FROM PROCESS WASTES

10.0. Introduction

The extraction of valuable metals or minerals from ores, the processing of concentrates resulting from beneficiation of these ores by pyrometallurgical and /or hydrometallurgical means and the commercial use of the extracted metals or minerals results in a wide variety of by-products. Some of these by-products contain residual metals or minerals of commercial value and may be reprocessed for the recovery of these additional and often different metals or minerals. Thus historically gold tailings produced in gravity plants may be reprocessed by cyanidation to recover fine residual gold values, tin may be recovered from zinc tailings, vanadium from tar sand tailings, uranium from gold tailings, pyrrhotite from nickel tailings, magnesium from asbestos tailings, as examples. Similarly metal values may be recovered from aqueous effluents by liming spent plating solutions or by hydrogen sulphide precipitation from acid mine drainage and occluded metals or minerals recovered from smelter or foundry slags. Finally a wide range of by-products, in the form of dusts, grindings, turnings, chips, spills, splatters and sprues result from the fabrication of metals

Many efforts are under way to minimize or reduce the volume of tailings generated and make the process more efficient. Some examples were described in Chapter 9. They have met with some success, but they will not solve the problem of the huge volume of accumulated tailings, effluent and sludge all of which are potential environmental hazards.

Treatment and disposal of mineral process tailings and metallurgical effluents and environmental standards to be met are described in a number of monographs and reviews. (Ritcey, 1992; Chalkley *et al.*, 1989; Aplin and Argall, 1973). That subject will not come in the scope of this chapter. The principal focus will be on recycling and resource recovery from tailings. It should, however, be noted (as will be explained in the chapter) that recycling of resources from the accumulated wastes has positive environmental impact, for minimizing health hazards due to toxic elements as well as for sustainable development. Therefore, both for economic as well as environmental reasons, resource recovery from process wastes is attracting serious attention in recent years.

Such resource recovery is important from two perspectives. First there is the value of the product recovered. It may be less than the cost of extracting the same metals and minerals from primary ores since the mining and milling costs have already been paid. Second is the resultant upgrading of the bulk material which may permit its use where previously concern with potential metal or mineral solubility or radioactive properties

may have inhibited such application. The use of this bulk material is addressed in Chapter 9 although to the extent that the bulk material such as mill tailings contains a substantial proportion of minerals such as calcite, dolomite, quartz, feldspar, chlorite, pyrite, or magnetite that are liberated such tailings are also a potential candidate for resource recovery. One example is the sludge generated in Canadian nickel mineral processing industry. It contains up to 6 percent nickel on dry basis in addition to iron and magnesium. The accumulated sludge could be a secondary source of nickel. Technically feasible and economically viable methods of recovery are greatly desired.

A second example is that of acid rock drainage (ARD), also referred to as acid mine drainage (AMD). It is generated by the oxidation of pyrite, which is the principal waste sulfide mineral occurring in sulfide mineral process tailings. The oxidation of pyrite produces sulfuric acid, which leaches into solution other metals occurring in the tailings. Many ARD systems are known to contain copper and zinc in significant concentrations, as much as 30 g/L zinc, and other metals like manganese and magnesium in lower concentrations.

This chapter discusses and provides examples of present or potential recovery of resources from the by-products of mining and processing of ores and concentrates, extraction, refining and fabrication of metals, plus the utilization of industrial minerals.

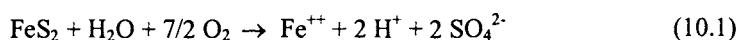
The chapter will describe some case studies of resource recovery from process wastes generated in different forms in diverse areas of mineral and metallurgical industry. They include mineral process tailings, metallurgical effluents, slimes and sludges produced in the tailing treatment processes, and solid wastes. Two sections are also devoted to survey the recycling of resources from exhaust batteries and spent catalysts. In addition to resource recovery, some of the wastes have been converted to useful byproducts, which will also be discussed.

10.1. Mineral Process Tailings

Almost all mineral processing operations, except those few, where the raw material (ore) to be processed is of high grade, generate huge quantities of tailings, which include those minerals, which are not usually of economical value in the operation. Such 'waste minerals' include silica, calcite and dolomite, silicate minerals and in the case of sulfide ores pyrite (FeS_2) and pyrrhotite (FeS). The common practice has been one of storing them in tailing ponds and recycling most of the water. The solid fraction is a potential secondary source of materials, some of which could result in economic spin off. Treatment of tailings to recover such resources is a growing area of research and development. The results of research are already being applied in some cases while others await applications under favorable economic situation. Some examples will be discussed in the present section.

10.1.1 Metal Values from Acid Mine Drainage (AMD)

Acid mine drainage (AMD), also called acid rock drainage (ARD) is a serious environmental challenge in sulfide ores processing areas. It is produced by the atmospheric oxidation of iron sulfides, notably pyrrhotite and pyrite in waste rock or tailing ponds by the following reaction (Kuyucak, 2000; Rao, 2003)..



The acid generated leaches out several other metals associated with the tailings and results in a solution which is still acidic and carries metal ions, mainly Cu(II) and Zn(II) besides Fe(II) and Fe(III) in significant concentration. Many investigations have been conducted to recover the metal values from ARD (Rao and Finch, 1992; Hammack *et al.*, 1993; Rao *et al.*, 1994).

10.1.1.1. Selective Separation and Recovery of Metals

Acid rock drainage is often treated by precipitating all metals as hydroxides by mixing lime to a pH of 9-10. The discharge water is practically free of dissolved heavy metals like Fe, Cu and Zn. The last two are considered to be toxic and their removal is essential before the reclaimed water is discharged, or recycled. This conventional method results in a bulky precipitate of metal hydroxides, but does not leave room to recover metal values, in particular, copper and zinc. In some of the ARDs, especially those from Canadian mines, zinc is found in significant concentration, sometimes, as high as 13 g/L (Rao *et al.*, 1994). In order to recover such metal values, selective precipitation methods based on pH control have been proposed (Rao and Finch, 1992; Rao *et al.*, 1994).

The recovery of zinc as sulfide is done by a three-step process.

In Step 1, iron is removed as ferric hydroxide by mixing lime or lime stone (calcium carbonate) to a pH of 3.5-3.7. If the ARD contains some of the iron in ferrous state, it has to be oxidized to the ferric state by an oxidant like hydrogen peroxide or ozone (Rao *et al.*, 1998). At pH ~3.5 ferric iron is completely precipitated while other metals, Cu, Zn, etc. remain in solution. This follows the principle of solubilities of metal hydroxides explained in Chapter 3.

In Step 2, zinc, copper and manganese are selectively precipitated as sulfides by sodium sulfide, CuS at pH 3.5, ZnS at pH 5.1 and MnS at pH 10.5.

In Step 3, the pH is raised to 10 to precipitate aluminum and the remaining copper, zinc and manganese. The metal levels in the discharge water range from 0.1 to 11 mg/L, almost entirely accounted for by magnesium. The process is schematically shown in Figure 10.1.

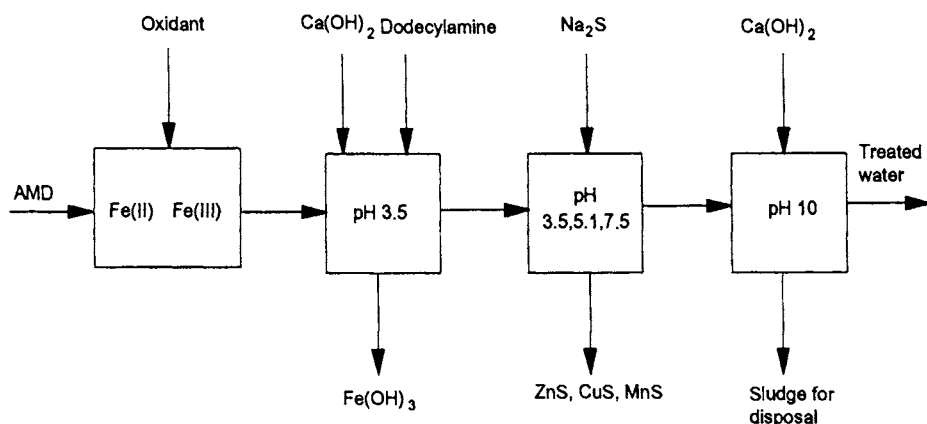


Figure 10.1. Flowsheet for three-step precipitation process to recover metal values from acid rock drainage (Rao *et al.*, 1994).

About 80 % of zinc is recovered by this process, the product assaying 30-35 % Zn. The lower grade is due to the precipitation of calcium sulfate as lime is used to set the pH. The product can be upgraded by separating calcium sulfate by precipitate flotation at pH ~4 using dodecyl amine chloride or sulfate as collector (Rao and Finch, 1997).

The three-step process also generates substantial quantity of ferric hydroxide (in Step 1). This could be a feed stock for preparing ferric sulfate, which is an excellent coagulant of use in industry (Rao *et al.*, 1991).

10.1.1.2. Calcium Silicate as Precipitant for Dissolved Metals

As an alternative to lime, which has been used for many years, in view of its abundant occurrence, to precipitate metal hydroxides, Pesic and coworkers (2001) have investigated calcium silicate and magnesium oxide as precipitants. They are by-products of magnesium smelting operations. Calcium silicate occurs as slag (Di-Cal) and magnesium oxide occurs as condensate (MgO). Both have neutralizing capacity, which could be exploited to neutralize acidic effluents and precipitate dissolved metals. The slag, Di-Cal described by Pesic and coworkers had 55-65 percent $\text{CaO} \cdot \text{CaSiO}_3$ and 20-30 percent $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$. The investigators have found that with the precipitates obtained by using Di-Cal, the rate of filtration is much faster than with the sludge produced by lime precipitation. This is attributed to flocculating properties of Di-Cal resulting in coarser precipitates and faster settling rates. It should, however, be noted that the quantity of Di-Cal required to reach alkaline pH is much greater than that for free lime. For example, in a mixture of metal solutions, 45 g Di-Cal is required to reach pH 9.0 whereas the quantity of lime to reach the same pH is 16 g. One of the reasons for such higher consumption could be the lower content of equivalent CaO in Di-Cal. Lime is 100 percent CaO while Di-Cal is a mixture of 55 % to 65 % and has lower neutralizing capacity. The requirement for greater quantities should not, however, be a serious deterrent. The use of slag generated in metallurgical operation, which would otherwise be considered as an industrial waste, to precipitate metals from metallurgical effluents, also a waste product, could be another example of industrial ecology.

An interesting finding of the work by Pesic *et al.* (2001) is with respect to the precipitation of selenium. They found that selenium is lost soluble from lime precipitates, and least soluble from MgO precipitates. Di-cal is a much better precipitant than lime. However, in presence of other metals, the precipitation of selenium is reduced probably due to competition of other metals for the precipitant.

10.1.1.3. The Green Precipitate Process

This is an alternative method of precipitating metals from ARD, developed in Australia. It is based on precipitating iron as mixed ferrous-ferric hydroxide by treatment with lime to a pH of 6-8. In this pH range all metal ions are precipitated. Iron is precipitated as a green precipitate of composition, $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ (Taylor *et al.*, 1998). This gives a more compact precipitate, which settles more readily than ferric hydroxide. The primary objective of this technique is treatment of ARD by bulk precipitation of metals. It is suggested to be an alternative to conventional treatment technique where lime is used to a pH 8-10 to precipitate all metals. Other metals, in particular, copper and zinc can be recovered by selective leaching. The inventors have reported that from a natural acid mine water, > 90 % copper and > 88 % zinc have been recovered. Details of such selective leaching are lacking. It is also obvious, application of this technique is

limited to acid mine water in which the ferrous ion concentration should be at least twice that of ferric ion on molar basis. Where the ferrous ion concentration is in excess, it can be brought to the required level by controlled oxidation, but if it is not already present at the minimum required level, the method is not applicable as reduction of ferric to ferrous cannot be done under ordinary conditions. That would require a strong reducing agent and elevated temperature, which would make the process uneconomic.

10.1.1.4. Biotechnology Method

A most promising route is based on the application of biotechnology.

The biotechnology based processes make use of sulfate reducing bacteria (SRB) (Hammack *et al.*, 1993; Rowley *et al.*, 1994).. Sulfate reduction is accomplished in a bioreactor where SRB grow on some form of solid support or in a sludge bed. Sulfate is metabolized and the hydrogen sulfide generated by the SRB contacts metal cations forming insoluble metal sulfides, which precipitate in the bioreactor.



where CH_2O represents organic carbon;



Both inorganic and organic nutrients may be used. Hydrogen is an inorganic nutrient. It may be produced by partial oxidation of methane or by the action of steam on methane (water gas reaction). Organic nutrients providing a reducing atmosphere are ethanol and simple sugars.

The reduction of sulfate to sulfide is biological process and the precipitation of metal sulfide is chemical process.

Rowley and coworkers (1994) have developed a novel, **Biosulfide** or Biogenic sulfide process, which separates the chemical precipitation process from the biological conversion of sulfate to sulfide. Raw AMD enters the chemical circuit and is contacted with hydrogen sulfide generated in the biological circuit. Some fraction of the volume of treated AMD enters the biological circuit for the biologically catalyzed conversion of sulfate to sulfide. The sulfide sludge is thus isolated in the chemical circuit, which averts the problem of their build-up in the bioreactor and is effectively separated from the biomass. Additionally, by operating a multi-stage chemical precipitation circuit the Biosulfide process facilitates the selective removal of metals. Selective separation is achieved by pH control in the reactors, as specific metals precipitate as sulfides at different pH ranges. Alkalinity requirements for the stepwise pH control are applied by the biological circuit. Alkalinity is produced simultaneously in the biological conversion of sulfate to sulfide in the form of carbonate.

Metal sulfide precipitates form rapidly creating a dense, stable sludge. By isolating the toxic fraction of the AMD stream in a sulfide sludge separate from the biomass sludge and from the metals considered to be valuable, the Biosulfide process can significantly reduce the volume of sludge requiring expensive disposal. The cost of treatment can be partly offset through significant recoverable metal sulfide concentrates to smelters. Metals readily removed as sulfides include copper, cadmium, zinc, arsenic, nickel, iron, lead, and antimony, among others. Molybdenum can also be removed, but the rate of reaction is lower. Aluminum, which does not form a sulfide can be precipitated as an hydroxide at a pH of 4 to 4.5.

A Biosulfide process schematic is shown in Figure 10.2. This is a 100 L system operated for a 75 hours continuous run treating an AMD of pH 2.45 and with the following metal concentrations in g/L: Fe, 2.3; Zn, 0.27; Cu, 0.19; Mn, 0.31; Mg, 1.5; Ca, 0.4, besides Co, Ni and As in smaller concentrations. The total sulfate concentration was 20 g/L. The chemical precipitation stage consists of three series-configured acrylic reactors of 6 L, 5 L and 6 L respectively. Each of the vessels is agitated by magnetic stirring and followed in the circuit by a 1.5 L cylindrical thickener. The first precipitation reactor is pH monitored. And the final two are pH controlled as desired. By peristaltic pump the AMD is transferred through the circuit for contacting with the bioreactor off gas.

The biological stage of the pilot system consists of two 40 L polyvinylchloride (PVC) anaerobic bioreactors. Solution exiting the chemical precipitation stage is mixed with nutrients in batches of 20 to 50 L to be fed to bioreactors. A single peristaltic pump moves the solution through the series configured bioreactor stage. Nitrogen gas flows through the system to carry the hydrogen sulfide produced to the chemical precipitation circuit. Bioreactors are maintained at 30 °C with submersible heaters.

The nutrient consists of 0.35 g/L ammonium chloride (nitrogen source), 0.06 g/L potassium dihydrogen phosphate (phosphorus and potassium source) and ethanol or methanol (carbon and hydrogen source) can be obtained their mixed culture from bog water.

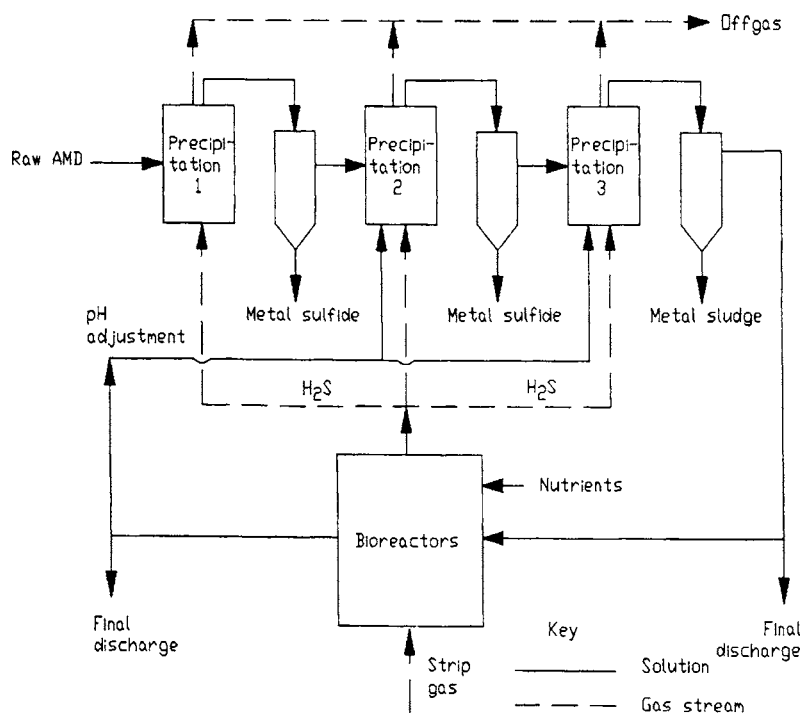


Figure 10.2. Schematic of Biosulfide process (Rowley *et al.*, 1994)

The operating conditions are summarized in Table 10.1. Product precipitation grades from 15 hours of operation are presented in Table 10.2. The results demonstrate the production of copper and zinc sulfide concentrates for sale.

Table 10.1. Summary of 75 Hours of Continuous Operation of Biosulfide Process.

Parameter	Hour 0 to 60	Hour 60 to 75
AMD treated,	44.3 L	10.30 L
AMD feed rate	0.74 L/hr	0.49 L/hr
Chemical stage retention	22.3 hrs.	33.7 hrs.
Bioreactor solution added	63.6 L	13.9 L
Recirculating load	144 %	190 %

On an average, sulfate reduction of 85 % is achieved by this process.

The advantages of separating the hydrogen sulfide generating bioreactor from the precipitation (chemical) reactors include the following (Hammack *et al.*, 1994):

1. potentially inhibitory or toxic metals in the wastewater do not contact the sulfate-reducing bacteria;
2. metal sulfide precipitation reactions take place under conditions, which are not conducive to the growth of sulfate-reducing bacteria;
3. individual metal sulfides can sometimes be selectively precipitated by controlling the pH of the wastewater within precipitators;
4. metal sulfides that are not processed for metal recovery are not contaminated or diluted with biomass or organic substrates.

Table 10.2. Analysis of Biosulfide Precipitation Products % (Rowley *et al.*, 1994)

Residue	Al	Cu	Fe	S	Zn
Pptn. #1	-	10.0	0.24	810.8	0.06
Pptn. #2	2.5	13.1	10.7	25.8	6.18
Pptn. #3	8.5	0.3	8.95	24.9	2.11

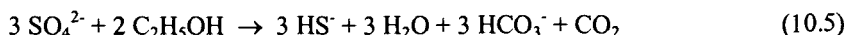
One possible drawback of this method is the formation of sulfur in those AMD samples which carry a large concentration of iron as ferric instead of ferrous. Hydrogen sulfide is oxidized to elemental sulfur by ferric ions by the reaction,



In addition to diluting and increasing the volume of the product sludges, the reaction also incurs substantial losses of sulfide, placing greater demand on the bioreactors. The only way to overcome this problem is to treat 'fresh' AMD where most of the iron is still in the ferrous state. In the samples containing high concentration of ferric ions a preliminary step to separate most of the ferric as hydroxide will be necessary. The Biosulfide process is an attractive alternative to conventional AMD treatment, particularly lime treatment which produces voluminous sludge which cannot be easily

handled. Dissolved metal concentrations are reduced to below discharge limits and the treatment meets discharge pH requirements. Large scale application of the process has been demonstrated in the treatment of AMD accumulated in a mine located near Vancouver, Canada, the Britannia mine where the on-going AMD problem is considered to be one of the worst. As compared to the conventional lime treatment process, the biogenic sulfide process has higher capital cost, but this is largely offset by lower operating cost. In particular, it eliminates the expensive (both from economic and environmental points of view) sludge disposal. Furthermore, it offers the potential for the recovery and recycling of metal sulfides (Rowley and Warkentin, 2001).

The principle similar to Biosulfide process has been applied to remove sulfur compounds from water and gaseous streams. The process has been described by de Vegt and coworkers (1998) and is called by trade name THIOPAQR. It has two biological steps. The first step is the reduction of sulfate to sulfide by SRB similar to the one used by Rowley's group. The reducing reaction in which ethanol is used as a source of hydrogen is



In the second step, SRB convert excess hydrogen sulfide to elemental sulfur. It is a biocatalyzed redox reaction



The chemical step, precipitation of metal sulfides by hydrogen sulfide is similar to the one described used by Rowley's group.

Table 10.3. Influent and Effluent Concentrations of the High Sulfate Water Treated at Kennecott Utah Copper (de Vegt *et al.*, 1998).

Parameter	Influent, mg/L	Effluent, mg/L
PH	2.3	8.5
Sulfate	30,000	<500
Aluminum	2,050	<2
Calcium	480	50
Copper	60	<0.1
Iron	675	<0.3
Magnesium	4,500	1.950
Manganese	330	0.3
Zinc	65	<0.1

A treatment plant following this approach has been installed at Budelco Inc., in the Netherlands. It is designed for an inflow of 300 m³/h of an influent containing 100 mg/L zinc and 1,000 mg/L sulfate and producing an effluent with < 0.3 mg/L zinc and 200 mg/L sulfate. The treatment plant has four main components: an upflow anaerobic-sludge blanket (UASB) reactor for the SRB process, including a gas-handling system; a

submerged fixed-film (SFF) reactor for the aerobic conversion of sulfide present in the SRB effluent to elemental sulfur; a tilted plate settler for the removal of solids; and a continuously cleaned sand bed filter, as a solids polishing step before discharge. (Figure 10.3).

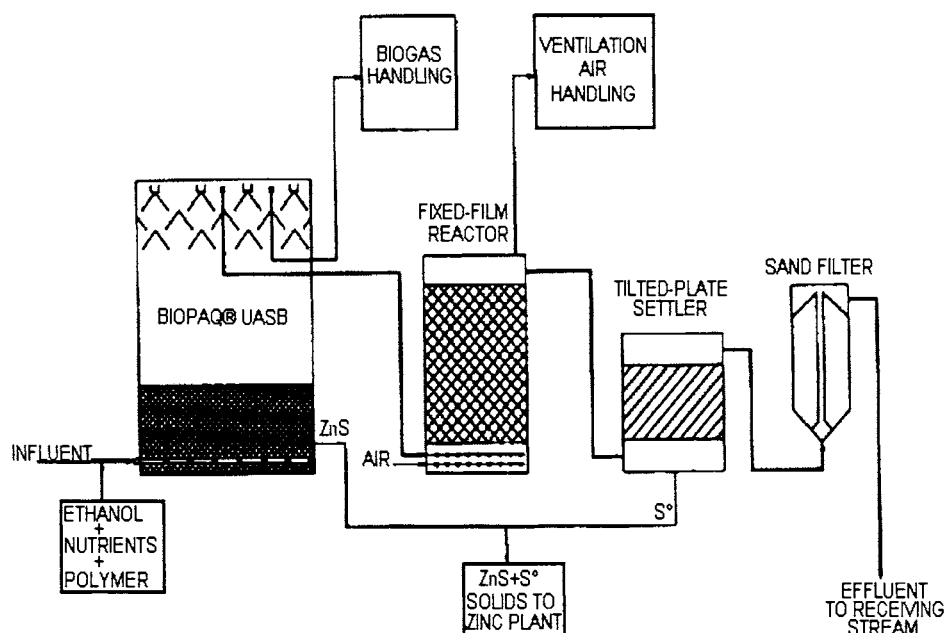
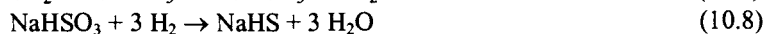
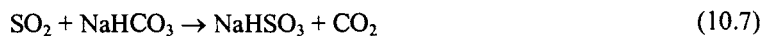


Figure 10.3. Simplified process diagram of biological metal removal and sulfate reducing plant (de Vegt *et al.*, 1998; with permission of the Society for Mining, Metallurgy and Exploration, Littleton, CO)

Another treatment plant on similar principles has been installed at Kennecott Utah Copper in Bigham Canyon, Utah. It is designed to treat streams with high sulfate concentration. The success of the operation is shown by virtually complete removal of copper and zinc and significant reduction in sulfate concentration. (Table 10.3).

A related application of this technology is to produce sulfide ion for the precipitation of heavy metals and/or elemental sulfur by the reduction of sulfur dioxide generated in the extraction of metals from sulfide minerals (van Lier *et al.*, 1999). Sulfur dioxide is first absorbed and neutralized by sodium bicarbonate to produce sodium bisulfite. The bisulfite is reduced to bisulfide in an anaerobic reactor:



Part of the sodium bisulfide is converted to hydrogen sulfide and the balance oxidized to sulfur:





Additional examples of applications of this technology for mine effluent treatment have been described (Boonstra *et al.*, 2001, 2002). It serves the dual purpose of water treatment and metal recovery from acidic effluents.

10.1.1.5. Ecological Engineering Solution

Another interesting approach, to some extent related to biotechnological route, is that developed by Boojum Technologies, Toronto, Canada. (Kalin, 2005). This is based on establishing conditions for prolific algal growth in a pond through which acid mine drainage flows. The algal material adsorbs the base metal impurities. The old algal matter with the metal loading gradually settles as sediment where, under anaerobic conditions are established acid is neutralized and the base metals fixed as sulfides. Inexpensive industrial materials or metallurgical wastes have been used for neutralizing acid. For example, suspension of 4 tons of magnesium scrap in a lake of 65 hectare area, consumes acid and raises the pH. Test results have suggested that another 16 tons of the metal scrap would raise the pH sufficiently to create conditions under which algae will proliferate and effectively neutralize the AMD, resulting in natural water. Periodically (once a century) the pond requires draining or dredging to permit recovery of the metal laden organic sediment for roasting to provide a base metal oxide product for conventional processing.

The ecological approach has also been investigated for the treatment of tailings from other mining areas, including pyrrhotite, uranium, copper-zinc and coal (Kalin *et al.*, 1991). Very inexpensive materials, peat and hay, straw and sawdust, which are readily available as agricultural and industrial wastes have been employed as carbon source for the growth of microorganisms. The process results in acid reduction and precipitation of metals as sulfides. It has been given the name, ARUM process – Acid Reduction Using Microbiology (Kalin *et al.*, 1991).

At this time, this ecological engineering approach where waste from one source is used to counteract waste produced in another source is mainly a remedial step, to reclaim water by neutralizing the acid. In a much longer term, probably after many decades of treatment, the sediments could become a rich secondary source of base metals.

10.1.1.6. Treatment of AMD Using Permeable Reactive Walls

Based on the same principles of biological reduction of sulfate, another process, where a reactive wall is made from the reducing materials has been developed (Blowes *et al.*, 1995; Benner *et al.*, 1999). The walls are installed in aquifers down gradient of contaminant source areas. The contaminated water is allowed to passively flow through the reactive materials of the wall, where the sulfate reduction and metal precipitation (Equations 10.2 and 10.3) occur.

The optimal mixture of materials for the wall should be reactive enough to remove the target contaminants from the flowing groundwater at its natural velocity, and sufficiently stable to remain active for an economically viable period of time. The usual mixture investigated by Blowes and coworkers (1995) consists of composted leaf mulch, pine mulch, and pine bark as the organic carbon sources, creek sediment as a source of sulfate reducing bacteria, agricultural limestone (CaCO_3) as a neutralizing agent, and coarse sand and gravel, to increase the permeability of the mixture.

10.1.2. Heavy Mineral Production from Oil Sands Tailings

The province of Alberta in western Canada is known for huge deposits of oil sands. They are mined for the extraction of bitumen. The extraction process consists of treating the bitumen rich sand with hot water by a process developed by Clarke (1944), a pioneer developer of Canadian oil sands resource. From the resulting emulsion bitumen is separated. Heavy minerals, occurring in the sand, have been found to accumulate in bitumen froth recovered in the extraction process.

Currently, approximately 200 million tonnes of oil sand is being mined annually by the processing companies in Alberta. Chemical analyses of exploration core samples have shown an average of 0.5 % titanium dioxide.

After the bitumen is extracted as a froth in separation vessels the froth is treated in a two stage centrifuge process with naphtha diluent to reduce solids and moisture in the product bitumen. Solids and water are removed from diluted bitumen by centrifuging and then discarded as tailings. A typical grade of the plant tailings is 11.5 % TiO_2 (titania) and 3.4 % ZrO_2 (zircon). The amount of froth tailings totaled 2.5 million tons in 1994, containing 166,000 tons of titanium dioxide. The distribution of titania and zircon around the major bitumen product circuits is shown in Figure 10.4.

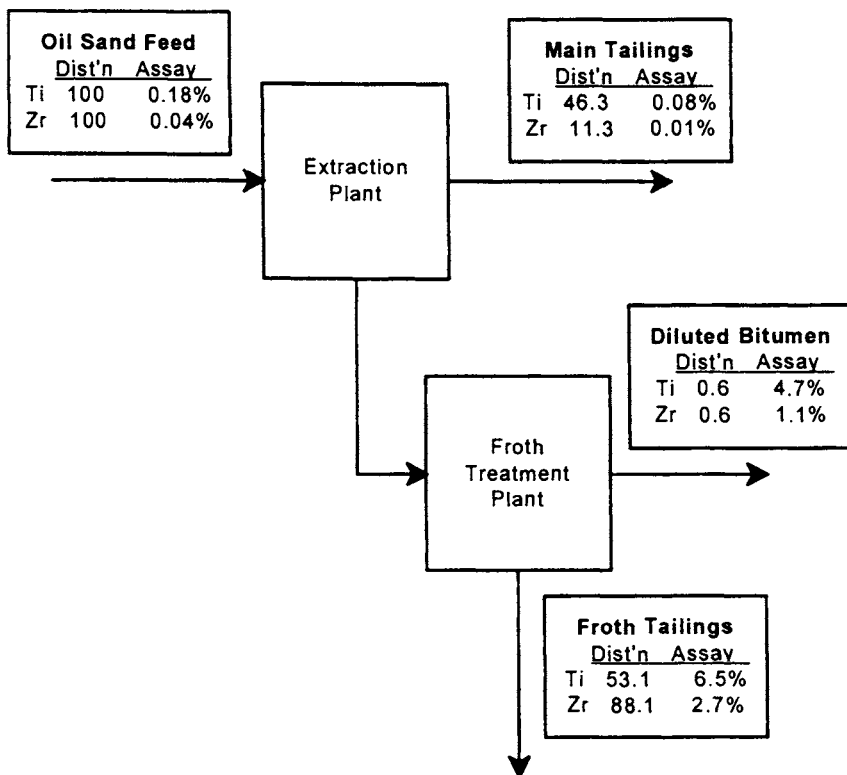


Figure 10.4. Distribution of heavy metals in froth treatment of oil sands (Owen and Tipman, 1998).

Over 50 % of the titanium in the oil sand and 90 % of the incoming zirconium report with the froth treatment tailings. Mineralogical analyses of the froth feed to froth treatment indicates the presence of ilmenite, leucoxene, rutile and zircon in the solids.

At the current level of production of 370,000 barrels per day the potential heavy mineral recovery from live tailings is estimated to be 430,000 tons per year (Owen and Tipman). Future expansion is planned to produce 910,000 barrels per day by 2007. This would generate 10.6 million tons per year of froth treatment tailings, containing 495,000 tons of titanium dioxide. The potential heavy mineral production rate is capable of exceeding one million tons per year as bitumen production approaches one million barrels per day.

Recovery of titanium and zirconium minerals can be achieved by employing mineral processing techniques. It is done in two stages. The first stage illustrated in Figure 10.5 comprises the use of hydrocyclones followed by bulk flotation. By this route almost 60 % silica is rejected. The bulk flotation tailings are returned immediately to the existing tailings circuits. The froth product is delivered by disc filters. The arrangement includes a tailings storage tank, sized for four hours of centrifuge plant tailings, a building containing a bank of flotation cells and ancillary equipment, and a concentrate storage tank, also sized for four hours.

The concentrate filter cake is oxidatively roasted to produce a dry concentrate with bitumen removed and pyrite oxidized. The amount of bitumen normally present in the roaster feed contains a significant fuel value. The dry concentrate and collection from the off gas cyclone/backhouse is conveyed to a bin.

In the second stage of processing illustrated in Figure 10.6 separate heavy mineral concentrates are produced. The dry concentrate is conveyed to an attrition mill where it is wetted and fine iron oxide particles are removed as slimes. Coarse agglomerates and oversize particles, including garnet and graphite are removed by a vibrating screen. Undersize from the screen is pumped to a classifying cyclone. The slimes pass overhead to the thickener. Sized and deslimed concentrate are collected as cyclone underflow. It is fed to a low intensity magnetic separator which pulls out ilmenite concentrate. The ilmenite is dewatered by a disc filter and conveyed to a storage bin. The non-magnetics flow to a set of spiral classifiers. The light fraction from the spirals are rejected as silica tailings to the thickener. The heavy fraction stream is subjected to high intensity magnetic separation. The non-magnetics produce a zircon concentrate, dewatered and stored. The magnetic stream is mainly rare earths. The rare earth concentrate is dewatered and conveyed to a storage bin. The spiral concentrator middlings are run through a high intensity magnetic separator. The non-magnetic stream is taken for reverse flotation to float silica which is transferred to the thickener. The sinks are collected as rutile concentrate.

The magnetics of spiral middlings are also subjected to reverse flotation. The concentrate consists of a tourmaline rich stream, and the sinks are a leucoxene concentrate. The leucoxene is dewatered and stored.

Plant tailings mostly consist of silica. After dewatering it can be used as an inert mineral suitable for landfill or even backfill. (The use of tailings as backfill will be discussed in Chapter 10). The second stage processing also produces an excess of clarified water. With appropriate safeguards it can be recycled in one of the extraction plants or returned to a water stream. The spiral concentrator middlings are run through a

high intensity magnetic separator. The mineral products recovered from a plant are described in Table 10.4.

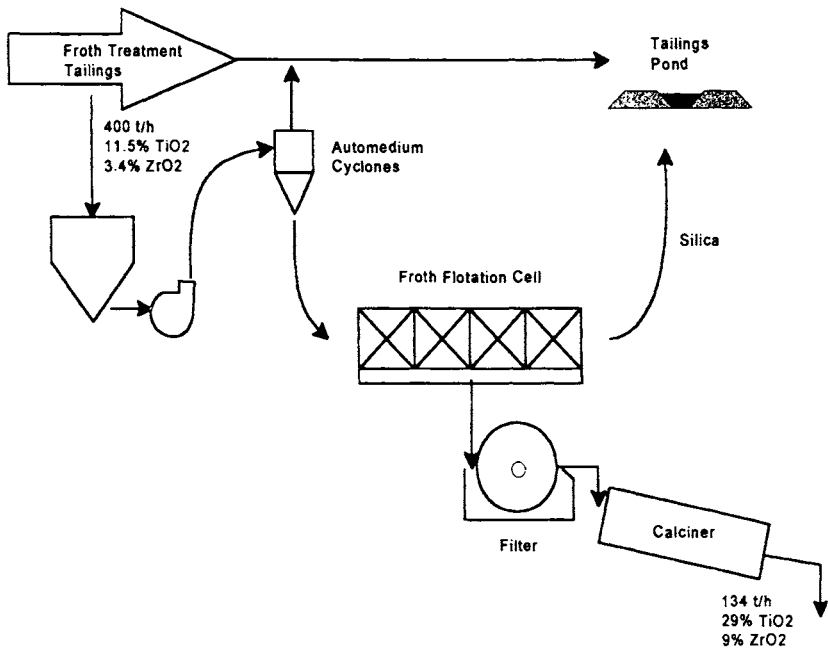


Figure 10.5. First stage mineral processing treatment of froth tailings (Owen and Tipman, 1998)

Table 10.4. Potential Heavy Mineral Production Rates.

(Dry) tons per hour	Product	(Dry) tons per year
11.4	Rutile	68,400
26.7	Leucoxene	160,000
7.9	Ilmenite	59,000
10.3	Zircon	61,800
1.3	Rare earths	7,800

Table 10.5. Production of Synthetic Rutile

Element	% assay in leucoxene	% assay in residue after leaching	% removal by leaching
Aluminum	1.9	2.3	11.5
Iron	16.4	2.2	90.1
Silicon	2.4	2.6	18.7
Titanium	36.7	40.7	2.4

Further processing of the products consists of treating specific minerals to convert them into saleable products. Leucoxene is subjected to reduction roasting to form ferrous and metallic iron from the ferric oxide present, followed by leaching with ammonium chloride. Processing of leucoxene to synthetic rutile removes over 90 % of the iron with 910.6 % recovery of the titanium. It is summarized in Table 10.5.

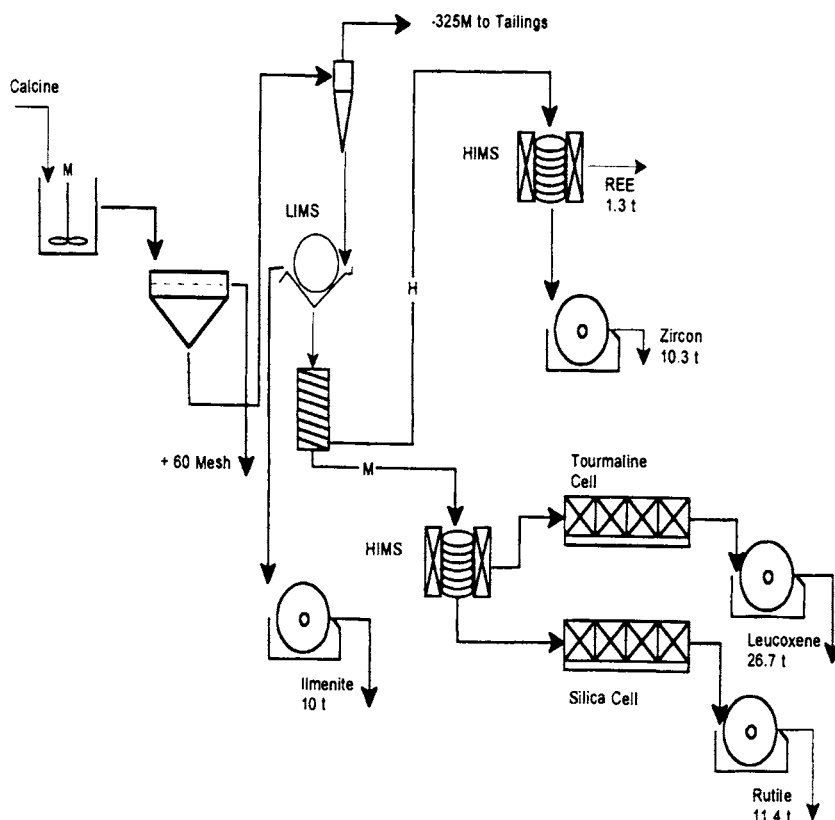


Figure 10.6. Second stage mineral processing and product separation (Owen and Tipman, 1998)

The silica content of the rutile in the concentrate is reduced by pressure leaching. By caustic pressure leach at 200 °C over 80 % silica can be removed with 100 % recovery of the titanium.

Both ilmenite and leucoxene are close to commercial grade products in all respects, but with lower calcium and magnesium content than hard rock ilmenite. This indicates a suitable feedstock for upgrading, but the economies of synthetic rutile production offer low rates of return than other processes and product options.

One significant product of commercial value is titanium dioxide pigment which can be produced from the processing concentrate. The results of low cost feedstock and relatively low energy requirement make the production of pigment feasible at a cost lower than the current world low cost (Sherritt International, 1996).

Production of heavy minerals and pigment can be amongst the lowest cost producers worldwide due in large part to the high grade of liberated heavy minerals in the tailings from the oil sands plants. The following financial summary shows the economic potential of utilizing the oil sand tailings.

Concentrator:

- 350,000 tons per year
- Capital cost - \$50 million
- Annual operating cost - \$14 million
- Product value fob West Coast of Canada \$51 million
- Annual revenue after product freight - \$42 million
- Internal rate of return – 19 %
- Net present value - \$40 million

Pigment Production

- 120,000 tons per year
- Capital cost - \$350 million
- Annual operating cost - \$177 million
- Annual revenue after freight – 4425 million
- Internal rate of return – 23 % after tax.
- Net present value- \$392 million

10.1.3. Recovery of Nickel Values from Pyrrhotite Tailings

The milling of nickel ores of Sudbury area in eastern Canada (Ontario province) has resulted in a large accumulation of pyrrhotite based tailings. They are relatively high in nickel content (~ 1 %) with about half that amount associated with the small pentlandite fraction (< 2 % w/v.) While the potential metal values in these tailings reach several million dollars in the production of only one year, they also represent a potential source of acidic heavy metal bearing drainage.

Several processing techniques have been investigated for the recovery of nickel from the pyrrhotite tailings. One promising approaches is based on biohydrometallurgy Tackaberry *et al.*, 1998). Solubilization of nickel values has been achieved using *Thiobacillus* (T.) *ferrooxidans* enriched with *T. thiooxidans*. With eight different T *ferrooxidans* strains nickel values are solubilized at maximum rates during the first 24-30 hours (~ 10 %) and increase to approximately 50 % after 28 days. (Figure 10.7). In the first six days pH of 3 has to be maintained by acid addition. The pH stabilizes to around 3.7 by 28 days (Figure 10.8). Nickel to iron ratios in the bioleach liquor goes to 0.225 as compared to the unleached solid tails value of 0.017. At a high pulp density of 20-25 % nickel extraction is 44 % and low acid consumption is observed with the presence of copper; however, Ni:Fe ratio is only 0.032 after 21 days as shown by the results recorded in Figures 10.9 and 10.10).

The highest rate of nickel extraction occurs within the first 24-28 hours but, unfortunately, high iron solubilization also occurs. Shorter leaching times to obtain maximum nickel extractions depend upon the ratio of ferric iron in solution to ferrous iron in precipitates. These considerations lead to two leaching options.

The first option would be tank leaching in a ferric sulfate process where the ferric sulfate is externally produced via bacterial oxidation using recycle leach liquor. This approach has the advantage of relatively fast kinetics and the possible recovery of sulfur

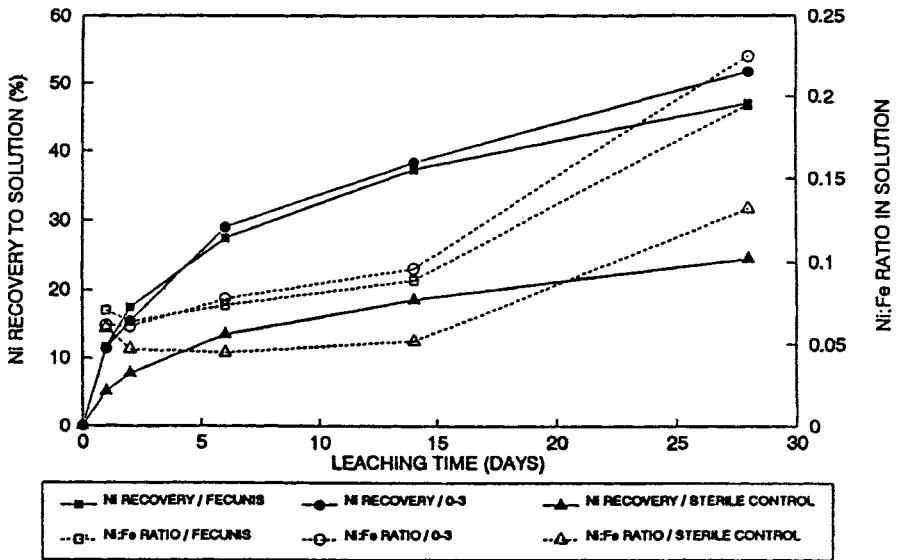


Figure 10.7. Leaching of nickel from pyrrhotite tailings with and without *Thiobacillus ferrooxidans*; kinetics of nickel recovery and selectivity of solubilization (Tackaberry *et al.*, 1998)

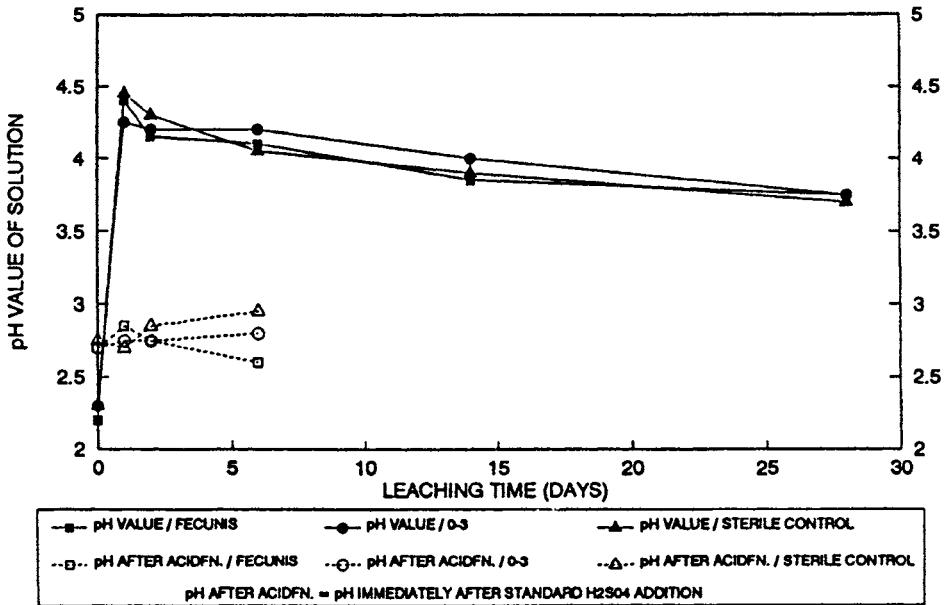


Figure 10.8. Leaching of nickel from pyrrhotite tailings with and without *Thiobacillus ferrooxidans* (Tackaberry *et al.*, 1998)

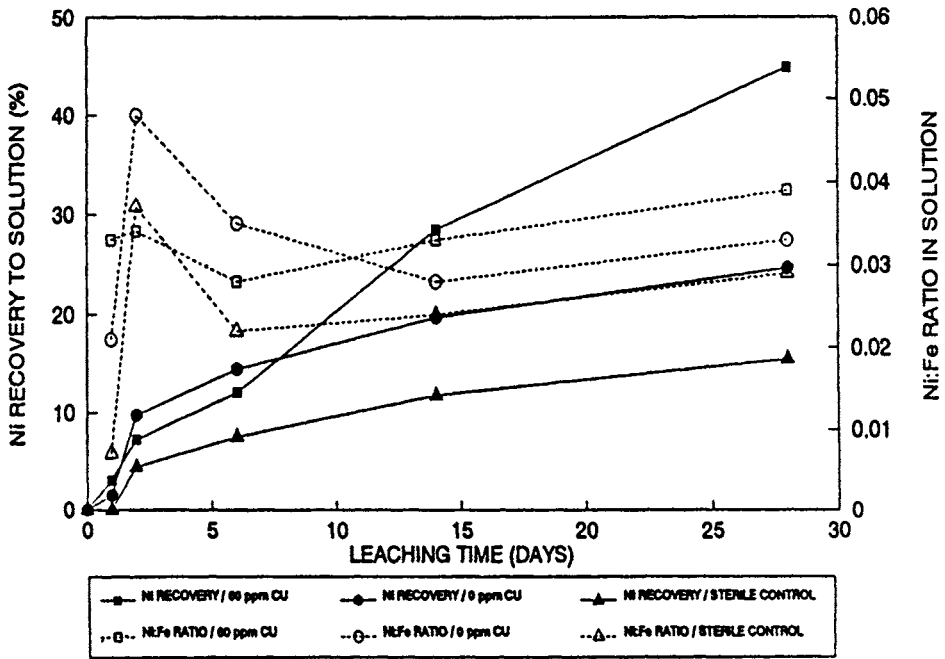


Figure 10.9. Effect of copper on nickel recovery and selectivity of solubilization in the leaching of nickel from pyrrhotite tailings with *Thiobacillus Ferrooxidans* (Tackaberry *et al.*, 1998)

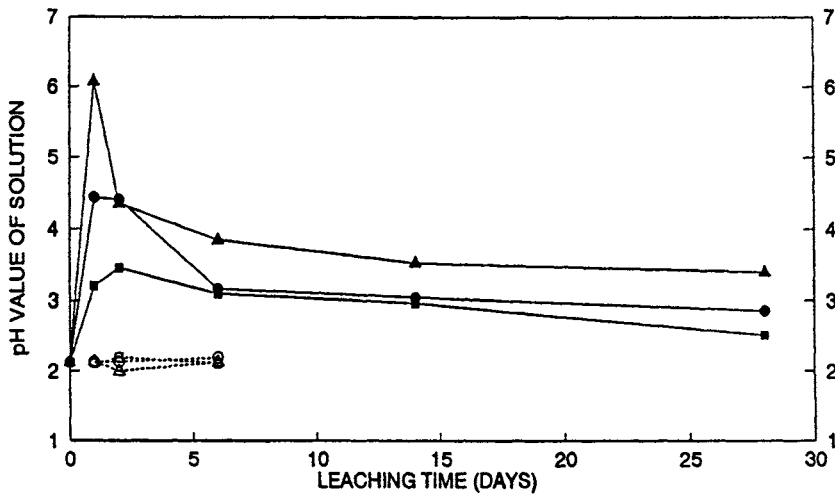


Figure 10.10. Effect of copper on pH in the leaching of nickel from pyrrhotite tailings with *thiobacillus ferrooxidans* (Tackaberry *et al.*, 1998).

from the residues. However, dewatering and storage of the iron hydroxide residues may be difficult.

The second option consists of agglomeration and heap leaching, which would require the blending of the pyrrhotite tailings with other chemically inert additives (e.g., other tailings or carbonate free sand) to avoid self-ignition. An even aeration and irrigation would be most critical for this type of operation. The leached tailings may be suitable for mining backfill or could be safely disposed off under the water table. Use of tailings for backfill has been described in Chapter 9.

With either of the two options, the reactivity of the final residue would be significantly lower than that of the original tailings thus lowering the risk of acidic tailings.

10.1.4. Recovery of Phosphate from Phosphatic Wastes

In the beneficiation of phosphate ores the tailings generated still carry significant phosphate content. The recovery has been difficult as the tailings carry a large proportion of clay minerals, magnesium oxide and iron carbonate mineral known as ankerite, an iron carbonate. Until recently, there was no suitable method for separating phosphate from such clayey wastes.

Progress has been made to recover some fraction of phosphate from these wastes. Separation of ankerite mineral has been attempted by magnetic separation with some success (Abdel-Khalek *et al.*, 2001). The magnetic stream enriched with phosphate is further processed by flotation to separate magnesium oxide. A product containing 31-32 % P_2O_5 by processing tailings with 20 % P_2O_5 has been produced (Abdel-Khalek *et al.*, 2001).

10.1.5. Recovery of Minerals from Tailings of Non-Ferrous Ores

When non-ferrous ores are processed for the recovery of economically valuable minerals often generates tailings, which could contain other useful minerals, which are not separated by the technique used. Often such tailings carry silica and clay minerals in major proportion. Some of them have economic potential. In addition, many tailings also carry base metal compounds. They may be recovered by further processing by different techniques. An example of such secondary processing is illustrated by a process developed to recover sericite from tailings of non-ferrous metal ores.

A lead-zinc ore occurring in China contains a clay mineral, sericite in significant proportion. It is subspecies of mica, of chemical composition, $H_2KAl_3(SiO_4)_3$. Because of its special physical properties, better flexibility, higher mechanical strength, heat resistance and lower coefficient of thermal expansion, it is widely used in rubber and plastics industry.

When the lead and zinc minerals (sulfides) are separated by flotation using xanthate, most of the sericite goes into tailing as clay minerals do not become hydrophobic by xanthates. In addition, the clay minerals fraction is very fine; especially, sericite is finer than other clay minerals and is not easily floatable. A mixed reagent containing long chain amines is used as collector and sodium fluosilicate as depressant (to minimize the flotation of quartz and other clay minerals) is found effective. About 28 % of sericite with a purity ranging from 58 % to 96 % could be recovered. The products are considered to be acceptable for use in rubber, plastics and coating industry (Chen *et al.*, 1998).

10.1.6. Recovery of Refractory Gold from Mill Tailings

Gold is conventionally recovered from the associated minerals by alkaline cyanide leaching. However, when gold occurs in encapsulation of micron size particles in cyanide unreactive minerals such as sulfides, silicates, or clay minerals it is refractory to conventional cyanide leaching. Occurrence of refractory gold in mine mill tailings has given incentive to alternative methods of winning the precious metal. One such method described by Haque and coworkers (1998) makes use of microwave preheating of the tailings to optimize gold recovery by alkaline cyanide leaching.

Some of the major mineral components of old mine mill tailings are goethite ($\text{FeO} \cdot \text{OH}$), jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), calcite (CaCO_3) and quartz (SiO_2).

The tailing sample is placed in an applicator. The ore bed is fluidized with air or nitrogen and simultaneously microwave heating is commenced. It is continued to a bed temperature of 400-420 °C at which point heating is stopped and fluidization continued until cool.

The microwave pretreated sample is next subjected to alkaline cyanide leaching step. The tailings are suspended to obtain a leach slurry with 33 % solids. The pH is set at 10.5-11.0 by sodium hydroxide. Oxygen gas is sparged through the slurry to obtain an optimum level of dissolved oxygen (DO). Lead nitrate, 0.5-0.8 g/kg solids is added to the slurry. Sufficient sodium cyanide is added to reach a cyanide ion concentration of 1 g per kg solid. The slurry is agitated for 48 hours. The solution phase of the slurry is separated by filtration. The filter cake is washed twice and dried to constant weight.

Microwave heating of the tailing selectively converts goethite to hematite and destroys or greatly eliminates jarosite (which would cause difficulty in solid/liquid separation). As a result of such pretreatment gold recovery by alkaline cyanide leaching has been found to increase between 90 % and 100 %.

The mill tailings may also be pretreated by sulfuric acid (100 ml acid per 500 g tailing and heated to 104-106 °C for 6 hours.) The acid completely decomposes calcite, but has no discernible effect on goethite, jarosite or quartz. Subsequent alkaline cyanide leaching yields gold recovery of approximately 70 %, significantly less than microwave treatment, but higher than the 50 % recovery usually obtained from untreated mill tailings.

10.1.7. Production of Briquettes from Coal Tailings

Demand for coal has been increasing steadily in the last few years. Coal tailings typically represent approximately 10 % of the run of mine (ROM) production and contain approximately 50 % proportions of inorganics and coal (Canibano and Leininger, 1987). In a colliery in Australia, such tailings are converted to briquettes (Radloff *et al.*, 2004). The plant consists of a double roll press taking dry (10-20 % by weight moisture content) coal washery fines and compressing them into a 50 mm briquette. Binders are used with the dry tailings feed material being compressed in a double roll press with 50 by 25 mm depressions. Briquettes are produced and stacked under a large drying shed for curing and hardening prior to delivery to the power station, where they are used as source of thermal power generation.

The production of quality briquettes requires the feed stock to be free of moisture. In the Australian colliery, heat from the sun is used to dry the tailings and only the dry surface material is reclaimed for feed stock. This ensures maximum effectiveness in the action of the binders leading to successful agglomeration.

10.1.8. Using Dolomite-type Flotation Tailings for Flue Gas Desulfurization

Many of the sulfide ores contain dolomite (calcium magnesium carbonate) as gangue mineral, which is rejected in the tailings when the sulfide minerals are recovered in flotation concentrate. The alkalinity of such tailings makes them a potentially attractive and inexpensive material to neutralize acidic gases producing calcium sulfate (gypsum) and magnesium sulfate:

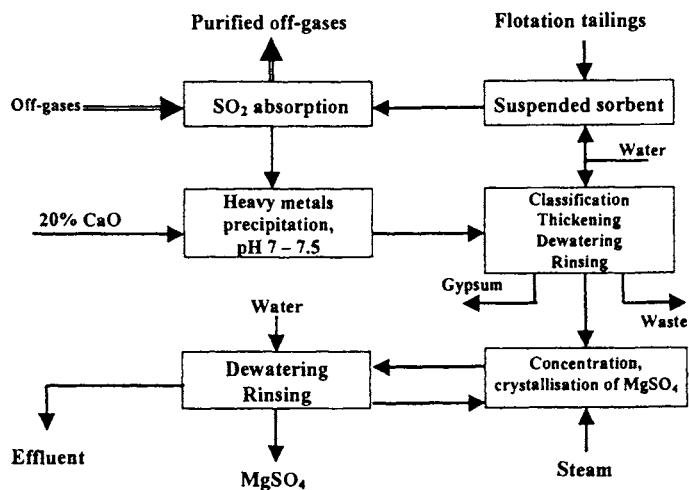
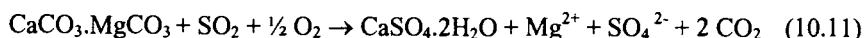


Figure 10.11. Flowsheet for production of magnesium sulfate from flue gas neutralization by flotation tailings (Chmielarz *et al.*, 2002)

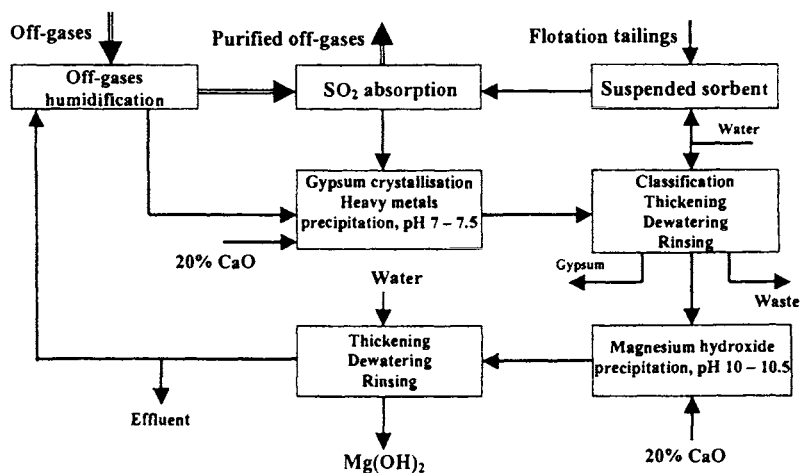


Figure 10.12. Flotation for production of magnesium hydroxide from the neutralization of flue gas by flotation tailings (Chmielarz *et al.*, 2002)

An interesting bench scale study on the absorption of flue gases carrying sulfur dioxide (generated in the roasting of sulfide ore concentrates) by Chmielarz and coworkers (2002) has produced promising results. Two tailings studied had 10.2% magnesium (zinc-lead tailings) and 7.6% magnesium (copper tailings) and about 20% calcium. The process differs in the two cases, as shown in Figures 10.11 and 10.12. Magnesium sulfate is produced as the end product. With the tailings of higher magnesium content, while from the tailings with lower magnesium content, magnesium hydroxide is produced, because in this case, the lower magnesium content does not produce sufficiently concentrated magnesium sulfate solution to crystallize the salt. Instead, by raising the pH of the solution magnesium hydroxide is produced. In both case, 20% lime is added to produce gypsum, which separates along with heavy metal sulfates (formed by the small concentrations of such metals as copper and zinc present in the tailings).

10.2. Metallurgical Effluents and Residues

Metal processing industry is the second principal source of 'waste'. This occurs in the form of effluents and residues, which are a source of environmental hazard as they often contain toxic metals and cannot be disposed off without appropriate treatment. Any liquid discharged into the environment must meet environmental regulations, which specify upper limit of each metal in the discharge liquid. Appropriate treatment techniques are required both to meet environmental regulations as well as to recover metal values, otherwise lost in the effluents.

10.2.1. Recovery of Nickel from Sulfate Metallurgical Effluents

Solvent extraction technique has been applied for the recovery of several metals, in particular, nickel and cobalt from metallurgical effluents. Recovery of nickel from a sulfate effluent of a large tankhouse has been achieved using versatic acid (Cole and Nagel, 1997). An organic phase consisting of 1 M versatic acid in a commercial solvent (Shellsol 2325) which serves as diluent (Cole and Nagel, 1997) produces a raffinate with < 10 mg/L nickel in five extraction stages operated at an aqueous to organic phase flowrate ratio of 3.8. The optimum pH profile is 6.3 in the first extraction stage increasing to 6.7 in the last stages, the pH maintained by 2.5 % ammonium hydroxide solution. The stripping of the loaded organic phase is completed in three stages using 100 g/L sulfuric acid at an organic-aqueous phase flowrate ratio of 20.

Table 10.6. Composition of Various Solutions in a Solvent Extraction Counter current Trial Using Versatic Acid (Cole and Nagel, 1997).

Stream	Feed	Raffinate	Loaded organic	Loaded strip liquor
Co	177	35	70	220
Mg	1480	1265	6	4
Ca	507	467	5	5
Mn	518	417	65	130
Fe	< 2	< 4	< 4	2
Cu	63	< 4	40	77
Zn	5	< 5	6	11
Ni	8500	191	7790	43300

Table 10.6 shows a typical composition of the feed, raffinate, loaded organic phase and loaded strip liquor. (See Chapter 4 for the chemistry of versatic acid).

The copper and zinc are extracted along with the nickel and are concentrated into the loaded strip liquor. Some 80 % of the cobalt in solution is extracted. Some manganese is also extracted, although at the pH of extraction (pH 6.3) it is expected that manganese hydroxide would precipitate from solution. Only traces of calcium and magnesium are carried into the organic phase.

When versatic acid is mixed with nitrogen donor synergists, the nickel extraction shifts significantly into the more acidic region. Figure 10.13 shows the extraction curves for nickel with versatic acid alone and in mixture with 4-nonyl pyridine which acts as synergist. The pH_{50} value (pH at which 50 % extraction occurs) for nickel shifts from 6.5 to 4.6 in presence of the synergist.

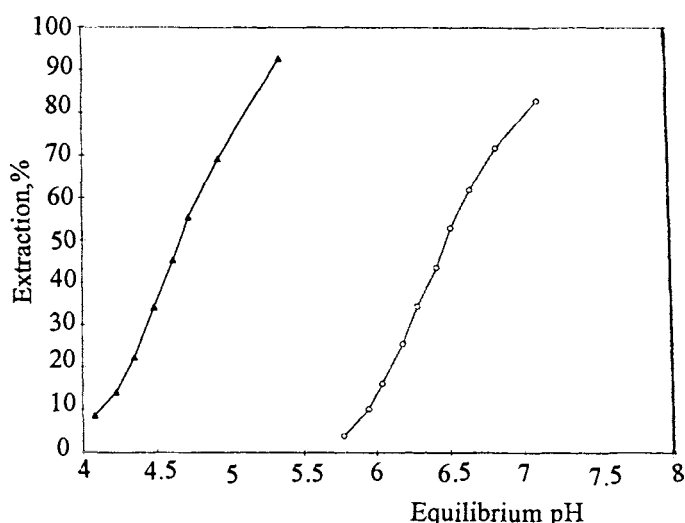


Figure 10.13. Extraction of nickel by 0.5 M versatic acid (triangles) and a mixture of 0.5 M versatic acid and 0.5 M 4-nonyl pyridine (circles) (Cole and Nagel, 1997)

Four counter current extraction stages operated at an organic-to-aqueous phase flowrate ratio of 2.4 reduces the nickel from 8.5 g/L to < 0.6 g/L. No precipitation of nickel or manganese hydroxides occurs at pH of 6. Stripping of the loaded organic phase is achieved with a strip liquor containing 60 g/L nickel and 50 g/L sulfuric acid. This composition simulates a typical anolyte from a nickel electrowinning circuit. At higher acid concentration an adduct of the 4-nonyl pyridine and sulfuric acid is formed. This is marked by the appearance of a third phase on start-up of the strip circuit; but it soon disappears.

A flowsheet to produce solution suitable for the electrowinning of high grade nickel from a dilute nickel sulfate solution is shown in Figure 10.14. The use of the versatic acid plus synergist system upgrades nickel and effectively reject calcium, magnesium and manganese into the raffinate at a pH that would result in no soluble loss of the extractant. Purification of the upgraded nickel solution with respect to the other base metals will be required before nickel can be electrowon from the solution.

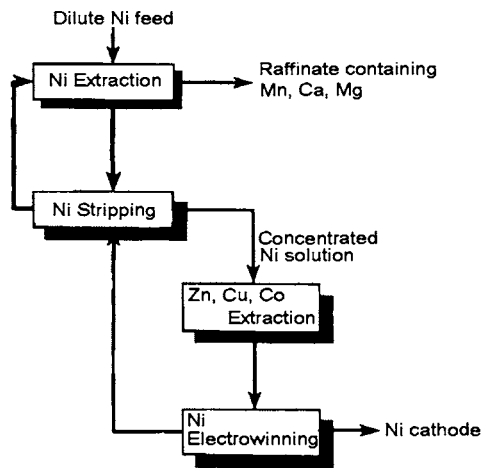


Figure 10.14. Flowsheet for the upgrading and purification of nickel using a versatic acid based solvent system (Cole and Nagel, 1997)

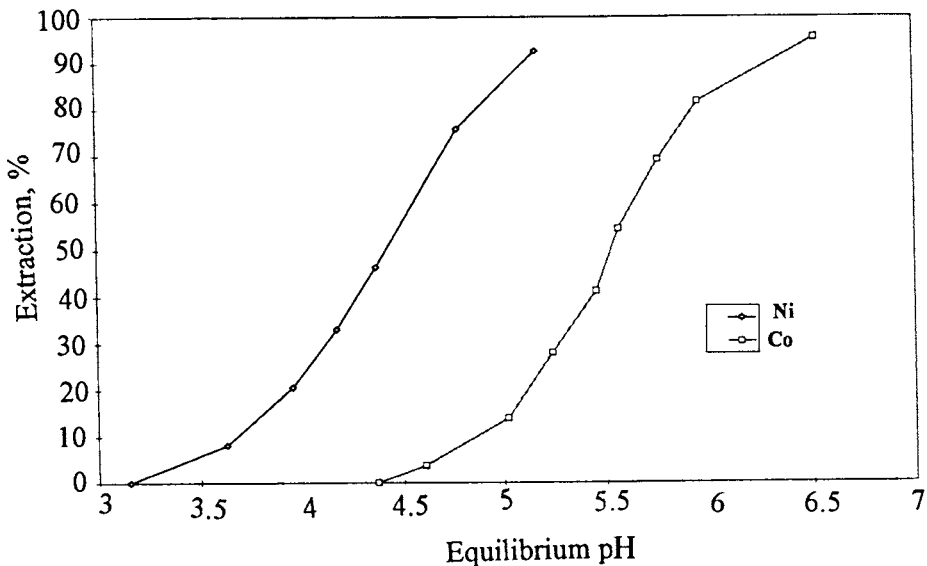


Figure 10.15. Extraction of nickel and cobalt by 0.5 M versatic acid 1 M 2—methyl decanloxime in Shellsol AB (Cole and Nagel, 1997)

When versatic acid is mixed with an oxygen-donor synergist the nickel extraction curve is shifted into the more acidic region while the cobalt curve is shifted into the less acidic region (Cole and Nagel, 1997). The separation between nickel and cobalt for an organic phase mixture of versatic acid and 2-methyl decanalo xime (2MDO, an oxygen donor synergist) is shown in Figure 10.15. The separation achieved by this organic phase system has been made use of in the development of a flowsheet to treat cobalt-containing

slags to produce cobalt cathode. The flowsheet is shown in Figure 10.16. By continuous counter current nickel concentration can be reduced from a level of 1 g/L to an acceptable level of 0.3 g/L in seven extraction stages using the versatic acid plus 2MDO mixture.

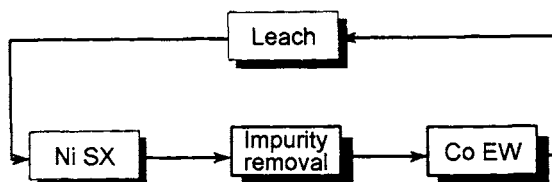
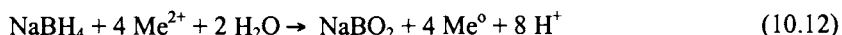


Figure 10.16. Flowsheet for the purification of a cobalt liquor derived from the leaching of cobalt slag (Cole and Nagel, 1998)

10.2.2. Metal Recovery from Spent Pickling Solutions

Plants manufacturing products of copper alloys generate waste materials along their production lines. These include slag, chimney dust, scrap turnings and spent acid pickling solution, which contain economically valuable metals, specially, copper and zinc. The physical state of pickling solution makes it possible to concentrate the valuable metals without extensive preparation stage. Part of the residual toxic metals can also be removed together with the copper and zinc, which reduces load on the wastewater treatment process.

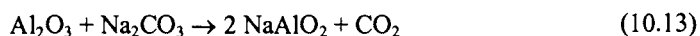
Cementation by iron powder is a convenient method to displace copper and zinc from pickling solution. Another reagent used is sodium borohydride (Guillermo *et al.*, 1995). It reacts by the following reaction:



The advantage of using this reagent is that it does not lead to the production of ferrous salt solution. The product formed is sodium borate, which is soluble and can be reclaimed as it is a useful industrial product.

10.2.3. Metal Recoveries from Red Mud

The major waste product generated in the alkaline extraction of alumina from bauxite (called Bayer process) is known as red mud, the red color caused by iron oxide of the ore. Approximately a ton of red mud is produced for every two tons of bauxite mined. Besides hematite, it also contains alumina and titanium dioxide in significant amounts. As with most tailings, red mud is an environmental liability. It is thick and the solids do not easily settle down. A pyrometallurgical process to recover metals from red mud has been described by Mishra and coworkers (2000, 2002). The red mud is first dried to remove moisture and some of the volatiles. A sample is heated in a magnesium oxide crucible to 400 °C for 2 hrs. in a nitrogen atmosphere, then cooled at 2°/min. The product is sintered with addition of stoichiometric amount of sodium carbonate (calculated on the basis of predetermined alumina content) to convert alumina to aluminum sulfate:



The mixture is heated in nitrogen atmosphere to 850 °C to 1100 °C for 2 hrs. The product is then cooled at 2°/min. It is leached in sodium hydroxide to dissolve sodium aluminate. The red mud is filtered, washed and is taken to recover iron. The iron oxide is reduced using petroleum coke at 900° to 1100 °C in nitrogen atmosphere. The iron is recovered from the red mud by magnetic separation. It is then leached in hydrochloric acid and the metal isolated by electrowinning. Alumina is recovered from sodium aluminate. About 90% reduction of iron and 83% recovery of alumina have been reported. They are, however, based on laboratory experiments. Investigations on a higher scale are required to determine feasibility of the process for processing large quantities of red mud.

10.2.4. Recovery of Metals from Low Metal Content Effluents

In addition to the specific examples of resource recovery from tailings discussed in the preceding sections, there are countless number of tailings, effluents and waste rocks, which still contain metal values in quantities, which could be recovered by appropriate technology. Some examples will be discussed in the present section.

10.2.4.1. Recovery of Copper from Low Metal Content Waste

Low metal content wastes occur in a number of areas. For example, shredding fluff of automobiles contain about 35 % copper. They have been processed by pyrometallurgical techniques. In a process developed in Japan, low copper containing wastes are melted in Mitsui furnace (See Chapter 6 for details). The molten metal is separated into copper rich phase and iron rich phase under carbon saturated conditions. (Carbon used in the form of coke reduces metal oxides). The copper content reaches 910.9 % (Tanno *et al.*, 2001). The process is schematically shown in Figure 10.17.

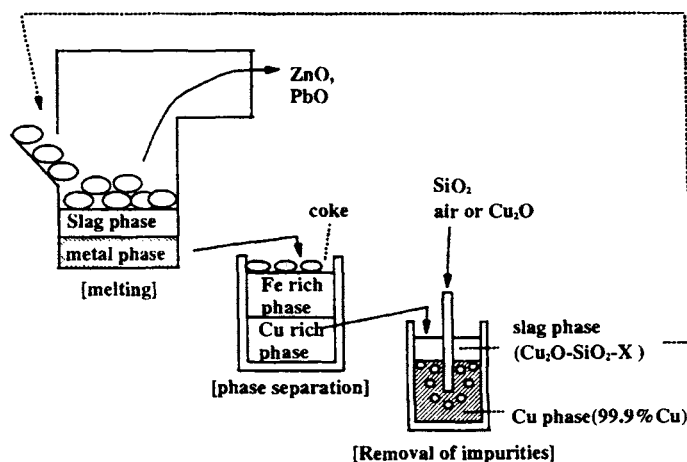


Figure 10.17. A schematic flow diagram of copper enrichment from low metal content waste and removal of impurities (Tanno *et al.*, 2001)

10.2.4.2. Metal Recoveries from Refinery Waste Electrolyte

In metal refining process by electrolytic methods, the residual electrolyte after recovering most metals still contains significant concentration of metals, which cannot be recovered by electrowinning. Up to 26 g/L Cu and 7 g/L Ni is found in a residual

electrolyte in a metal refinery in Iran (Asadi Nejad and Allahkaram, 2001). Solvent extraction is applied for the recovery of metals from such waste electrolyte. LIX reagent is used for the extraction of copper and nickel is extracted by versatic acid (see Chapter 4 for the Chemistry of these reagents and details of solvent extraction)). Over 95 % copper and nickel are recovered by the process.

10.2.4.3. Recovery of Heavy Metals from Metallurgical Effluents by Flotation

Metallurgical effluents containing copper, mercury, lead and cadmium can be processed by treatment with hydrogen sulfide followed by flotation of the sulfides. Such a separation method has been described by Nesbitt and Davis (1994). A laboratory waste solution from a copper operation is treated with gas mixtures rich in hydrogen sulfide. Metal sulfide precipitates are formed at gas/liquid interface. Copper, mercury, lead and cadmium are precipitated at $\text{pH} < 3.5$. Iron and zinc are not precipitated at this pH as their solubility products are higher (see Chapter 4). The precipitated sulfides are treated with sodium (or potassium) alkyl dithiophosphate, which is a mineral collector for sulfides. The sulfides are floated in a column flotation cell of the type shown in Figure 10.18 (Basic principles of flotation are explained in Chapter 3).

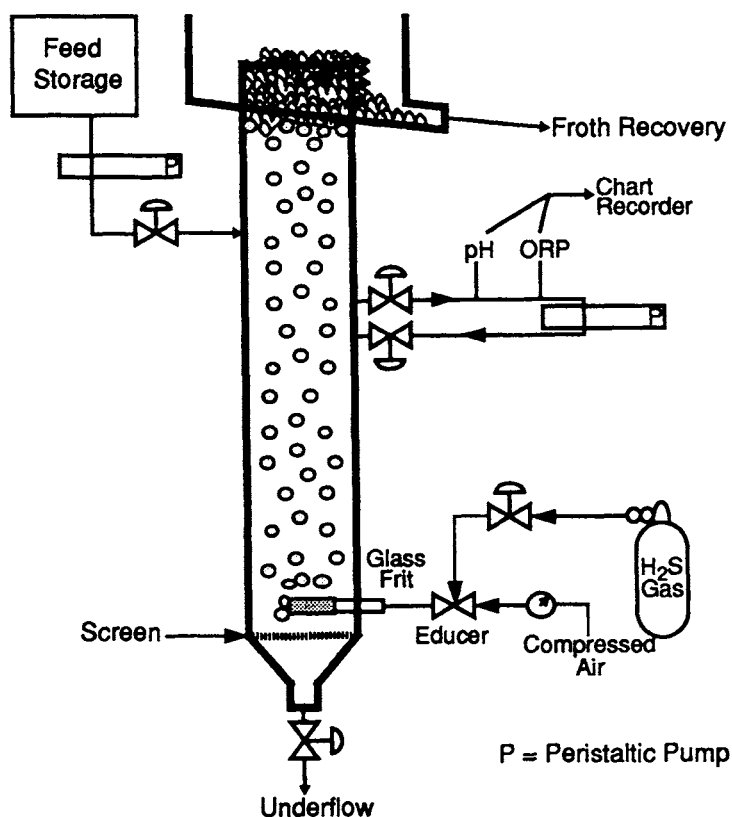
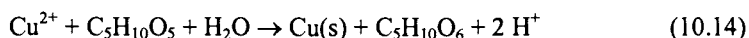


Figure 10.18. Schematic diagram of column flotation cell (Nesbitt and Davis, 1994)

Over 95 % of lead, mercury and cadmium are removed, while zinc remains in solution. Further selectivity will require finer pH and reagent control.

10.2.5. Recovery of Metals from Waste Streams by Reduction Using Organic Waste

Dissolved metal ions in effluent streams can be reduced by organic compounds at elevated temperature. For example, cupric ions are reduced to copper metal by a carbohydrate:



Essentially, the alcohol group (CH_2OH) of the carbohydrate is oxidized to aldehyde (CHO) group by the metal ions.

This principle has been applied for the development of an attractive process to recover metals from waste streams using organic waste streams containing carbohydrate type compounds (van der Weijden *et al.*, 2001). The reaction is conducted in an autoclave or a plug flow reactor at temperature about 180 °C. As the pH drops with reaction, the reaction would slow down at lower pH. By controlling the pH with sodium hydroxide up to 99 % copper could be removed from a dilute waste stream of copper using xylose, which is a carbohydrate obtained by dilute acid hydrolysis of wood at temperature > 140° C. Copper metal is formed as a fine powder.

Many example of such treatment have been described by van der Weijden and coworkers. The technique whereby the waste streams from two sources, one organic and the other metal containing effluent mutually interact producing reusable metal and producing a cleaner effluent is an excellent example of ecological engineering.

10.2.6. Germanium Recovery from a Non Ferrous Leach Residue. (Henry *et al.*, 2004)

Germanium is a rare metal used in semiconductors and other electronic devices. There are few natural minerals of germanium In 2000-2001 as germanium prices reached a height of approximately 600-800 USD/kg GeO_2 . It often occurs with other non-ferrous metallic ores and is found in metallurgical residues from which it is recovered by hydrometallurgical processes. Chemical composition of one such residue is shown in Table 10.7. It is a leach residue from a non-ferrous metal producer. One of the major challenges in this process is the varying Ge content as it depends on the process conditions of supplier. Another challenge is the Si and Al content, which causes difficulties in solid liquid separation work. Additionally, the high chloride content could result in material of construction constraints.

Table 10.7. Non-ferrous Metal Products in the Leach Residue

	H ₂ O	Ge	Cl	Fe	M ²⁺	Al	Si	S	As
%	60	0.3-0.7	4-9	30-48	3-8	0.3	3-5	1	0.1-0.2

A hot sulfuric acid leach is used to extract germanium from the feed material. The main co-extracted metals consist of: iron (50 g/L), but also elements such as silicon, aluminium as well as significant quantities of non-ferrous metals (M^{2+}).

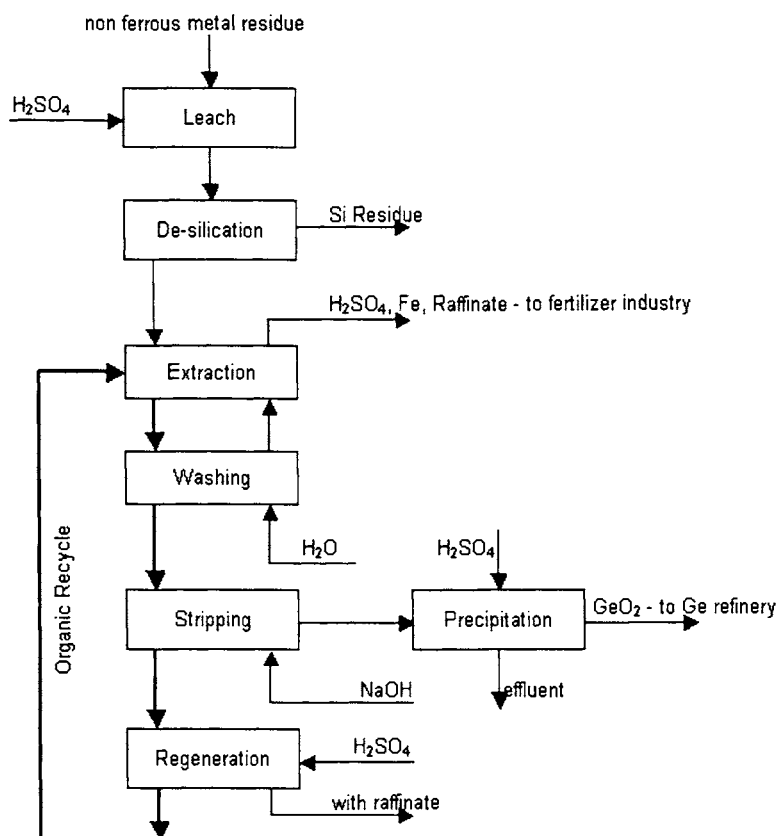


Figure 10.19. Schematic flow diagram - germanium recovery treatment (Henry *et al.*, 2004)

A de-silication process is used to remove silicon from the leach liquor. This significantly improves solid liquid separation properties as well as the down stream solvent extraction process. Table 10.8 presents the chemical composition of the pregnant leach liquor after de-silication. The process flowsheet is shown in Figure 10.19.

Table 10.8. Leach Liquor Composition

G/L			mg/L					
Fe	H ₂ SO ₄	M ²⁺	Ge	Si	Al	As	Ca	Na
50	100	11	1000	1-3	250	200	20	4000

The pregnant leach liquor advances to a solvent extraction circuit (2), in which germanium is selectively separated from the ferric sulphate liquor. The germanium free raffinate containing all acid, iron and other impurities is sold to a phosphoric acid producer in the area, in which the raffinate acidity is used to leach calcium phosphate rock while producing gypsum. Iron is recovered further downstream in the phosphoric acid purification process and used as iron units in fertilizer compounds. This represents

an enormous economic advantage in terms of savings, which would otherwise have been consumed by the neutralisation of acid and the precipitation of iron in the raffinate.

The loaded organic is washed with hot water in one stage to remove entrained organic, significantly increases reagent consumption in the stripping phase. The washed organic advances to the stripping stages, in which the germanium is extracted from the organic phase into the aqueous phase. The solvent extraction strip liquor is neutralised batch-wise to precipitate relatively pure germanium dioxide. On average the precipitate (assumed to be $\text{Na}_3\text{HGe}_7\text{O}_{16} \cdot 4\text{H}_2\text{O}$) contains 48% Ge. This material is sold to germanium refiners for the fabrication of optical fibres and catalysts.

Table 10.9. Germanium concentrate composition

	H ₂ O	Ge	Na	Si	Fe	As	M ²⁺
%	40-45	47-52	7	<0.04	<0.01	<0.01	<0.1

10.2.7. Metal Recovery from Zinc Cements

Zinc cements are metallurgical residues typically consisting of copper (15-20%), nickel (2-5%), zinc (20-30%), cobalt (5-7%) and minor quantities of cadmium and thallium. A specific flowsheet (Figure 10.20) has been developed at Hydrometal to treat such materials and to separate them into copper, cobalt, nickel and zinc concentrates. As this was a batch process, it meant that considerable storage capacity had to be put in place. For that purpose the old zinc plant clarifiers have come to good use. Intermediate precipitates are also stored on site or another process has to be developed

Table 10.10. Copper concentrate composition

	H ₂ O	Cu	Zn	Cd	Co	Ni
%	35	50-70	5-10	<1	<1	<1

Low cost residual sulphuric acid is used to leach the cements and produce a copper concentrate/residue containing more than 50% Cu. High copper grades reflect the presence of metallic (or undissolved) copper. Copper co-dissolution depends mainly on the 'freshness' or oxidation state of the cement. An old or severely oxidised cement lead to high copper co-dissolution, resultant high acid consumption and subsequent high consumption of a copper precipitating/neutralising agent. Additionally, the copper grade of the leach residue/precipitate is affected as precipitated copper (as hydroxide or carbonate) has a lower copper grade per definition than undissolved metallic copper. Alternatively zinc dust has been used as well to re-cement dissolved copper and produce a higher copper grade cake.

The pregnant de-copperized leach solution is further purified by removing cadmium and thallium using a zinc dust cementation process. Often, high copper co-dissolution during leaching results in insufficient copper precipitation and consequent high zinc dust consumption since all zinc is consumed by dissolved copper. As the zinc dust consumption is high even under optimal conditions and a high zinc content (~40% Zn) cement is produced. Possible methods to use this contaminated zinc dust elsewhere in this The purified solution, principally a zinc cobalt nickel solution advances to a cobalt precipitation stage in which cobalt is oxidised from Co^{2+} to Co^{3+} and precipitated as cobaltic hydroxide using sodium hypochlorite and caustic soda. The pH of the reaction is

controlled by addition of caustic soda to prevent formation of chlorine. Final cobalt concentration in the filtrate is less than 1 mg/L. The cobalt is precipitated in a different part of the plant more suitable for the use of chlorides and chlorine formation. Zinc co-precipitation is significant at this stage, therefore a purifying stage is introduced to selectively re-leach zinc while upgrading the precipitate in cobalt (typically more than 47% Co). The re-leached zinc units (with some re-leached cobalt units) are precipitated at pH 9 and recycled within the flowsheet.

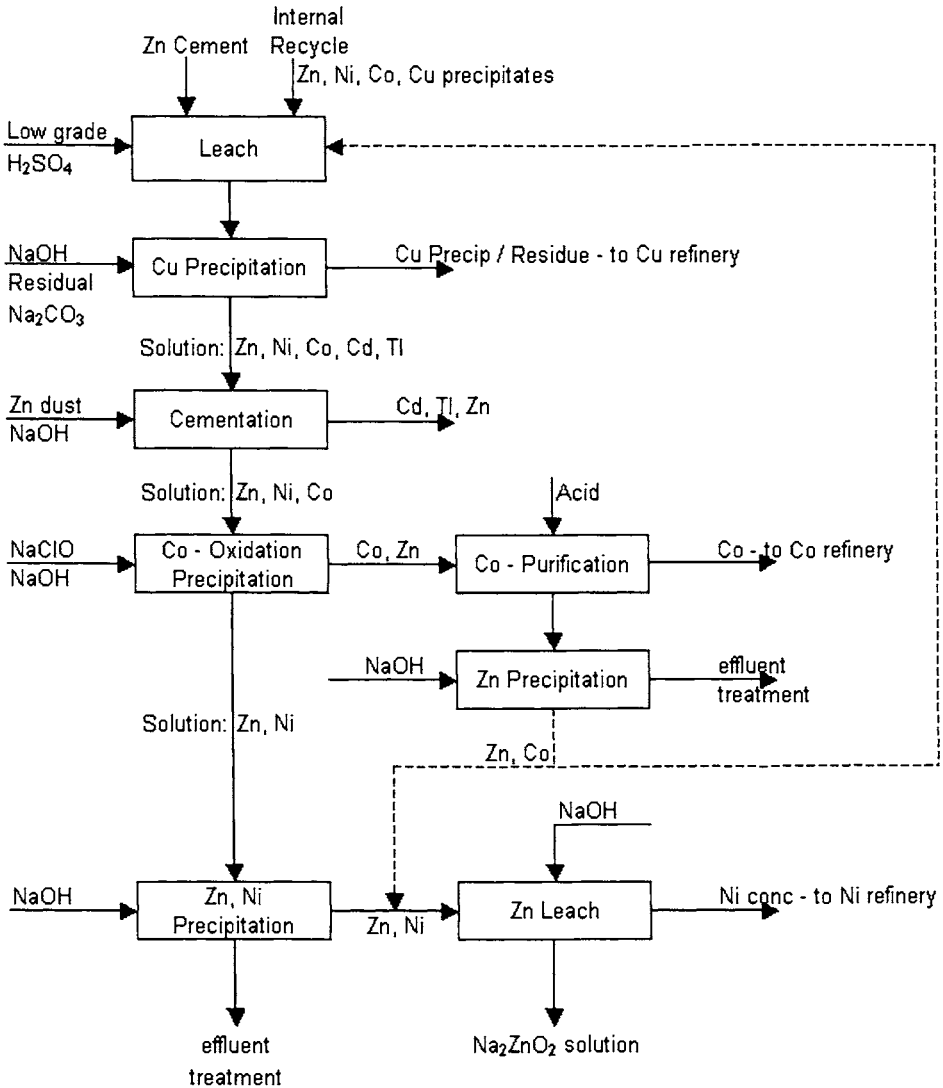


Figure 10.20. Schematic flow diagram of zinc cement treatment (Henry *et al.*, 2004)

Table 10.11. Composition of Cobalt Concentrate

	H ₂ O	Co	Zn	Fe	Mn	Cd	Cu	Ni
%	35	>47	3	3	2.5	<0.1	<1	<0.3

The filtrate, principally nickel and zinc, advances to a second precipitation circuit in which all remaining soluble metals are precipitated as hydroxides (~4% Ni, ~60% Zn) around pH 9. The zinc nickel hydroxide cake is leached in hot caustic soda to produce a sodium zincate solution and a nickel concentrate (leach residue). The sodium zincate solution (40 - 42 g/L Zn), upon purification by zinc dust, is sold to nearby industries for the production of zinc oxide, while the nickel residue/concentrate (20–30% Ni) is sold to the nickel refining industries.

10.2.8. Recovery of Gallium from Bayer Liquors

Bayer process is a one of the commonly used processes for extracting aluminum from bauxite ore. It is leached in sodium hydroxide, which chemically dissolves aluminum oxide to form sodium aluminate, from which aluminum hydroxide is precipitated. Details are described in hydrometallurgy text books; see, for example, Habashi (1970).

As the bauxite ore contains gallium as oxide (Ga_2O_3) in small concentrations, which is also leached by sodium hydroxide forming sodium gallate (NaGaO_2). As gallium is a relatively rare element, used in semiconductor industry, and there are only a few primary sources available there is incentive to recover gallium from the secondary source.

A chelate forming resin, with amidoxime groups, represented by $\text{R}-\text{C}(=\text{NOH})\text{NH}_2$, (trade name, Duolite ES-346, manufactured by Rohm and Haas) where R denotes the resin matrix has been described by Riveros (1990).

10.2.9. Recovery of Silver from Photographic Process Waste

Silver is a most common metal used in photographic and x-ray films. The used films are therefore a rich secondary source of silver.

Recovery of silver from photographic wastes has been done by various methods. As it is a noble metal, it can be easily displaced from soluble silver salt solutions (most commonly silver sulfate) by a base metal. Zinc is most commonly used. Disadvantage of this method is that it will result in the production of a large volume of zinc nitrate solution, which has to be treated to recover and recycle zinc, which can be done by precipitation as zinc hydroxide or zinc sulfide.

Al alternative method is electrowinning. The photographic film is first leached in nitric acid. The resulting silver nitrate is electrolyzed with a steel cathode and copper anode. The steel cathode is brushed to remove the deposited silver. The cathode is then re-cleaned and used for electrowinning another batch. The extraction efficiency can be enhanced by the presence of cyanide in the electrolyte as silver forms argentocyanide complex. (Basics of electrowinning are explained in Chapter 2). A saturated solution of meshed cassava has been used as an inexpensive source of cyanide (Ajiwe and Anyadiegwu, 2000).

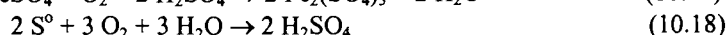
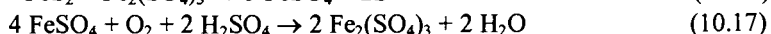
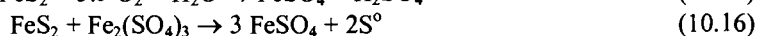
10.2.10. Recovery of Cobalt from Cobaltiferous Pyritic Waste

Bioleaching has been applied to recover metal values from pyritic wastes generated as flotation tailings. An example is found in the recovery of cobalt from cobaltiferous pyritic material, investigated by Morin and coworkers (1995). The material is separated

by flotation and contains about 80 % pyrite and 1.38 % Co, 0.14 % Cu and 0.12 % Ni. Cobalt is mainly disseminated in pyrite in unidentfied form. A small fraction occurs as siegnite $[\text{Co,Ni})_3\text{S}_4]$ and pentlandite $[(\text{Ni,Fe,Co})_9\text{S}_8]$ -bravoite $[\text{Fe,Ni,Co})\text{S}_2]$ association. He gangue minerals are mainly quartz, silicates and gypsum.

Leaching is done in 20 L baffled tanks in cascade. Bacterial colony from mine water, consisting of *thiobacillus ferroxidans* and *thiobacillus thiooxidans* is enriched by the 9K medium (Silverman and Lundgren, 1959; see Chapter 4). The basic medium has the composition, in g/L, $(\text{NH}_4)_2\text{SO}_4$ 3.7, H_3PO_4 0.6, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.52 and KOH 0.48.

The following leach reactions take place:



Limestone is used to control the pH between 1.1 and 2.0 in the leaching process at 35° C. After the leaching of metals, the pH is raised close to 3 to separate iron as jarosite (a complex iron hydroxide) precipitate, according to the reactions:

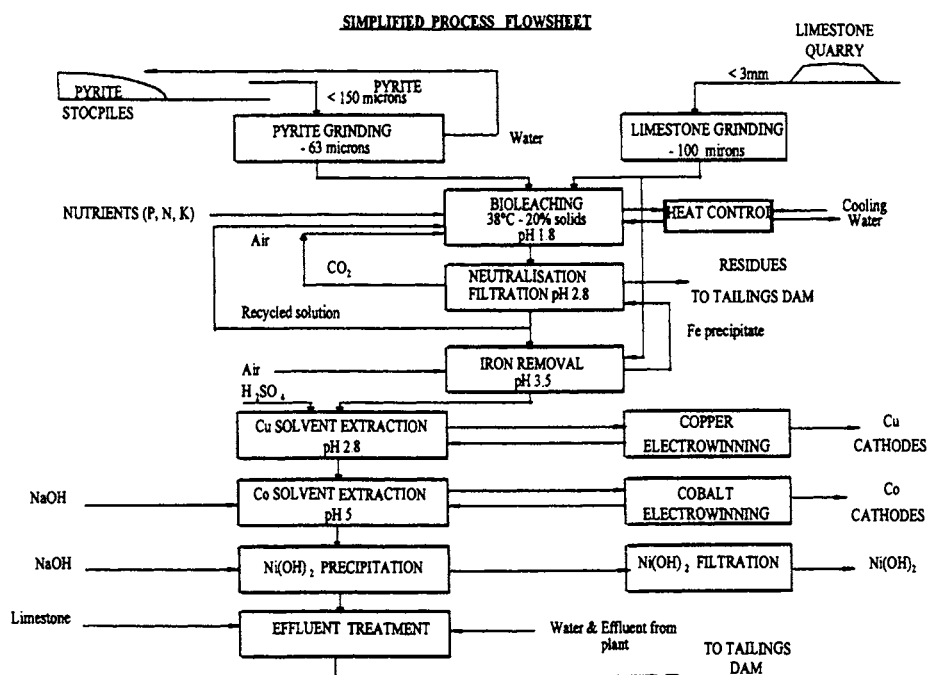
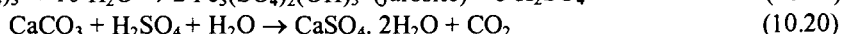
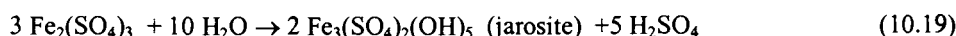


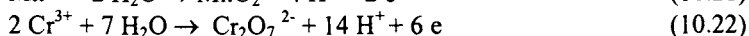
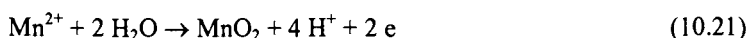
Figure 10.21. Flowsheet for the treatment of cobaltiferous pyrite ((Morin *et al.*, 1995)

Following the separation of iron, copper, nickel and cobalt are separated by solvent extraction. Copper is first recovered by LIX (oxime) reagent. It is tripped from the organic phase by sulfuric acid and recovered by electrowinning. After copper removal, the pH is raised to 4.5-5 by caustic soda and cobalt is extracted using Cyanex 272 (phosphonic acid) at 50-60° C. That is also stripped by sulfuric acid from the organic phase and recovered by electrolysis in cells with lead anodes and stainless steel cathodes. Finally, nickel is recovered as hydroxide by precipitation with sodium hydroxide at pH 8. The flowsheet of the process is shown in Figure 10.21.

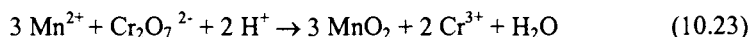
10.2.11. Chromium from Chromate Waste

The electroplating industry generates large quantities of chromate or dichromate waste. As chromium is a highly toxic metal, discharge of such wastes is environmentally unacceptable. Removal and recovery of chromium from such wastes is an economic as well as environmental necessity.

A chromium recovery method where chromium is reduced to the trivalent state, separated from other dissolved metals by cementation by manganese, followed by electrolysis to recover chromium metal has been described by Becker and coworkers (1994). In the first step chromate is reduced to chromic compound by reduction by sulfur dioxide. The solution, pH 2.2-2.5, now contains chromic sulfate along with several other metal sulfates, of which copper is the dominant. Manganese powder is added, which displaces these metals by cementation reaction (explained in Chapter 4). The solution is then sent for electrolysis in a set-up with an anode of lead alloy carrying a layer of lead dioxide by passivation of the metal, and stainless steel cathode. Chromium is discharged at the cathode. The oxygen discharged at the anode oxidizes the lead to produce lead dioxide. Two other electrochemical reactions occur at the same time: oxidation of manganese ions to form manganese dioxide; and oxidation of chromic ions to form dichromate:



However, dichromate is not found in the anolyte, which is explained by its reduction to chromic state by manganese dioxide:



10.2.12. Extraction of Metals from Industrial Hazardous Wastes

Many metallurgical industries generate hazardous wastes containing dissolved toxic metals. Examples are, steel industry, which produces fumes from smelting operation, the non-ferrous mining industry (from the smelting and refining of the metals produced), and the plating industry. Some of the residues are processed before they are classified as wastes. The non-processed wastes, amounting to several hundred tons per year are discarded as hazardous. Often they contain valuable metals in concentrations higher than the original ores from where they were extracted. For example, pentlandite ore processed for extracting nickel, occurring in Sudbury region of Canada contains 5-6 % Ni. Some of the waste sludge stored in tailing ponds contains 7-8 % metal. Production of metals from such wastes should be very profitable as they do not require mining and grinding, two

principal steps, which significantly contribute to the cost of recovering metals from natural virgin sources. It is, however, necessary to develop economically feasible techniques to achieve metal recoveries from such waste sludges. An example is illustrated by a hydrometallurgical flow sheet developed to recover several metals from the wastes generated in plating industry (Pommier, 1998). It is shown in Figure 10.22.

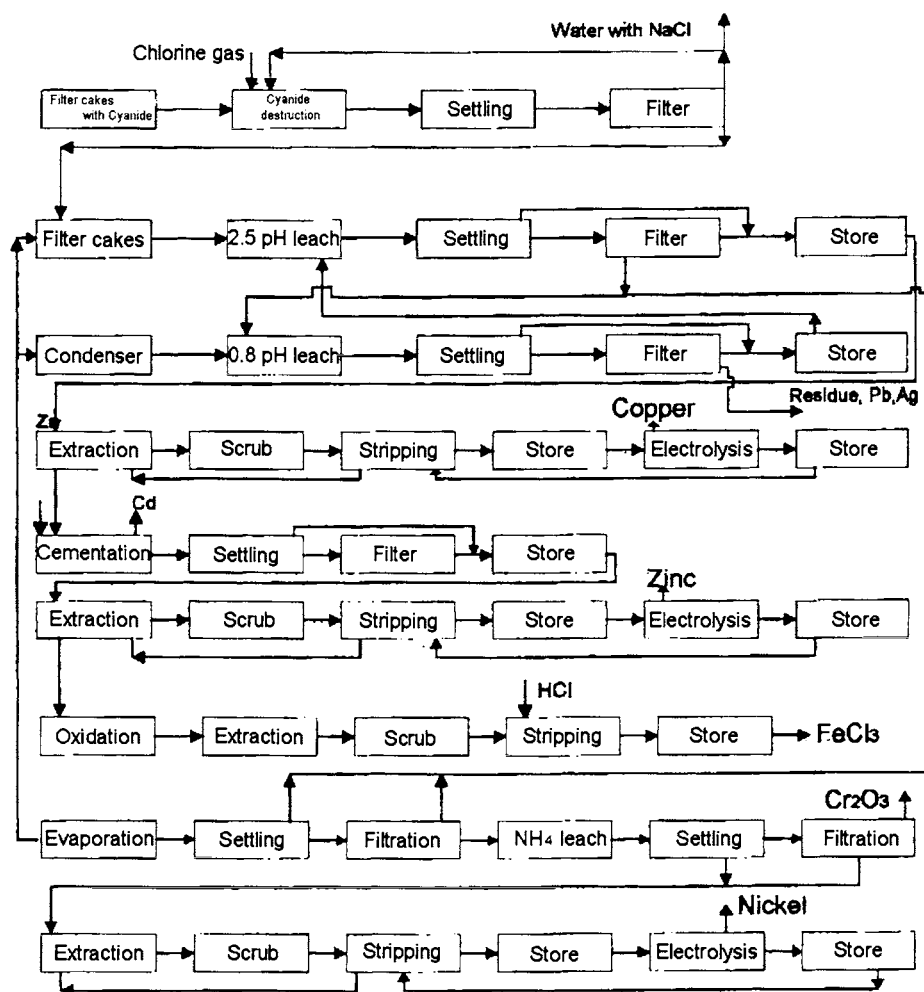


Figure 10.22. Extraction and refining of metals from filter cakes, containing cyanide produced in the plating industry (Pommier, 1998).

Waste residues are first leached in sulfuric acid at pH 2.5 to dissolve the metals of interest. The extraction is completed by lowering the pH to 0.5. The liquor from this operation is used to leach new filter cake at pH 2.5. The residues of three leaching operations at pH 2.5 and 30 % solids by weight are sufficient to produce one low pH leaching approximately the same solids concentration, using tanks of similar capacity.

The two stage leaching procedure generates a clean liquor for metal extraction, a clean plant residue and a build up of "impurities" within the leaching circuit. The impurities may be extracted after they have reached maximum concentration, by simple pH adjustment and filtration. A stream of the low pH liquor is diverted to a pH adjustment tank, the pH adjusted to 2.5 and from the precipitate build up, those metals whose hydroxides are soluble at pH 0.5 but insoluble at pH 2.5 are filtered.

The metals dissolved at pH 2.5 are separated by solvent extraction (SX). Using either LIX or DEHPA (see Chapter 4 for the chemistry of these compounds) extractant diluted in kerosene. One SX step, one scrubbing step and one stripping step, at pH 1.5 leads to almost complete recovery of copper (~ 3 ppm in the residual liquid) and an electrolyte with copper in high concentration (~ 30 g/L). Copper is separated by electrolysis.

Cadmium and lead, which may be present in the electrolyte are removed by cementation. Zinc powder is added to the copper free liquor. This precipitates any lead and/or cadmium. A portion of the cathodic zinc may be used in place of zinc powder.

The copper-free solution, freed from cadmium and lead, is sent for extracting zinc by solvent extraction using D2EHPA. Stripping is done by sulfuric acid at pH 1.0. The zinc free liquor contains 2 ppm of zinc and the zinc electrolyte contains 35 g/L zinc. After the extraction, scrubbing and stripping, zinc is separated by electrolysis using stainless steel cathodes. The electrolyte is recycled for stripping.

The copper-free solution, freed from cadmium and lead, is sent for extracting zinc by solvent extraction using D2EHPA. Stripping is done by sulfuric acid at pH 1.0. The zinc free liquor contains 2 ppm of zinc and the zinc electrolyte contains 35 g/L zinc. After the extraction, scrubbing and stripping, zinc is separated by electrolysis using stainless steel cathodes. The electrolyte is recycled for stripping.

Oxygen is bubbled through the zinc-free solution for about an hour to oxidize all iron to ferric state. The liquor at pH 1.0 is sent to another solvent extraction using D2EHPA, which extracts all the oxidized iron. It is stripped with a concentrated solution of hydrochloric acid to produce ferric chloride for the market.

The residual liquor is evaporated at 120 °C to precipitate both chromium and nickel and the concentrated sulfuric acid is recycled to low pH leaching stage. The precipitate of nickel and chromium sulfates is treated with a 50-50 mixture (by weight) of ammonium hydroxide and ammonium carbonate, at pH 10, which dissolves the nickel and generates a chromium oxide residue. The nickel solution is processed by solvent extraction using D2EHPA. The nickel in the extract is recovered by electrolysis. The chromium sulfate precipitate is roasted at 450° C to produce chromium oxide for marketing.

This is an innovative process serving dual purpose of recovering metal values from a metallurgical waste and producing a harmless residue of small volume.

10.3. Recovery of Metal Concentrates from Waste Sludges

The sludge produced by lime treatment of industrial effluents often contains many impurities associated with the cupric hydroxide. Several treatment steps are required to obtain the desired purity copper hydroxide concentrate. In a process described by Jandova and coworkers (2000), the sludge is first leached in dilute sulfuric acid at pH 0.9-1.0. This dissolves the cupric hydroxide along with several other metal oxides. The acid leach residues are separated by a solid liquid separation step. The copper is precipitated by 50 % sodium hydroxide, pH 6.0, followed by a second solid-liquid separation step. The cupric hydroxide precipitates is still contaminated. It is calcined at

800-900 °C. This produces cupric oxide. The aluminum oxide present as an impurity is converted to iron aluminate (FeAl_2O_4). In the next step of acid leaching with 1 M sulfuric acid, cupric oxide is selectively leached while the iron aluminate remains insoluble. The purified copper solution is treated with 50 % sodium hydroxide to precipitate cupric hydroxide concentrate. The flow sheet of this process is shown in Figure 10.23.

10.3.1. Recovery of Metals from Acid Mine Drainage (AMD) Sludge

In many mining areas the AMD produced is still treated with lime, which precipitates all residual heavy metals producing a sludge and releasing water containing mainly dissolved calcium and magnesium. The sludge is stock piled in tailing areas and is an environmental hazard. Further, it contains metal values, copper, zinc and nickel depending upon the composition of the original ore, and large proportion of ferric hydroxide.

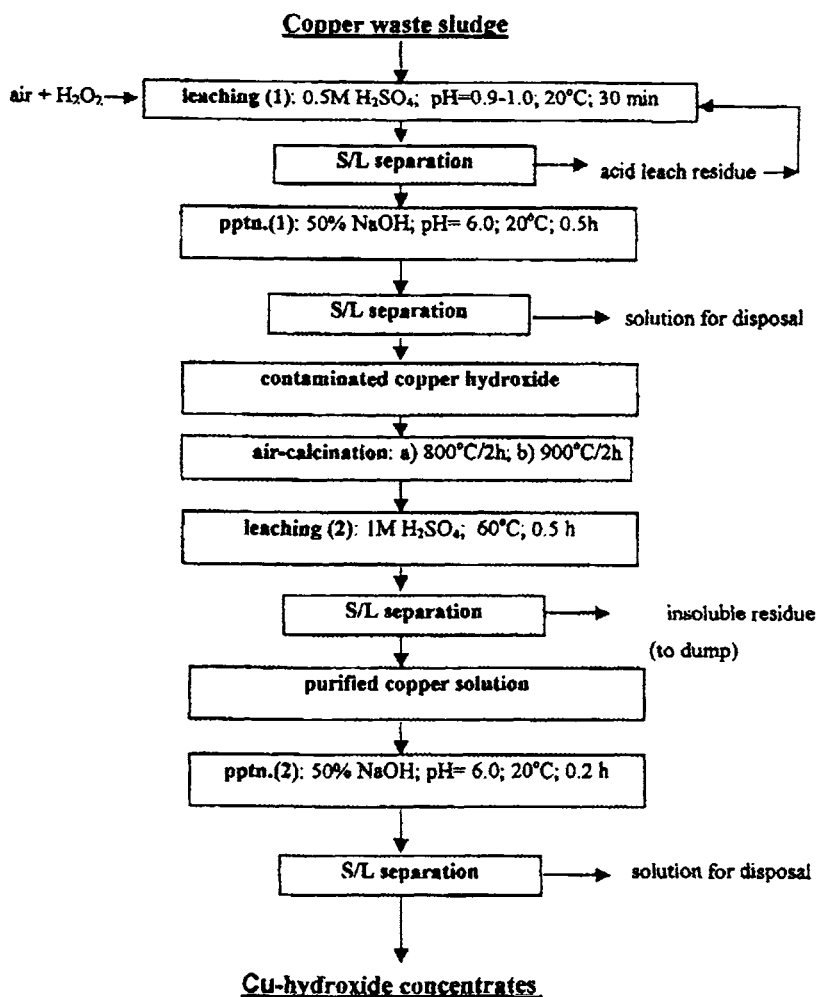
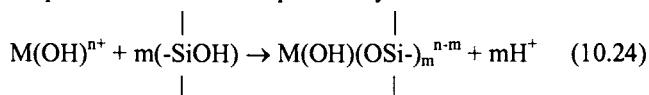


Figure 10.23. Flowsheet of processing copper waste sludge (Jandova *et al.*, 2000).

In a novel method developed by El-Ammouri and coworkers (2000) the sludge is first leached with sulfuric acid to pH ~3.5 to selectively leach all metals hydroxides except ferric hydroxide. The metals are then recovered by adsorption by activated silica sol. It is based on the adsorption of cations onto silica gel. In general, metal removal begins at pH levels slightly below the values for the precipitation of the corresponding metal hydroxide. The adsorption mechanism is expressed by



As this is a cationic reaction, the adsorption is pH dependent. Similar reactions have been reported for metal adsorption (El-Ammouri *et al*, 1998; Rodgers, 1999).

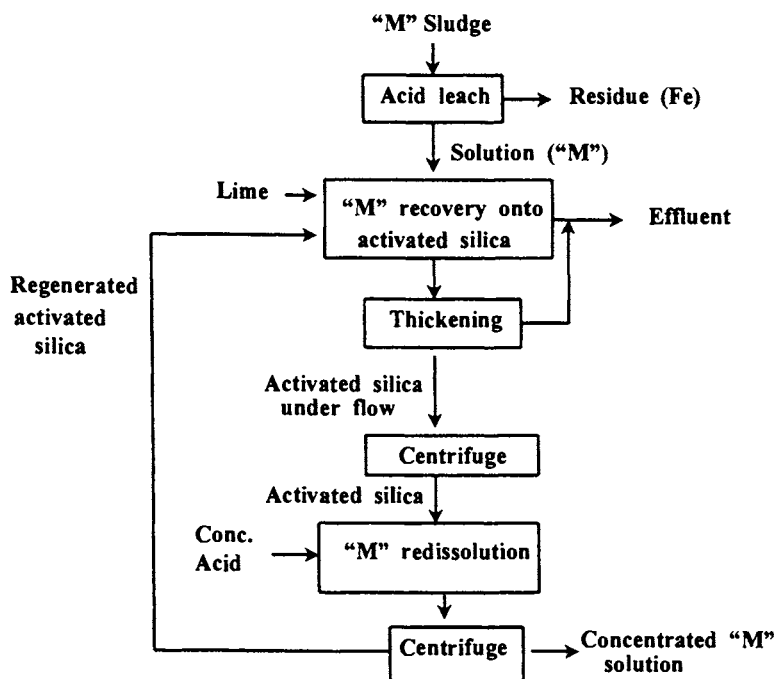


Figure 10.24. Sludge treatment using activated silica sol (El-Ammouri *et al.*, 2000)

After sulfuric acid leach and phase separation by settling, activated silica sol is added to the leach solution at a controlled metal/silica ratio to pH 8.5, controlled by lime ('M' recovery box in Figure 10.24). After the addition of sol and lime, the metal (nickel or zinc) is incorporated into the sol and calcium precipitates as gypsum. The metal-sol phase settles readily into a layer giving a sharp interface and a clear supernatant. Settling can be enhanced by centrifugation. A small volume of concentrated sulfuric acid is added to the metal-sol phase ('redissolution' in Figure), followed by centrifugation/separation. This produces a concentrated metal solution and the silica sol is recycled. The process is described in Figure 10.24.

Activated silica is a polymeric form of silica. It is prepared by adding sodium silicate solution to deionized water to give a solution at pH 11.2. Polymerization is initiated by

mixing 10 % sulfuric acid with gentle agitation. The agitation is stopped after acid addition is completed. Total polymerization occurs in about 18 minutes. The activated silica is diluted by an equal volume of water after 9 minutes of gelation to stabilize the sol. The final colloidal sol used for metal adsorption has 1 w/w % SiO₂ in the form of long chain negatively charged silicate polymers. Further details are described in the paper by El-Ammouri and coworkers (2000). The mechanism of gelation and determination of gel times have been described by Iler (1979). The term 'active' refers to the polymerization process still being active, though retarded by dilution.

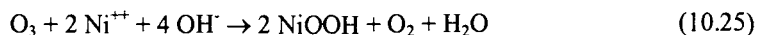
The method, applied to a nickel sludge containing high proportion of magnesium hydroxide produced 100 % nickel recovery at pH 8.5 with up to 90 % magnesium rejection. The redissolution step (pH ~1.5) produced a solution containing about 15 g/L Ni as nickel sulfate, sufficiently concentrated solution for the electrowinning of nickel. With a zinc hydroxide sludge, from an initial 5 g/L Zn in leach solution, a 45 g/L solution of Zn as zinc sulfate is produced. One problem encountered is entrapment of solution with the recycled silica, which will require silica sol to be washed before recycling.

10.3.2. Metal Recovery from Hydroxide Sludges

Many years of the mining and processing of nickel sulfide ore in Sudbury nickel belt (in the province of Ontario, Canada) has led to the generation of huge quantities of waste sludge. Nickel sulfide ore, mainly consisting of pentlandite nickel iron sulfide, and pyrrhotite (non-stoichiometric iron sulfide) is processed by flotation whereby pentlandite is separated as concentrate and the tailings consisting of most of the pyrrhotite along with dolomite and silica gangue and residual nickel sulfide are discharged into tailing ponds where they accumulate. The solid settles down producing the sludge and the supernatant water is recycled. While the disposal of sludge in the tailings ponds is common practice in mineral processing operations and meets the current needs and environmental regulations of mining industry, it is not the best practice as in the long term the tailing ponds will represent land, which is set idle and is not aesthetically pleasing. Further, the accumulated sludge containing significant quantity of nickel, which is a toxic metal, is a potential environmental hazard. There is growing need to reduce the solid content in the tailing ponds and produce nontoxic sludge, which can be safely disposed off, or used for beneficial purpose. Sludge in the tailing ponds of Sudbury region contains 5-7 % Ni mostly as hydroxide and is associated with Fe (~ 10 %), Mg (~ 10 %) and Cu (~0.5 %) as hydroxides and Ca (~3.5 %) as sulfate. It is thus a significant potential secondary source of nickel. Several hydrometallurgical methods have been investigated for metal recovery from hydroxide sludges.

10.3.2.1. Nickel Recovery by Acid leaching and Ozonation

A novel route to recover nickel as nickel oxide has been investigated by Calzado and coworkers (2005). It is a 2-stage process. In the first stage, the sludge is leached with sulfuric acid at pH 3.2. The leach solution containing nickel and magnesium sulfate is separated from the ferric hydroxide by filtration. In the second stage, nickel is separated by treating with ozone, which oxidizes nickel present as Ni²⁺ to Ni³⁺ in accord with the equation:



As indicated by the equation, the oxidation of Ni^{2+} takes place with hydroxyl ions by ozone. It is, therefore, necessary to raise the pH to an optimum level to provide enough hydroxyl ion concentration. Calzado and coworkers have found that pH should be maintained at 7 for continuous reaction. The pH of the leach, initially at 3.2 is lowered to 7 by sodium hydroxide and maintained at that value by adding more sodium hydroxide as is necessary.

By this oxidation 99% of soluble nickel has been recovered as nickel oxide-hydroxide (NiOOH) precipitate. The resulting compound, nickel oxide-hydroxide is a black solid, which readily settles down and can be easily separated. It is suggested as a potential feed stock to recover nickel metal by direct reduction or to manufacture nickel compounds. The leach residue containing 0.5 % Ni and 11 % Fe passes the standard leachability test (described in Chapter 2) after mixing with lime to raise the pH and can be disposed off. Alternatively, it can be used as feed stock to produce ferric sulfate, which is a useful industrial coagulant. The physical properties of nickel oxyhydroxide and parameters for bench scale process have been discussed by Calzado and coworkers (2005).

Economics of this process is determined by the cost of ozone. That should be manageable with the availability of portable ozone generators, which can be installed on mine site. Another economic factor is cost of sodium hydroxide. This has to be offset by recovering sodium sulfate, which is produced by neutralization of the sulfuric acid in the system.

10.3.2.2. Metal Recovery by Amine Complexation and Electrowinning

An alternative approach to selective recovery has been explored, based on the formation of an amine complex by nickel. Nickel forms a soluble complex with diethylene triamine (DETA), $\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}_2$ by co-ordinate bonding (explained in Chapter 4), with metal to DETA molar ratio 1:2. (Rao *et al.*, 1995). Ferric hydroxide is not affected as ferric ions do not form ammine complex. Ethylene diamine, (EDA) $\text{C}_2\text{H}_4(\text{NH}_2)_2$ can be used in place of DETA. Mixing the hydroxide sludge with slightly ore than stoichiometric proportion of

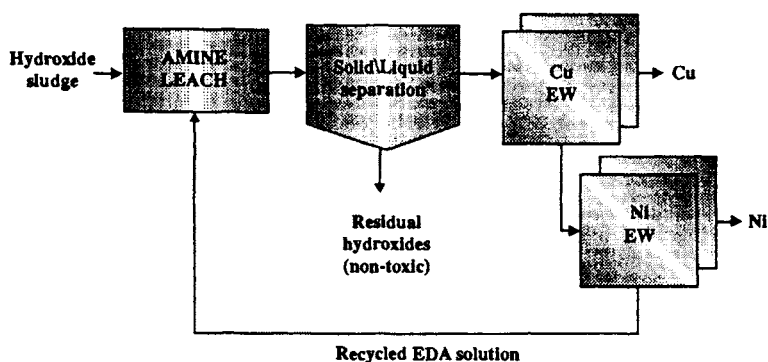


Figure 10.25. Potential process flowsheet for recovery of copper and nickel from hydroxide sludge using an EDA leach/electrowin process (Gelinis *et al.*, 2002)

amine (1:2.4) leads to almost 90 % metal extraction as soluble amine complex. Copper and nickel can be recovered from this solution by electrodeposition by method developed

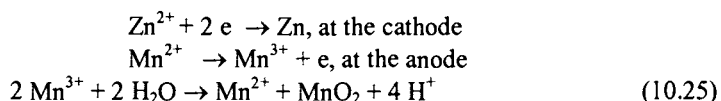
by Gelinas and coworkers (2002). From a mixture of copper and nickel, current efficiencies above 95 % can be achieved in the deposition of copper. When the concentration of Cu in solution reaches 100 mg/L, nickel deposits are obtained at current efficiencies above 90 %. When metals are deposited from the amine complexes the amine remains stable and is recovered in the cell for re-use. The results reported so far are from bench scale research. It is an attractive method of recovering metals requiring mainly only consumption of electricity, and as a result, will have few environmental concerns, as the reagents are recycled. A potential flowsheet is shown in Figure 10.25.

10.3.3. Metal Recovery from Wastewater Treatment Plant Sludge

Another example of metal recovery from sludge produced by lime treatment of acid mine drainage has been described by Pesic and coworkers (1996), and Binsfield and coworkers (1996). A unique feature of this sludge is that, besides iron and zinc, it contains manganese in significant concentrations.

In the first stage, the sludge is leached in sulfuric acid in presence of sulfur dioxide, which is used to reduce the manganese occurring as Mn(III) to soluble Mn(II). The sulfur dioxide also reduces some of the iron from Fe(III) to Fe(II). This is reoxidized by hydrogen peroxide and precipitated as ferric hydroxide at pH 3. The excess peroxide is removed by reaction with manganese dioxide. In the next step, copper and cadmium in solution are separated by cementation by zinc dust (see Chapter 4 for an explanation of cementation). After separating these metals, any cobalt and nickel are separated as complex compounds by reacting with 1-2 nitroso-naphthol and nioxime respectively at pH in the range 3.0-5.0.

Zinc and manganese are recovered by simultaneous electrowinning with lead-silver (1%) anodes and aluminum cathodes. Zinc is deposited as metal at the cathode, while manganese is recovered as manganese dioxide at the anode. The manganous, Mn(II) ions are anodically oxidized to Mn(IV). The electrochemical reactions are as follows:



The role of the anode is to produce manganese dioxide by the anodic oxidation reaction. The oxidized manganese ions react with oxygen in water to produce manganese dioxide precipitate. As the precipitate is carried back to the anode, more manganese dioxide is incorporated onto the initial deposit. The end result is small flakes of brownish black deposit. Manganese dioxide is not a conductor, and its excessive deposit on the anode can increase the electrode resistance, causing a drastic drop in current efficiency. This is minimized by using a material, which minimizes the deposition of manganese dioxide on the anode, which results in most manganese dioxide precipitating in solution as the reaction continues on the anode. Lead, lead-silver alloy, stainless steel or titanium are found to be suitable anode materials for this purpose. The flowsheet of the entire process is shown in Figure 10.26.

Optimum cathodic and anodic current densities are 600 and 160 A/cm², respectively. The electrowon zinc is of high quality and can be stripped easily. The highest possible zinc concentration is desired. Increases in manganese concentration have a positive effect on anodic current efficiency. The current efficiency becomes unacceptably low when the

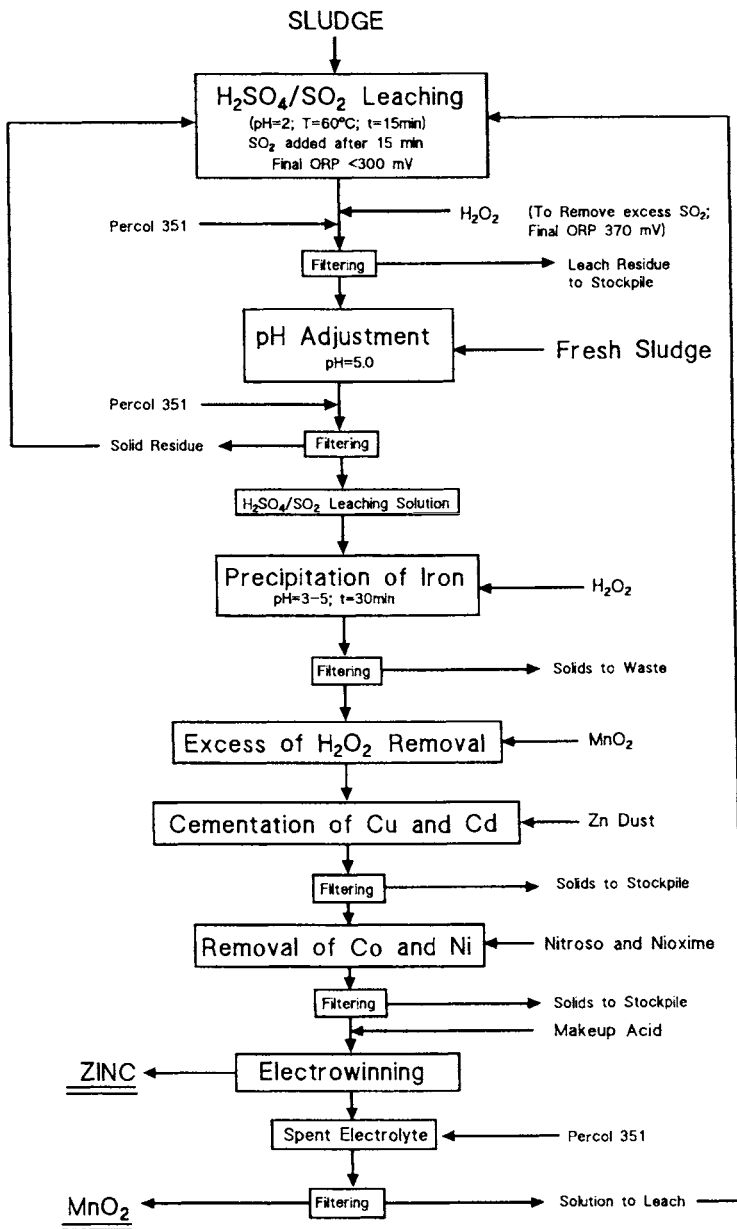


Figure 10.26. Flowsheet for recovering zinc and manganese from an ARD sludge (from Pesic *et al.*, 1996)

manganese concentration drops below 0.3 M. Initial acid concentration of 0.25 M acid is required to promote conductivity and high current efficiencies. Adequate stirring is also

required to aid in carrying manganese dioxide and Mn(III) ions away from the anode surface.

10.3.4. Resource Recoveries from Metal Hydroxide Sludges.

Electroplating industry generates liquid wastes, which often contain significant quantities of dissolved metals. These are precipitated as hydroxides, which form a sludge. For recovering the metals, the sludge is dissolved in sulfuric acid to produce metal sulfate solutions. The metals are then recovered by electrolysis. The relatively simple principle has been applied for the recovery of nickel from an electroplating waste liquid (Soloabal, *et al.*, 1999).

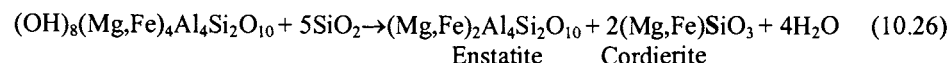
In some instances it would be more economical to recover the metal in the plating bath as metal compound. An example is the conversion of aluminum from the metal finishing bath to aluminum sulfate (Saunders, 1987). The dissolved metal is first precipitated as hydroxide by caustic soda (NaOH). The aluminum hydroxide forms as a gelatinous precipitate. This is treated with a polymeric flocculant and separated by filtration and thickened. The hydroxide sludge is treated with sulfuric acid to produce aluminum sulfate. This is a valuable industrial chemical with excellent coagulating properties and used in municipal water treatment.

Electrowinning technique has been used to recover metals from many metal waste solutions from a number of sources. Electrowinning cells of various designs have been described. By electrowinning two metals consecutively, alloys can be produced. An example is found in a paper by Diaz and coworkers (1999). The concept is still to be developed for industrial application.

10.3.5. Producing Refractories from Asbestos Wastes

Asbestos is the term used for all materials, which after appropriate preparation, provide heat-resistant fibers suitable for spinning. It is used in over 3000 products, asbestos cement, insulation, asbestos board, brake- and clutch-linings, textiles, reinforced plastics and resins. Recent environmental regulations, especially in European Community, prohibit the use of asbestos as a raw material in industrial products. It has also to be eliminated from all structures and systems where it has been used before. This has resulted in enormous amounts of asbestos waste waiting to be processed. Disposal in landfill sites generates toxic wastes and is environmentally unacceptable. Chemical treatment with hydrofluoric acid, which destroys the structure of the fibers and silicate minerals, has been attempted (Geffers *et al.*, 1993). That is not, however, a satisfactory solution as hydrofluoric acid itself is a highly toxic chemical and is not generally favored.

An attractive process of treating asbestos waste to produce a silicate mineral of practical use has been developed by Abruzzese and coworkers (1998). It is called "Cordiam" process as it leads to the synthesis of an aluminosilicate mineral called cordierite. The refuse containing chrysotile or amphibole asbestos is mixed with kaolinite or kaolinite-illite clay and sintered at temperature 900-1000° C. The sinter reaction is represented by the equation:



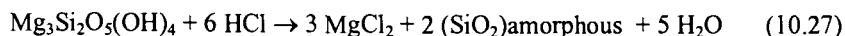
This process potentially eliminates asbestos wastes and converts it into a useful material. Cordierite has low coefficient of thermal expansion and excellent thermal shock resistance, which makes it specially suitable for applications for insulation in electronics. It is also used in the preparation of porcelains, refractories and enamels. Another promising application is that of high temperature molecular filters for automobile catalytic converters (Helferich and Schenk, 1989).

10.3.6. Recovery of Magnesium from Asbestos Processing Wastes

In addition to waste asbestos accumulated as a result of declining use of the material (Section 10.3.5) there are also huge dumps of asbestos tailings accumulated over many years of asbestos mining. A spectacular example of such tailings is found in the province of Quebec in Canada, where, until recently, asbestos mining has been a major economic activity bringing in handsome revenue to the province. With growing health concerns, the use of asbestos is discouraged in many European countries, resulting in reduced demand for this material. The tailings, accumulated as a result and are stock piled, mainly (> 90 %) consist of serpentine, a complex magnesium silicate of composition, $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ containing 23 percent by weight of magnesium. There are minor amounts of magnetite (Fe_3O_4) and awaruite (Ni_8Fe_3). The processes developed are still to be fully developed addressing some environmental concerns like hydrogen chloride emission, and progress is being made in that direction.

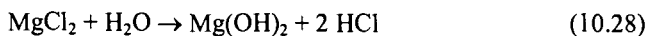
10.3.6.1. Hydrometallurgical Process

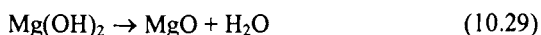
Magnesium is rapidly leached from the serpentine in hot concentrated hydrochloric acid to form soluble magnesium chloride and insoluble amorphous silica, which is pseudomorph of the original serpentine particles.



At 100° C, the initial rate of magnesium dissolution from 230 g/L of asbestos tailings increases as the 0.3 power of the HCl concentration. The terminal magnesium concentration increases with concentration of the acid up to 5.0 M HCl, but is insensitive to higher concentrations of acids, indicating the nearly complete leaching of all the available magnesium. The leaching of iron parallels that of magnesium, but iron reprecipitates from the weakly acid media. Minor amount of silica is also leached, but the extent of silica dissolution increases as the acid concentration decreases. The silica concentration rises rapidly to a maximum value (< 0.5 g Si/L) and then declines gradually to some terminal value. Both the maximum and terminal silica concentrations decrease as the concentration increases. The rate of magnesium dissolution in 7.0 M HCl increases moderately with increasing temperature. The rate of dissolution of iron is less temperature dependent, presumably because of the presence of easily leached magnetite. The magnesium leaching rate is nearly independent of the particle size of serpentine for particles 12-1000 μm range. This is thought to be the result of the diffuse nature of the reaction zone (Dutrillac *et al.*, 2001).

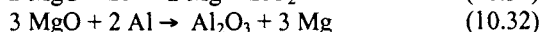
The magnesium chloride is hydrolyzed by steam to produce magnesium hydroxide, from which magnesium metal is produced by carbon reduction of the oxide.





10.3.6.2. Pyrometallurgical Process

A pyrometallurgical route to recover magnesium by treating the asbestos tailings in a plasma furnace has been developed and is called Magram (acronym for MAGnesium Recovery from Asbestos and related waste materials) process) (Chapman *et al.*, 1995). It is based on the high temperature reduction of magnesium oxide produced in the furnace by silicon and aluminum:



A schematic of the process is shown in Figure 10.27. The plasma reactor consists of a water-cooled cylindrical steel shell lined with a high grade refractory, which is chemically resistant to the slag melt. The furnace is powered by a DC hollow graphite electrode supported by a vertically moveable clamp arm/mast assembly. Argon is injected down the center of the electrode to stabilize the transferred plasma arc. The anode, in electrical contact with the melt, is built into the furnace hearth and is externally connected to the power supply. The calcined raw material consisting of asbestos waste, dolomite and alumina are pre-blended with the metal reductant, ferrosilicon and fed at a controlled rate to the furnace. The solid materials are rapidly assimilated in the slag bath. The volatile magnesium vapor exits via the furnace exhaust, and is recovered as a liquid melt in the condenser unit. The off-gas from the condenser is flared to ensure combustion of any entrained metal particulates prior to gas cleaning and venting to atmosphere. Slag and metal are intermittently tapped from the furnace.

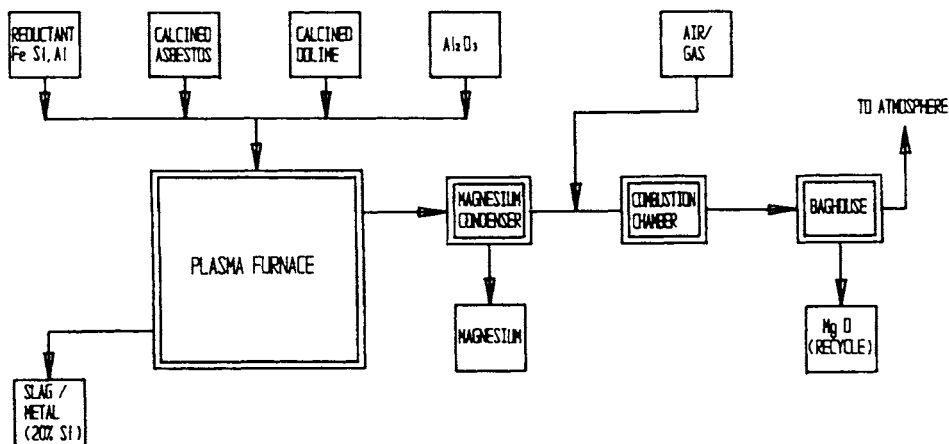


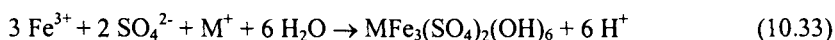
Figure 10.27 MAGRAM process flow sheet (Chapman *et al.*, 1995)

The process generates slag, which would normally consist of silicates and aluminosilicates. In order to obtain slag of a desired composition, which is sufficiently fluid and can be easily tapped, the feed material of asbestos wastes is enriched with

dolomite and alumina. The quantities required to be added are estimated by setting up a mass balance. From the composition of the asbestos tailings, the quantities of silica and alumina produced are calculated from stoichiometric equation. The balance of silica and alumina desired to obtain slag of the desired composition are then calculated and corresponding quantities of dolomite and alumina are added to the feed.

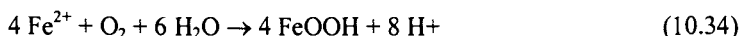
10.3.7. Recycling of Zinc Hydrometallurgical Wastes by Self-propagating Reactions

Electrolytic zinc production process generates over a million tons of wastes each year, produced in the process for removing iron from the electrolyte before electrolyzing for zinc. In one process called the jarosite process, the ferric iron is precipitated as jarosite, which is a complex iron hydroxide.



where M^+ is a monovalent cation, sodium, potassium, ammonium or hydronium. Precipitation occurs at pH 1.5 and 95 °C by adding the reagent, usually an ammonium or a sodium salt.

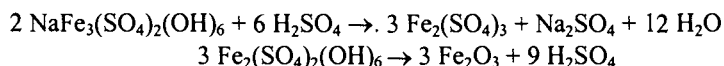
In another process the iron is removed from the zinc sulfate solution by precipitation as hydrated ferric oxide, FeOOH . Ferrous iron in solution is oxidized by air at 90 °C and pH 3.0. The oxidation is catalyzed by copper in the leach liquor.



The oxidation is catalyzed copper present in leach liquor. These wastes, which typically contain from 25 to 50 % of iron oxides, are considered hazardous and toxic due to the presence of heavy metals like lead, cadmium and copper as well as arsenic and zinc. If the toxic components are removed, the zinc compounds can be recycled to sphalerite (zinc sulfide) roasting plant to recover zinc.

10.3.7.1. Conversion of Jarosite to Hematite

Jarosite can be converted to hematite by thermal decomposition in sulfuric acid. The reaction, investigated by Dutrizac (1990) takes place in two stages: formation of ferric sulfate by reaction with sulfuric acid, followed by hydrolytic decomposition of ferric sulfate to ferric oxide (hematite):



Increasing acid concentration favors the dissolution of jarosite, but it reverses the hematite precipitation reaction and tends to form basic iron sulfate, which generates considerably less acid:



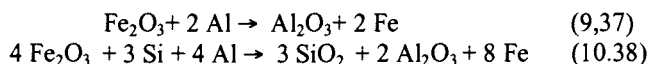
Optimum temperature for decomposition is 225 °C. The precipitation of hematite is facilitated by seeding with a crystal of hematite.

One drawback in this process is the deportment of arsenic (originally from the zinc feed material) as arsenate to hematite causing inadvertent contamination.

10.3.7.2. Production of Glass from Goethite Waste

Treatment of goethite waste to produce glass-ceramic sheets has been described by Pelino and coworkers (1996). Essentially, the process requires mixing goethite waste with raw materials and other residues to obtain a glass with adequate properties. The following materials are used for this purpose: sand, tuff, feldspar, limestone, dolomite, pumite and glass cullet. A typical composition given by Pelino and coworkers is, 42.6 % goethite, 17.8 % sand, 15.2 % feldspar, 21.4 % limestone, 1.8 % magnesium oxide, 1.5 % titanium dioxide, 0.35 % coal. Glass-ceramic sheets and tiles are made directly from the molten glass batch by progressive cooling, from 1450 °C to 850 °C at 20 °C/min cooling rate; 30 minutes isothermal step at 850 °C; from 850 °C to room temperature at 20 °C/min. With such treatment approximately 75 % crystalline phase is produced. The glass ceramics thus made exhibit hardness and resistance, which are higher than those found in industrial basalt glass ceramics obtained from fused rocks (Strnad, 1986).

Another method to treat the ferric oxide component by aluminum and silicon functioning as reducing agents has been proposed by Orru and coworkers (1999). The reactions are as follows:



These are highly exothermic reactions and are called thermite reactions, which are self-propagating due to the heat produced and require no external heat source once the reaction is initiated. The aluminosilicates produced form a glassy structure and take within it toxic metals, lead and cadmium. This can be potentially useful for glass-ceramic industry.

10.3.8. Titanium Dioxide from Titania-Rich Pigment Sludges

A plant producing titanium dioxide pigment produces a sludge which is still found to contain a total of about 54 % titanium dioxide and 27 % silica. Of the titania content 42 % is soluble in sulfuric acid. In order to permit recycling of the sludge it is necessary to reduce the silica content and increase the soluble TiO₂ grade. The possibility of achieving this goal by mineral processing techniques has been demonstrated by Belardi and Piga (Belardi and Piga, 1998). The process flowsheet is shown in Figure 10.28.

The material is dispersed by strong agitation. Next, the coarse and fine fractions are separated by a centrifugal wet gravity separation step. The cleaning stage for maximum reduction of the silica content comprises a rougher flotation step using a phosphoric acid ester (SM 15) as collector. In the acid pulp (pH 2.5) this reagent is selective to titanium bearing minerals. Further purification of the titanium dioxide is done by a series of three cleaner flotation steps. For the cleaner flotation hydrofluoric acid is used as depressant for silica. In the final beneficiation stage a concentrate of titanium dioxide is obtained by wet high intensity magnetic separation. An intensity of 2.1 Tesla is found to ensure the highest titania extraction efficiency.

The final product contains 79 % TiO_2 total with 76 % soluble and 4.4 % silica. Recovery of soluble titanium dioxide is 73 % considering that in a full scale closed circuit the only final tailings are those from the gravity and rougher flotation sections. By adding another cleaner stage the silica content can be reduced to 2 % which would permit recycling of the material whose grade and particle size make it suitable for recycling.

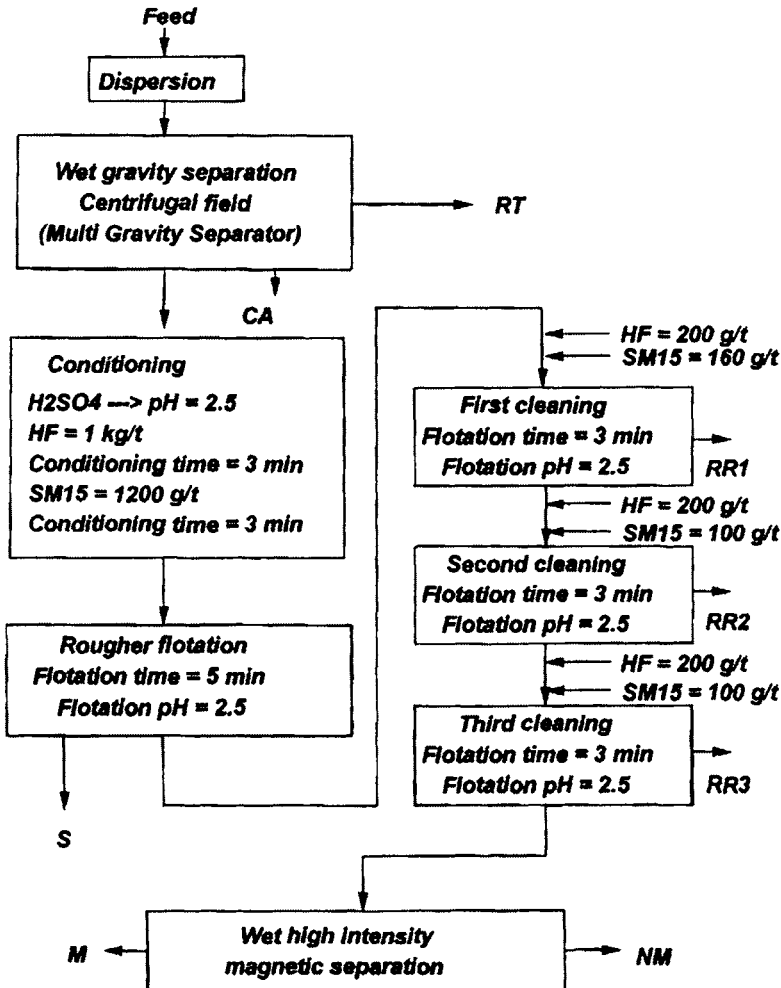
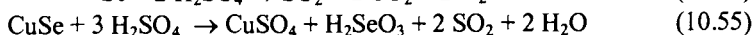
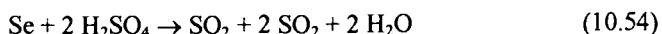


Figure 10.28. Integrated circuit for the beneficiation of titanium dioxide sludge (Belardi and Piga, 1998)

10.3.9. Recovering Selenium and Tellurium from Slimes

Selenium and tellurium are placed in the same group (6A) of Periodic Table in rows 3 and 4. Corresponding to sulfur they occur in one of the three oxidation states, the negative divalent state as metal selenides, positive tetravalent state as alkali metal selenites or tellurites (analogues of sulfite) or in the positive hexavalent state as alkali

Selenium and selenides remain unchanged under these conditions because of their greater resistance to oxidation. They are roasted at higher temperature, 500-600 °C to produce selenium dioxide, from which the element is recovered by reduction by sulfur dioxide.



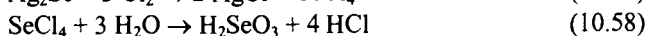
Significant quantities of sulfur dioxide are generated. When the temperature is lowered, the reaction is reversed resulting in the reduction of selenium dioxide to selenium:



When tellurium is present, the tellurium dioxide formed remains in the sulfated slimes. The process has been successfully applied for the complete removal of selenium from copper anode slime (Hyvarinen *et al.*, 1989).

10.3.10.5. Chlorination Process

In the chlorination method developed by Hoffmann (1989), selenium or selenide is converted to selenium chloride, which is then hydrolyzed to produce selenous acid:

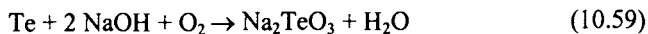


Wet chlorination of is done by sparging slimes slurried in water or hydrochloric acid with chlorine gas (or other oxidants like sodium chlorate liberating chlorine and hydrochloric acid), at about 100 °C. Under these conditions, selenium and selenides rapidly oxidize and dissolve.

Drawbacks of the chlorination method are the corrosive nature of the chlorinating agent, which makes it necessary to use media which can withstand the action of chlorine and the nonselective action of chlorine on other elements present in the slime, which also form soluble chlorides.

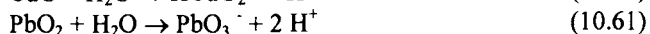
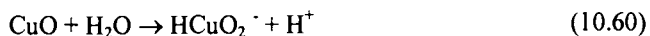
10.3.10.6. Alkaline Leaching Process

A hydrometallurgical process developed by Rhee and coworkers (1997) involves alkaline leaching with oxygen and removal of impurities by precipitation as sulfide by sodium sulfide, followed by electrowinning. Tellurium and selenium are solubilized forming tellurate and selenate respectively:



(similar reaction occurs with selenium).

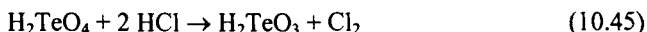
Copper and lead are oxidized to cupric oxide and lead dioxide respectively. Some of these oxides get resolubilized forming bicuprite and plumbate respectively.



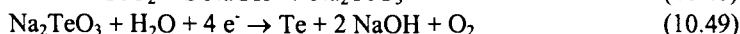
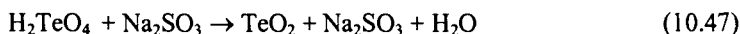
10.3.10.2. Soda Ash Roasting Process

Roasting with soda ash (sodium carbonate) at 530-650 °C results in the conversion of selenium and tellurium to sodium selenate and tellurate respectively. The tellurate, being highly insoluble remains as residue while the selenate is dissolved. Sodium selenate is leached in water and is reduced to sodium selenide, which is then oxidized by blowing in air through the solution. In one process charcoal is used as reductant. In another process the reduction is done in concentrated hydrochloric acid or ferrous iron salts catalyzed by chloride ions as reductant.

The sodium tellurate is converted to telluric acid by dilute sulfuric acid. Tellurium is extracted by reducing telluric acid by hydrochloric acid and sulfur dioxide:



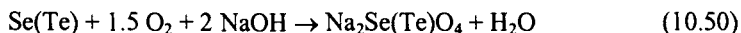
An alternative method is reduction by sodium sulfite to form tellurium dioxide, which is dissolved in sodium hydroxide to produce sodium tellurite. The element is recovered by electrolysis.



The regenerated alkali is recycled.

10.3.10.3. Alkaline Autoclaving Process

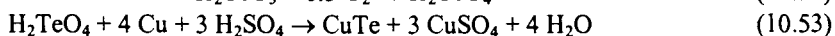
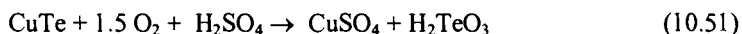
In this process the slime is oxidized in alkaline solution under pressure to convert the elements directly into their hexavalent state:



Although the process is fast, it has drawbacks. Consumption of both oxygen and alkali could be higher than that corresponding to stoichiometry as the silica and lead present in the slime will also be converted into sodium silicate and plumbate respectively.

10.3.10.4. Sulfation Roasting Process.

This process is suitable for the selective separation of tellurium and selenium from copper refinery slimes. By treatment with oxygen at 120 °C and 50 psi (345 kPa) telluride is oxidized to tellurate. Tellurium is recovered from the tellurate by cementation with copper.



The copper telluride is now in a purer form than in the slime. The element is extracted from it by alkaline leaching and electrowinning.

metal selenates or tellurates (analogues of sulfate). Both are rare elements; there are not many primary sources of their occurrence. They are recovered as by-products of other metal-winning processes, in metal refinery slimes

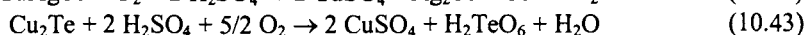
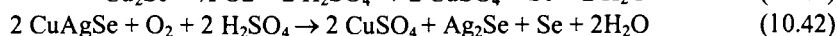
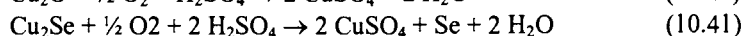
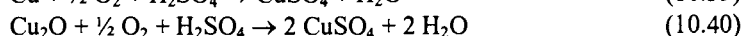
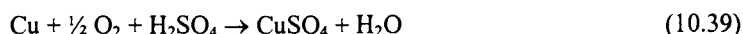
Most tellurium occurs as by-product in copper refinery wastes along with selenium and several other elements and is called tellurium cement (Te-cement).. Most metals occur as oxides and some sulfides. It is generally considered as an undesired impurity to be eliminated from anode slimes (from the electrorefining of copper). Recovery of tellurium leads to reduction slime of toxicity of the slime, which thus serves as a secondary source of tellurium. Composition of a typical tellurium cement (Table 10.12) shows that the material contains significant proportion of copper in addition to tellurium

Table 10.12. Chemical Composition of Tellurium Cement (Rhee *et al.*, 1997)

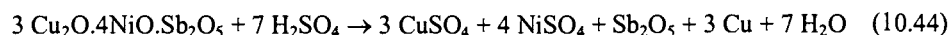
Element	Percent weight	Element	Percent weight
Te	21.7	Zn	0.29
Se	0.59	Cu	32.9
As	1.30	Sb	1.28
Pb	0.55	Mg	0.10
Fe	2.15	Bi	0.52
S	6.51	O	26.80

10.3.10.1. Recovering Selenium and Tellurium from Copper Refinery Slimes

The anode slimes contain copper, mostly as cuprous oxide and additionally, a variety of cuprous silver selenides, cuprous telluride and small quantities of elemental copper. The copper interferes with the processing of the slime to recover selenium and tellurium, especially in pyrometallurgical processing. The first step in the slime processing is therefore decopperizing. This is done by pressure oxidation to convert copper compounds to cupric sulfate by oxygen introduced into the reactor at a pressure of 30-80 psi. (205-550 kPa) (Hoffmann, 2000; Wesstrom, 2000). The following reactions take place:

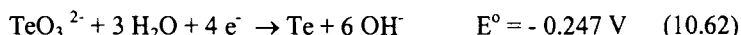


The slime may sometime contain cuprous oxide in combination with nickel oxide and antimony oxide. The compound has been named 'kupferglimmer' (Hoffmann, 2000). The dissolution of this compound does not require oxygen, but it has to be digested in higher quantity of sulfuric acid to leach it producing cupric sulfate and nickel sulfate:



Four methods have been described by Hoffmann, (1991). They are all based on converting the elements in the slime to a compound to facilitate separation, then extracting the elements from the compounds.

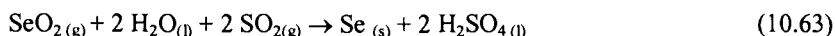
The metals thus dissolved are precipitated by sodium sulfide. Tellurium is recovered by electrodeposition. The electrochemical reduction reaction is expressed as



Electrowinning is conducted at constant applied voltage with stirring. High purity (99.9%) tellurium can be recovered.

10.3.10.7. Selenium Extraction by Vacuum Distillation

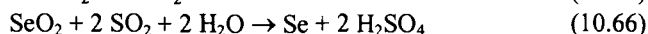
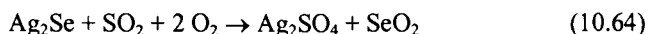
In a laboratory study Klenovcanova and Imris (2002) have recovered selenium from anode slime by roasting followed by vacuum distillation. Selenium in the slime is evaporated as selenium dioxide by the oxidation roasting of anode slime in a multi-hearth furnace at 720-825 °C. The off gas with selenium dioxide and sulfur dioxide and roasting dust generated in the furnace are then absorbed into dilute sulfuric acid solution in water scrubber at a lower temperature of about 60 °C. In water scrubber selenium dioxide is reduced to selenium by sulfur dioxide:



The precipitated selenium with dust carryover from roaster and other volatile compounds collected in water scrubber are filtered from the solution as selenium concentrate.

Vacuum distillation takes advantage of high vapor pressure of selenium. The investigators have determined the optimum conditions under which evaporation of impurity components (arsenic antimony and sulfur) is minimized and high purity selenium is recovered: evaporation temperature 280 °C, condensation temperature 120 °C and vacuum from 3910.6 to 666.6 Pa.

The reduction process with sulfur dioxide is also used to recover selenium from copper anode slime, where selenium occurs as silver selenide. (Jarvinen, 2000). It is first converted to selenium dioxide by heating at 600 °C with air, oxygen and sulfur dioxide. The selenium dioxide is then reduced by sulfur dioxide:



The selenium, purity 910.5%, is recovered from the gases with water and sulfur dioxide gas. Silver, recovered by electrolysis of silver sulfate is a valuable by-product of the process.

10.3.10. Precious Metals from Copper Anode Slimes

Copper anode slimes tend to contain varying quantities of copper, tellurium, selenium, bismuth, silver, arsenic and precious metals. Table 10.13 gives an overview of some of the materials that are treated during the last few years. The objective of treating these materials is to produce a concentrated final product high in silver and precious metals. Due to the expensive nature of these materials they are treated in a separate, well cleaned plant, designed to minimize the loss of material. Small polypropylene filter presses and a glass lined reactor are used. Strict analytical controls are also performed in

between treatment stages to confirm a zero loss of precious metals. As all reactions are performed batch-wise, the possibility always existed to cement co-dissolved precious metals by means of zinc or copper dust. Copper dust is preferred as it does not cement dissolved copper

Table 10.13. Composition of Anode Slimes Treated at Hydrometal

%	A	B	C
H ₂ O	20-35	40	2-8
Cu	20-35	30	30-40
Te	20-30	30	5-10
Se	5-10		
Bi	3		20-25
Ag	2-3	2-7	2-3
As	2-3		5-10
Pb	15-20		

Generally the first stage in treating materials such as these is to de-copperize them by a hot sulfuric acid ~ 100 g/L H₂SO₄ leach with or without an oxidant such as sodium chlorate (NaClO₃) or hydrogen peroxide (H₂O₂). An excess of oxidant generally leads to a loss of precious metals contents in solution. If other recoverable quantities of metal are leached they are selectively precipitated at their hydrolysis pH. In the case of a high bismuth content in the slimes, a soluble chloride salt is added during the leach to solubilize the Bi, which may subsequently be selectively precipitated (60-65% Bi, <1% Cu). Otherwise, it is neutralized to pH 9 and the copper is precipitated as copper hydroxide (50-60% Cu, <1% Bi) and sold to copper refiners or recycled elsewhere in the plant. For example, copper hydroxide material may be used as a neutralising agent in the cement treatment process described above to neutralise the leach liquor of a highly oxidised (thus high Cu tenors in solution) cement. The leach residue, which often still contains considerable quantities of copper and/or other recoverable metal is treated by a second leaching step. During this stage of the flowsheet different options are available to proceed.

The higher Te materials (A and B) were treated by a strong caustic leach leaving the silver and precious metals in the residue. Good leach efficiencies depended strongly on the oxidation state of tellurium. Te⁴⁺ dissolves easily in caustic solution, but not in acid, and Te⁶⁺ dissolves easily in acidic solution but not in caustic solutions. Other anion forming metals such lead, arsenic, selenium are solubilized at this stage as well.

Acidifying the caustic tellurate solution to a pH of 5 to 6 resulted in a precipitate containing all Te (and other metals). Depending on the composition of the concentrate a releach/re-precipitation stage would be applied to upgrade the Te concentrate and separate it from lead and selenium. If the purity of this precipitate was sufficient and it was found to be economically feasible, the possibility existed to proceed towards production of metallic tellurium by means of Te electrolysis.

The low Te materials (C) are subjected to another sulphuric leach to increase copper recovery as well as to solubilize tellurium (as Te⁶⁺). Hydrogen peroxide is used to maximize Te and Cu recovery. Once again after each leach batch, analytical control samples were taken prior to proceeding. Cementation of precious metals could be carried out if required. Tellurium and copper were precipitated by hydrolysis and sold to

tellurium and copper refineries and consequently does not lead to high consumption of metal dust. A generalized flow diagram is presented in Figure 10.29.

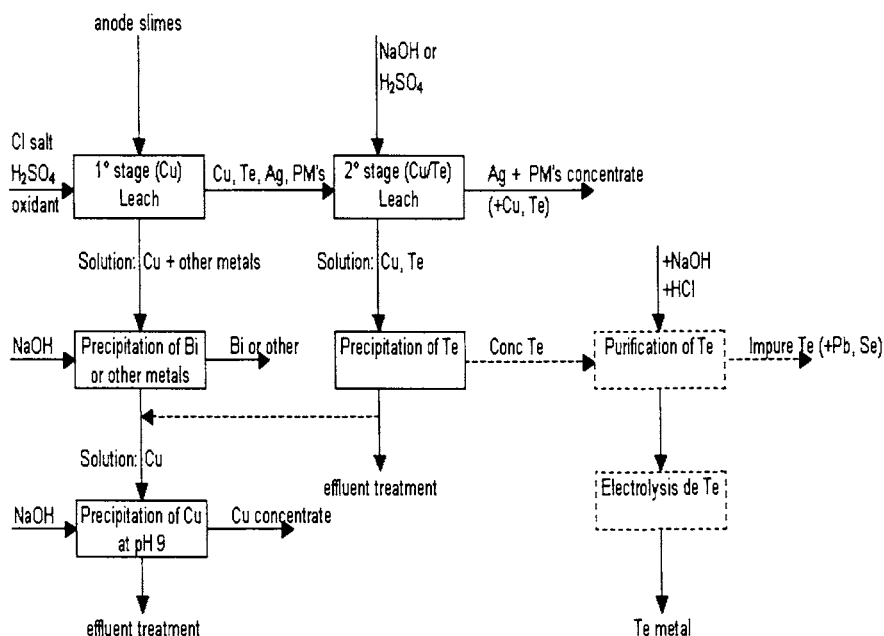


Figure 10.29. Generalized flow diagram for anode slime treatment (Henry *et al.*, 2004)

10.3.11. Tungsten, Niobium and Tantalum from Carbide Sludge

Tungsten carbide is used for various metallurgical tools because of its hardness. Tool scrap is an important secondary source for recycling tungsten, niobium and tantalum. Unclassified scrap is alkali roasted to convert tungsten carbide to tungstic oxide or sodium tungstate, followed by leaching, purification and conversion of to pure tungstic oxide. Cobalt is recovered by acid leaching. The sludge remaining contains niobium, tantalum and titanium together with some tungsten and cobalt. It is a potential source of all these metal values. A typical sludge contains 48.5 % tungsten, 4.1% cobalt, 5.6% niobium, 7.2% tantalum, 11.6% titanium (Gupta and Suri, 1994).

A processing scheme, shown in Figure 10.30, to recover tungsten, cobalt, niobium and tantalum has been developed by Gupta and Suri (1994). The sludge is treated with alkali to recover nearly 50% of tungsten as sodium tungstate. The residue after the alkali leaching is leached with hydrochloric acid to partially recover cobalt in solution. The resultant material is roasted with soda ash to convert the tungsten carbide to sodium tungstate. Additional amounts of tungsten and cobalt are recovered by a sequence of water/alkali leaching followed by acid leaching. The residual sludge is low in tungsten and cobalt. This is dissolved in hydrofluoric acid and treated by solvent extraction to recover either mixed niobium-tantalum oxides or separated oxides.

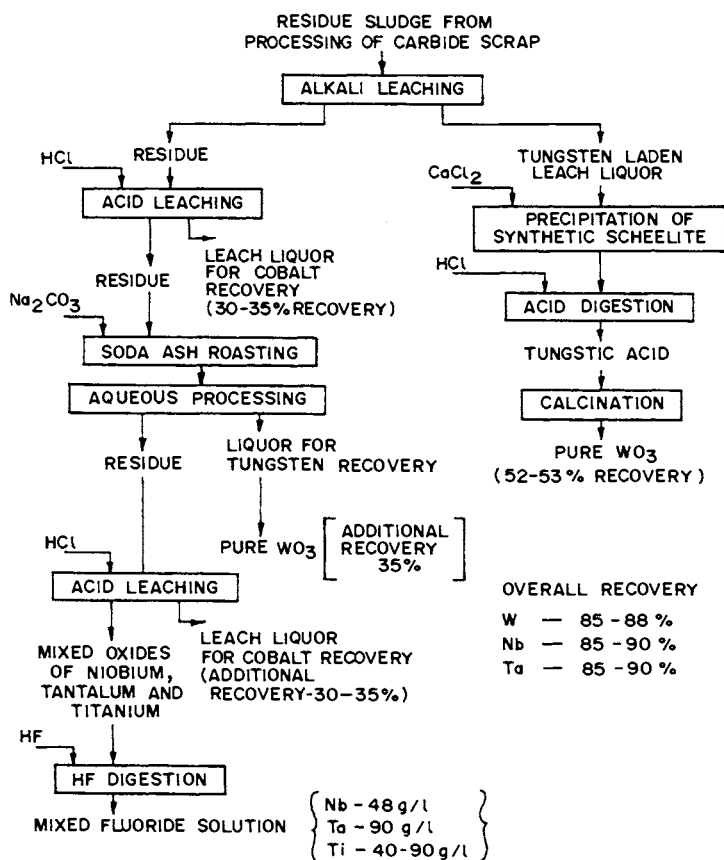


Figure 10.30. Flowsheet for metal recoveries from carbide sludge (Gupta and Suri, 1994)

10.3.12. Recovery of Mercury from Contaminated Soil

An innovative fluidized bed thermal desorption system has been developed to recover mercury from contaminated soil (Harris and Baum, 1996). Referred to as Thermal Recycling System (TRS), it is mobile thermal desorption system with a processing rate up to 5 tons per hour. The system includes a continuous feed system, all radiant heat, inert gas atmosphere, hot gas filter, two-stage cooling, and a water treatment system. The process flow diagram is shown in Figure 10.31.

10.3.13. Recovery of Minerals from Over Burden Rock at Lignite Quarries

Lignite extraction works from quarries generates large quantities of waste material containing several valuable minerals. Those of special interest are oxides of titanium and zirconium. Georgescu and coworkers (2001) have developed a flow sheet to recover such metal values applying mineral processing physical separation techniques; see Figure 10.32.

The material is prepared by washing and wet classification at 1.6 mm. The material then goes to gravity separation on concentration cones and helical separators in several treating stages. This is the preconcentration stage. The tailing fraction is sent to magnetic

separator to separate quartz, alumina and alkalis in nonmagnetic fraction. The final concentrate on spirals is dried, heated and screened (at 0.315 mm) and sent to electrostatic separator. This separates conductive minerals, ilmenite, magnetite and gold. The nonconductive fraction consists of zircon, garnets and quartz. Further gravity separation of nonconductive fraction by table concentration leads to production of zircon concentrate with 52.6 % ZrO_2 . This is useful in ceramic industry. The components of the conductive fraction are sent to magnetic separator ($H = 800\text{--}1,000$ Oersted) in four stages to separate magnetite, ilmenite and gold concentrates. The final products are magnetite (20.2 % TiO_2), ilmenite (45 % TiO_2) and a gold product (50-100 g/t). (For details of gravity separation techniques, see Chapter 3).

STEP ONE:

Contaminated soil is screened and crushed so the material sent into the processing unit is uniform in size.

STEP TWO:

The contaminated soil is heated to a temperature of up to 1,200 degrees Fahrenheit so that the contaminants in the soil are vaporized.

STEP THREE:

The vapors are cooled and condensed for collection in liquid form. Depending on the nature of the contaminants, the liquid is then recycled, further processed, or destroyed.

STEP FOUR:

The heated soil is then cooled, tested for contamination levels, and returned to its owner for use as back-fill, or sent to a landfill as daily cover.

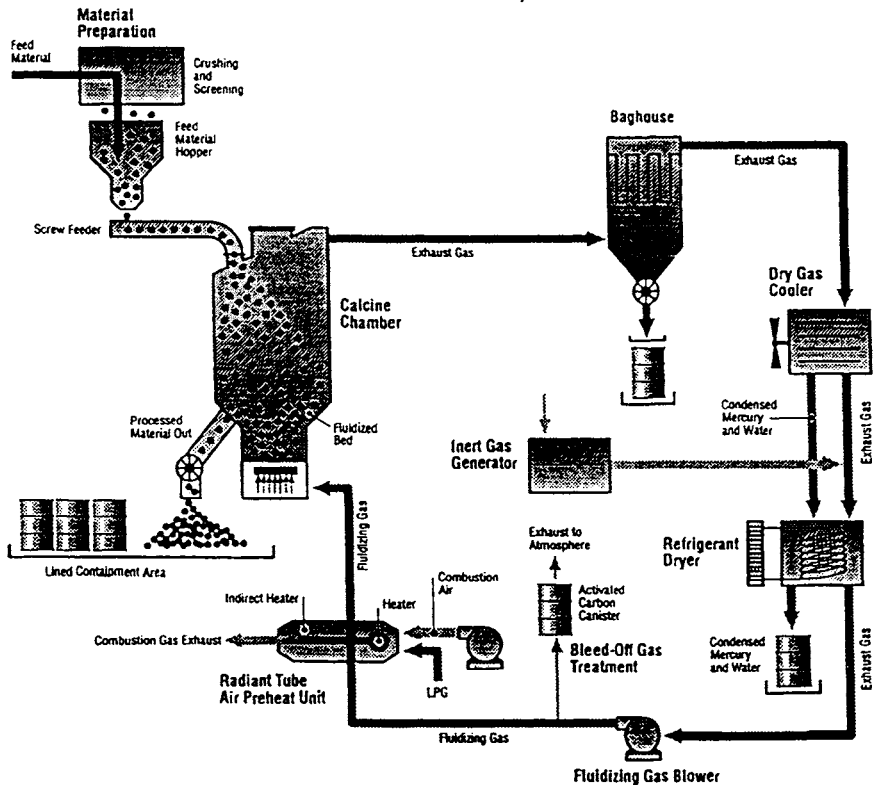


Figure 10.31. Process flow diagram to recover mercury from contaminated soil (Harris and Baum, 1996)

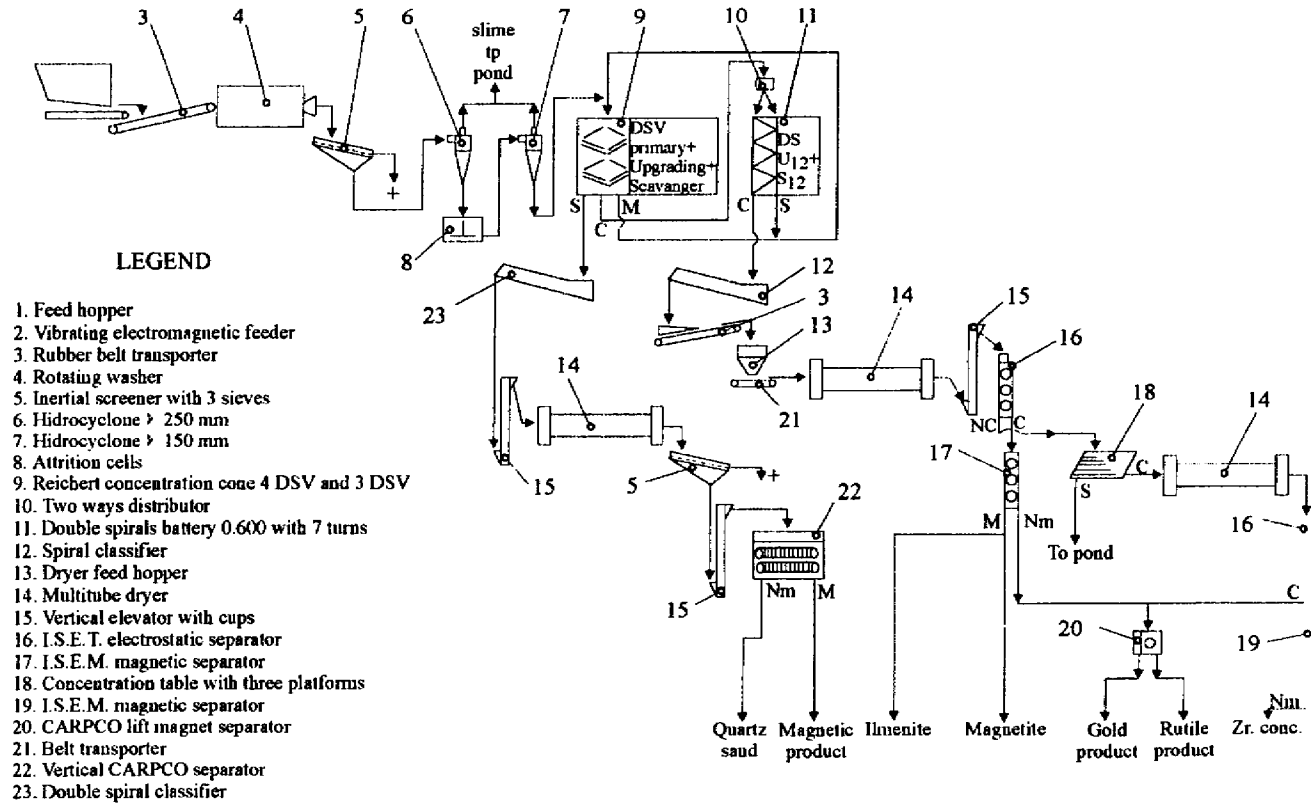


Figure 10.32. Flow sheet for recovering valuable minerals from overburden rock (Georgescu *et al.*, 2001)

10.4. Solid Wastes

Some of the metallurgical operations do not use water. The material is processed as dry solids in granular or powder form. The 'waste' generated in such operations occur are treated by techniques used for processing dry material.

10.4.1. Recycling from Foundry Sands

Greensand (sand bonded using clay and water) is a widely used moulding material in use; about 70 % of foundries use this type of material. Silica sand is generally used while specialist sands such as zircon and chromite may be used for higher temperature casting. The sand is mixed with bentonite clay and some water, rammed into the required pattern shape and may or may not be dried to form a mould. When the molten metal is poured, the clay binding at the surface is burnt. If the temperature of the clay reaches 300 to 600°C (depending on the source and clay type), water and clay structure is lost, but can be replenished, but at 400 to 700°C the hydroxyl ions in the clay structure may be lost. They cannot be replaced, and the clay cannot be rejuvenated with water to be used as a binder. Above 870°C the clay reacts with the surface of the sand forming a hard brittle shell around the sand and particle Shpektor *et al.*, 1990).

Sodium silicate binders are used extensively in both mould and core making, and reuse of the sand causes a build up of silica gel, and higher requirements of sodium silicate solution (Jain, 1979). Organic resin binders such as furan resins and phenol formaldehyde readily burn off at the surface when metal is poured. As a result, they are extremely useful as core sand binders, as the sand can easily be removed after use, without damage to the internal features of casting. They are used in shell moulding, when high dimensional accuracy is necessary in the finished casting. Incomplete burning off, however, causes build up of these resins and increased binder requirements and acid demand (used as hardening agent). These binders are expensive, increased requirements mean that it is more economic to replace or clean the sand after several uses; Burns, 1986). Other additives such as coal dust and fibrous material can also build up on the surface of sand particles and must be removed after several cycles.

At present, wet, dry and thermal reclamation systems are used for reclamation of the sand. In all of the systems the sand must first be prepared by removing metallic materials and crushing and screening to expose particle surfaces to permit efficient cleaning.

Dry processing is carried out by mechanical or pneumatic scrubbing. Mechanical scrubbing involves the sand being thrown by a revolving wheel onto an attrition surface where the coatings are broken and removed by impact. After several cycles, the fines are removed either by screening or by air suction. In pneumatic scrubbers the sand particles are blown at high velocity at a target plate of hardened metal. This breaks the coatings, the sand falls down the scrubber to an outlet chute and air suction at the top removes the spent binder. Clay coatings and some furan resin are removed by these methods.

Wet scrubbing can be either gentle washing to remove coatings, or attrition scrubbing of a slurry. The main disadvantage of this process is the amount of water required, which can be up to 10 times the weight of the sand. The major advantage is the effectiveness of wet scrubbing at removing both fines and carbonaceous material along with good clay removal (Hoyt, 1988).

Thermal processing is the most widespread method of sand reclamation. All organic binder systems, sulfur, nitrogen rich compounds, and carbonaceous materials can be removed, with the coatings acting as fuels and reducing energy requirements. The

temperature should be over 800° C, which results in high fuel cost. Crushed sand can be easily fluidized with hot air and combustion occurs evenly on all sides of the particles allowing efficient removal of binders (Lavington, 1985).

Pocock and Veasey (1995) have demonstrated the potential of reclamation of used sand from a greensand foundry which produces automobile parts. Used sand is disposed on average of 500 tons per week. Used sand in the size range between 1 mm and 90 μ m is used for the cleaning process.

The first step is wet attrition which is conducted in a laboratory flotation cell fitted with attrition scrubbing attachments (Figure 10.33). Prior to attrition, metallic materials and metal oxide coated sands are removed by magnetic separation. About 23 to 26 % by weight of the material is removed by this separation.

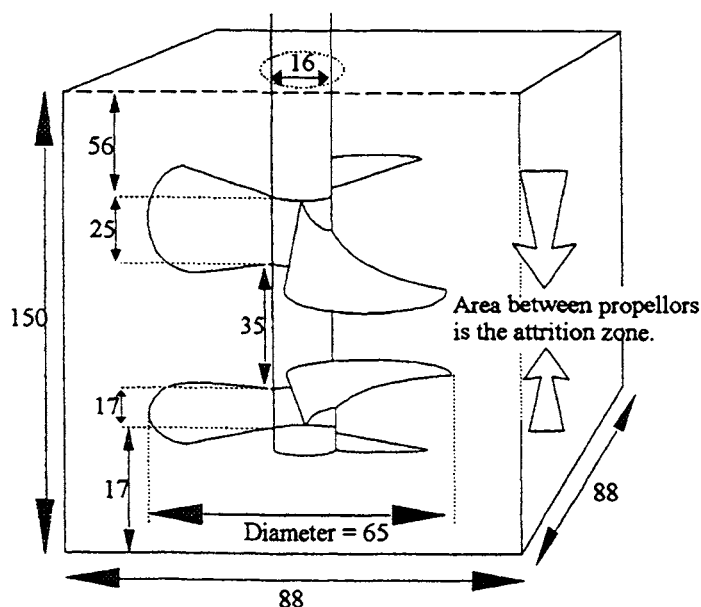


Figure 10.33. The attrition cell used for cleaning foundry sand, (Pocock and Veasey, 1995)

Table 10.14. Comparison of Treated and Untreated Sand Characteristics.

Scrubbing time (min)	Average AFS number	Percent material retained over 3 fractions	Specific Area (m ² /g)	Percent loss on ignition	Percent removed by scrubbing
Untreated	58.24	82.89	1.27	3.41	-
30	62.44	83.68	0.48	2.74	10.59
60	63.17	84.01	0.34	2.60	8.78
90	61.59	84.22	0.32	2.66	10.74

Notes. The AFS (American Foundrymens Society) number is a measure of the sand fineness. This is calculated from the size distribution by multiplying the percentage retained on each sieve by the mesh size of the previous (larger aperture) size. The products are then added and divided by 100 to give the AFS number. Thus, the finer the sand, the higher the number. The size distribution and AFS number affect the finish, permeability, binder requirement and strength of moulds and cores. The proportion of fines should be monitored before re-use to avoid any problems with mould and core making.

The Loss on Ignition (LOI) is the percentage of the material which will burn off when casting is carried out. As any volatile and organic matter is likely to burn off this usually constitutes the LOI.

The next step is scrubbing. The material from the attrition cell is scrubbed using 1050 cm³ of slurry in a cell with speed adjustable rotor. Rotor speeds up to 2000 rpm and pulp densities up to 80 % solids have been employed. The fraction, -90 µm material produced by scrubbing is removed by wet scavenging after every 30 minutes. Make up samples are added to the +90 µm material to maintain the required pulp density. The results of the treatment showing a comparison of the characteristics of treated and untreated sands are shown in Table 10.14.

The AFS number above 60 obtained by treatment is acceptable for re-using the sand. The LOI decreases significantly which is an indication that coal dust and clay are removed from the attrition cell. Increased scrubbing time has little effect on the amount of material removed but is beneficial to the size distribution and the surface area of particles.

10.4.2. Silicon from Semiconductor Scrap

Producing semiconductor grade silicon (SEG-Si) requires a large amount of energy (450 kWh/kg). It is a principal component of solar cells, but as a result of high cost, only small amount of silicon is currently used. If the scrap silicon generated in semiconductor industry and in the conventional method of silicon manufacture is processed, and upgraded by economically viable technique, that will potentially increase the availability of high grade silicon.

A method to produce high grade silicon by electron beam (EB) heating has been developed by Yamauchi and coworkers (2004). The EB apparatus has two electron guns, a cold hearth, a water-cooled copper crucible and several sensors. Each gun has a maximum power of 200 kW. A cross section of the apparatus is shown in Figure 10.34.

About 5 kg of scrap silicon is placed on the hearth as raw material. The silicon is melted by electron beam. After exposure to a vacuum, the refined liquid silicon is poured into the carbon crucible. In the first stage melting an ingot is produced. This is further refined by a second stage melting by electron beam. By this technique, a high grade silicon is produced. The concentration of impurities are Fe, 0.4 ppm, Cu, 0.06 ppm and Ti, 0.04 ppm. Antimony is completely removed (not detectable). This is considered to be sufficient to meet SEG-Si specifications.

10.4.2.1. Reusing Waste Silicon in Wafer Manufacturing Process

Silicon wafer is building block in integrated circuit in electronic industry. The manufacturing process of silicon wafers produce considerable amount of waste silicon

along with silica. This product is potentially valuable for the manufacture of silicon compounds. Two compounds, which have been synthesized are tetramethoxy silane (TMOS) and silicon carbide (Sinha, 1998).

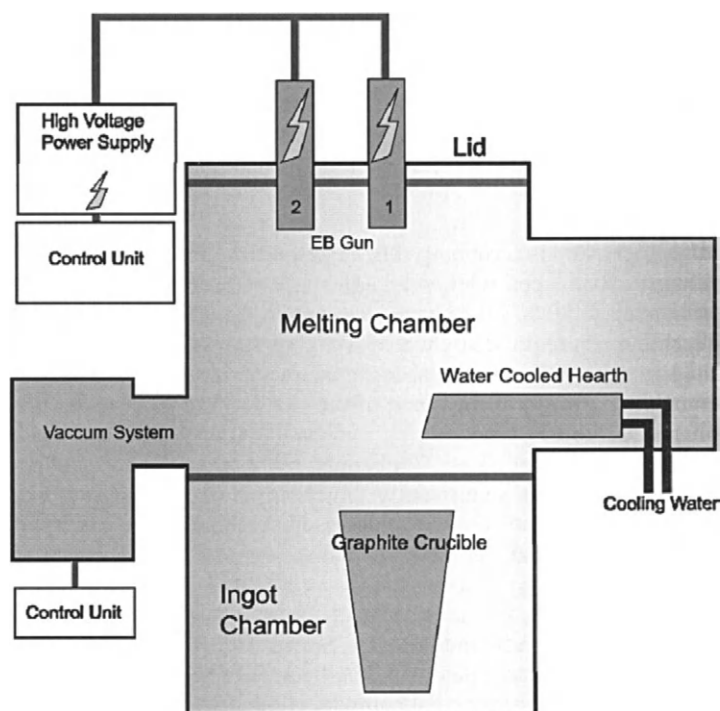
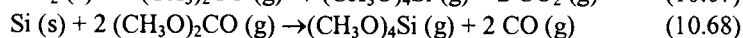
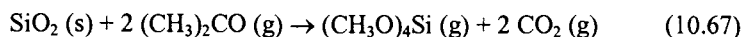


Figure 10.34. Schematic of Electron Beam Furnace for the Production of High Grade Silicon from Recycle Feed (Yamauchi *et al.*, 2004)

For the synthesis of TMOS, the solid waste is treated with a mixture of methanol and potassium hydroxide. Pellets of silicon enriched solid impregnated with potassium hydroxide (by methanol acting as solvent) are formed in an extruder. The pellets are then dried to evaporate the methanol and sent to a moving bed reactor, where they come in contact with dimethyl carbonate (DMC) in gaseous state at around 300 °C and at atmospheric pressure. The DMC is heated near its boiling point (92 °C) and is transferred to the reactor by helium as carrier gas. The products are condensed and the unreacted DMC is separated from TMOS by distillation. The chemical reactions are the following:



A variety of organosilicon compounds are derived from TMOS. It is an important key step in the synthesis of silicone polymers, production of glasses and in the production of ceramics and is also used as starting material for the production of high purity silica.

For the synthesis of silicon carbide, the solid waste is mixed with carbon black and the mixture heated in a furnace to 1500 °C. The product is a low grade silicon carbide, which might be usable as a refractory material. Though this is less valuable than TMOS, silicon carbide is much less toxic and environmentally safer compound.

10.4.3. Resource Recovery from Aluminum Electrolytic Cells (Pots)

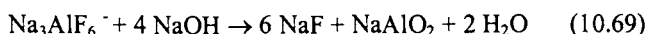
During the life of Hall-Heroult electrolytic cells to extract aluminum, fluoride salts and sodium penetrate into the carbon blocks, and eventually into the alumina refractory lining. This occurs usually after 3-8 years' service due to the stresses and erosion, which cause attack of the iron collector bars and refractory lining by bath electrolyte or liquid aluminum metal. The electrolytic cells, referred to as pots, are withdrawn from service and the cathode lining replaced. Excess bath and liquid metal are siphoned off and as much as possible of loose alumina removed. The cooled remaining lining is broken up and dug out of its steel shell. Iron and large pieces are manually removed. The carbonaceous material and the refractory lining are considered to constitute spent potlining or pot liner (SPL). This material is environmentally hazardous as it contains significant concentrations of toxic compounds including cyanides and fluorides. In contact with moisture, SPL can also potentially generate ammonia, methane and other flammable gases. About 35 kg of SPL is generated per ton of aluminum produced (Kimmerle *et al.*, 1994). Several valuable products can be recovered from SPL, thus minimizing potential environmental hazard.

10.4.3.1. Leach Process

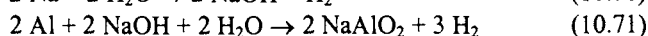
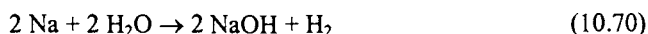
A process named as Low Caustic Leach and Liming (LCL&L) has been described by Kimmerle and coworkers (1994). The flowsheet (Figure 10.35) comprises five blocks: dismantling and crushing; grinding and classification; extraction and leaching of SPL; cyanide destruction and crystallization of sodium fluoride from leachate; and causticization of the sodium fluoride vapor.

The pots are dismantled to remove the bath and excess alumina and aluminum metal. The SPL is segregated manually into carbon rich and refractory rich fractions, which are separately crushed and homogenized. The SPL fractions are then crushed in an impact crusher to an average 20 mm size and separately ground using a hammer mill to reduce the aggregate size to an average of 0.5 mm.

The finely ground SPL is digested in hot, dilute sodium hydroxide solution. This procedure extracts into the liquor fluorides, alumina, some silica, and free and complex cyanides. The cryolite in the SPL dissolves forming sodium fluoride and aluminate:



Any sodium and aluminum metal dissolves with the evolution of hydrogen:



Aluminum nitride and carbide dissolve to form aluminate, and generate ammonia and methane respectively:

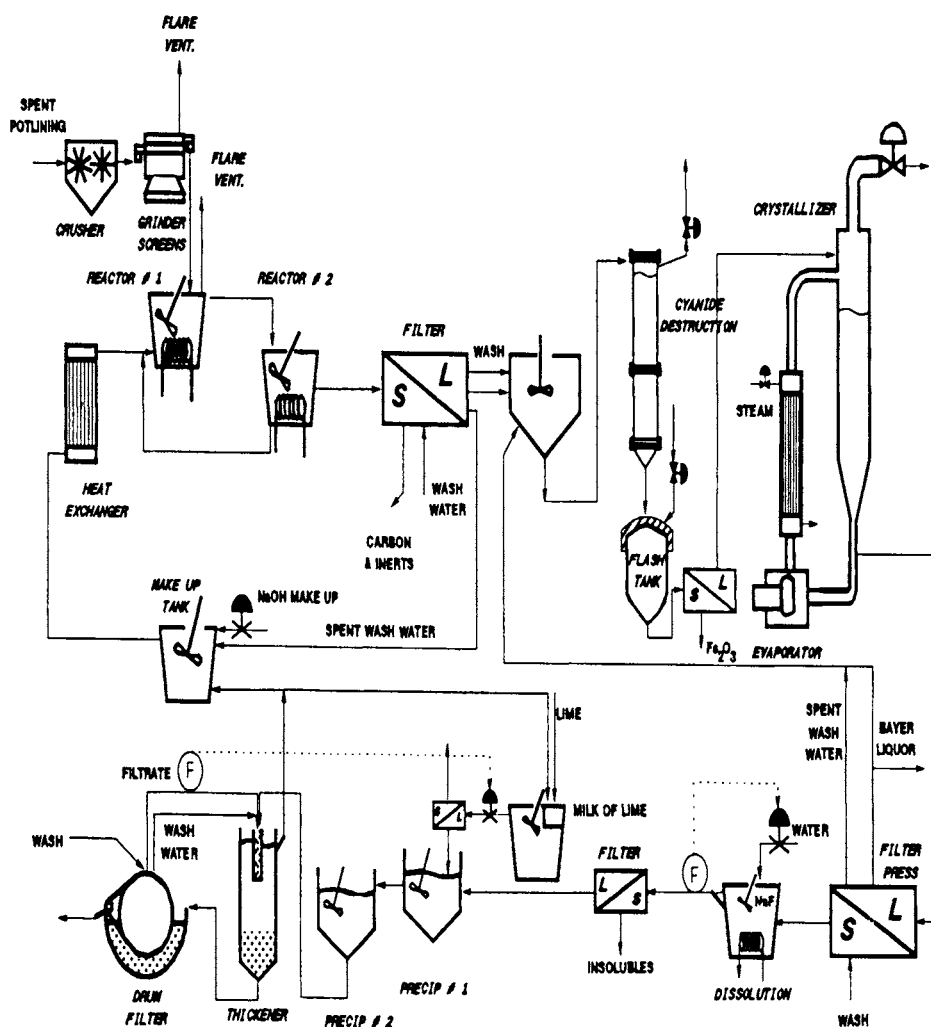
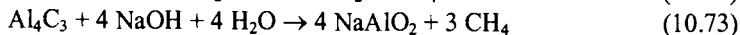
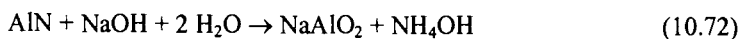
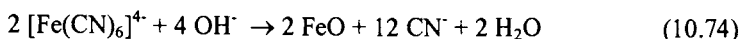


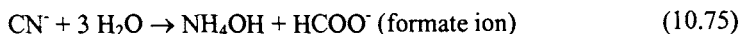
Figure 10.35. Treatment of SPL by Low Caustic Leaching and Liming Process (Kimmerle *et al.*, 1994)



In order to destroy cyanide, which is found to the extent of 600 mg/L, the caustic leachate from the digestion units slightly enriched with sodium hydroxide to reach 60 g/L concentration. The liquor then enters a cyanide destruction unit, which is a heated stainless steel plug flow reactor. Any ferrocyanide present is first hydrolyzed:



which is followed by the hydrolysis of cyanide itself:



The clean caustic leachate goes to an evaporator-crystallizer where the concentration of sodium hydroxide is raised to a point (around 225 g/L) to crystallize out sodium fluoride. As the leachate is further evaporated, the solubility of sodium fluoride is further reduced as sodium carbonate and alumina start to coprecipitate. The sodium fluoride slurry is continuously filtered to produce two value-added products, the concentrated alumina rich liquor, called Bayer liquor, and sodium fluoride crystals of 95 % purity. Purity can be improved by a single re-precipitation. The sodium fluoride is re-dissolved and the coprecipitated insoluble impurities are filtered out. The sodium fluoride is then neutralized with stoichiometric addition of calcium hydroxide in cascading precipitators to produce calcium fluoride. This is used as feed stock to produce aluminum fluoride while the caustic liquor produced is returned to the extraction step of the process.

10.4.3.2. Pyrometallurgical Method

An alternative method to process SPL is by smelting it in an Ausmelt furnace (described in Chapter 6). The process consists of two stages, smelt stage and digest stage; see Figure 10.36.

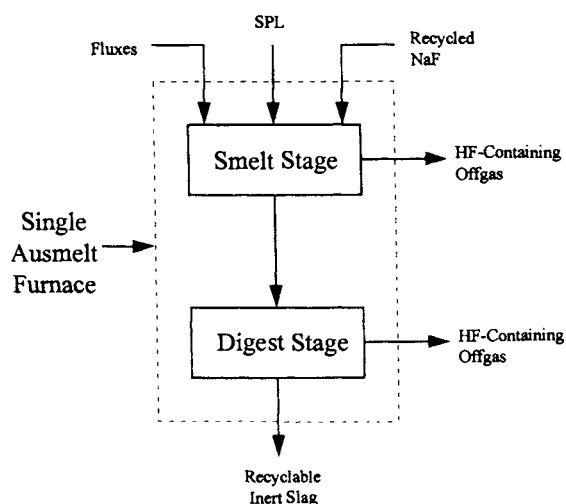


Figure 10.36. Simplified flowsheet for recycling SPL in Ausmelt system (Matusiewicz *et al.*, 1996)

In the smelt stage the SPL is smelted with a flux, which can be steel mini-mill slag or limestone, and sodium fluoride fume recycled from subsequent stage. This produces a slag, which assists the process by exposing fresh carbon surfaces for further reaction, dissolving the high melting point refractory components like alumina and controlling the distribution of fluorine in the system. When the furnace is filled to the maximum operating depth, feeding of SPL, fluxes and sodium fluoride fumes is stopped and conditions adjusted to remove further levels of fluorine as hydrogen fluoride. This is the

digestion stage. When sufficient fluorine is removed to levels to meet the environment criteria, the molten slag is tapped and quenched using water to granulate the slag. The granulated slag is a potentially useful product in building and industrial applications (see the Section on Slag in Chapters 8 and 10.). From the off gas the hydrogen fluoride is purified by scrubbing with sulfuric acid in a rectifier column. This produces > 99 % pure product. It is used to produce aluminum fluoride by reacting it with aluminum hydroxide. The overall flowsheet of the entire process is shown in Figure 10.37.

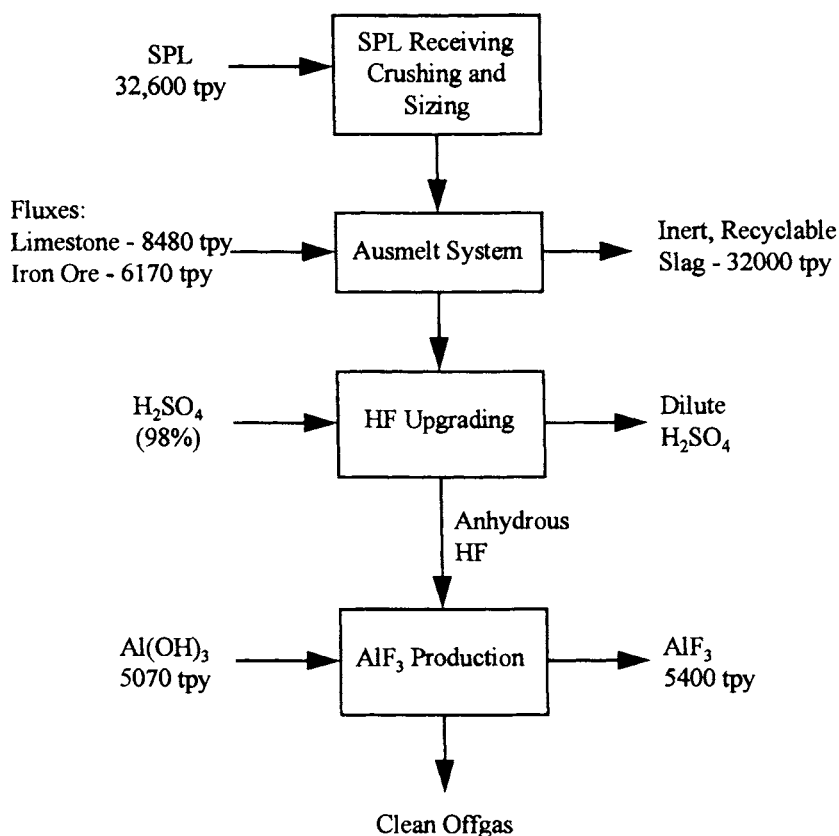


Figure 10.37. Flowsheet for recycling SPL (Matusiewicz *et al.*, 1996)

10.4.4. Conversion of Aluminum Waste into Glass-Ceramic Products

A process to convert spent pot lining waste to glass and ceramic type products has been described Balasubramaniam and coworkers (2000). The SPL waste is homogenized by grinding to <100 μm size. The powder is blended with glass formers like boric acid and network modifiers like sodium and calcium oxides and melted in a muffle furnace at about 1300 °C. The molten mass is cast into steel molds and annealed at temperature in the range 500 to 600 °C. The glass produced is converted into glass-ceramic material by a controlled thermal treatment in the temperature range 600 to 750 °C. The glass-ceramic materials are said to possess superior mechanical properties. They can be tailor made to a

desired color and texture by an appropriate combination of composition and heat treatment.

10.4.5. Use of Spent Refractories from Other Metals Manufactures

Refractories are used in the construction of ladles and furnace linings in extractive metallurgical industry. Once they are no longer effective, they have to be disposed off. The accumulating spent refractories are another burden on land fills and environmental liability. The problem can be considerably mitigated by recycling or otherwise using the components of the spent refractories.

The principal components of refractories are alumina, silica and magnesia. This composition makes it a possible raw material for producing Portland cement. Smith and Peaslee (2000) have investigated this route. Spent refractory bricks are ball milled to $< 44 \mu\text{m}$. The ground refractory (12 wt %) is mixed with 68 weight % alumina, 16 weight % silica and 4 weight % ferric oxide. The mixture is heated in an alumina crucible to 1550°C . This results in the formation of a cement with 8 % tricalcium aluminate, 14 % dicalcium silicate, 67 % tricalcium silicate and 11 % brownmillerite. (See Chapter 8 for details on mineralogical properties of slag). The composition is close to that of commercial cement used in construction.

The basis of fluidizing a bed of solids is to temporarily suspend particles by air flow. It is desirable to have the particles homogenous. This is done by particle sizing, which includes a soil shredder, vibrating screen, and a rock crusher. This enables a variety of soil types (clays, silts, sands, rocks) to be processed to produce a somewhat homogenous feed material. Desorption of mercury takes place inside of a closed chamber, called a calcine chamber. It has two parts: the gas room (upper) and the fluidized bed (lower). Soil processed with the material-sizing equipment is conveyed to the top of the calcine chamber and dropped through the gas room into the bed. Temperature is maintained at approximately 650°C (1200°F). The soil is retained at this temperature for about one hour. Inert gas is injected into the system at several locations to reduce the oxygen concentration. The process gas exiting the system contains soil fines, which are removed by passing through a baghouse operating at the high temperature required. The mercury and mercury compounds are condensed in a gas cooling system and passed through a water treatment system. This removes all mercury compounds from the condensate producing elemental mercury and water. Mercury is sold to a refiner and water is recycled to the processed soil for cooling purposes.

While the system is primarily designed to remove and recover mercury from contaminated soil, it can also remove any contaminant with a boiling point of 500°C or less. They include many organic compounds and PCBs.

10.4.6. Metal Recoveries from Alloy Grinding Wastes

Significant quantities of waste are generated in the grinding of hard face alloys. Approximately 1.6 million kg of hardface alloys are annually converted through grinding operations to a finely divided waste material (Redden *et al.*, 1988). They contain significant quantities of nickel, chromium, cobalt and tungsten.

In a process for treating such grinding wastes, developed at the U.S. Bureau of Mines (Redden and Swarup, 1995), cleaned grindings are dissolved with chloride lixiviants (Hydrogen chloride and chlorine), which produces a residue and a chloride leach liquor. The leach residue containing tungsten trioxide (which is not leached by HCl) is leached

with sodium hydroxide to form sodium tungstate, from which calcium tungstate is precipitated by the addition of calcium chloride. Iron, cobalt, manganese and nickel chlorides are sequentially recovered from the leach liquor by solvent extraction operation which produces strip liquors from which high grade metal products could be recovered. The final raffinate is purified chromic chloride solution. The various recovery operations are schematically shown in Figure 10.38 (placed on page 441, following Figure 10.39).

10.4.7. Recovery of Lead as Lead Monoxide from Lead-Containing Solid Waste

In addition to spent lead batteries from which the metal is recovered (see Chapter 7), there are many lead-containing industrial products, which are disposed in hazardous waste facilities. In such solid wastes, lead occurs in many forms, including oxide, sulfide, sulfate, carbonate, or combinations of two or more; all of which are highly toxic. Environmental concerns have made it necessary to develop new technologies to remove and recover lead compounds from the accumulated waste. For any process to be environmentally acceptable, it should be both efficient in lead removal and also free of any potential for uncontrolled emission of lead. It should also be able to treat the different compounds of lead occurring in the solid waste.

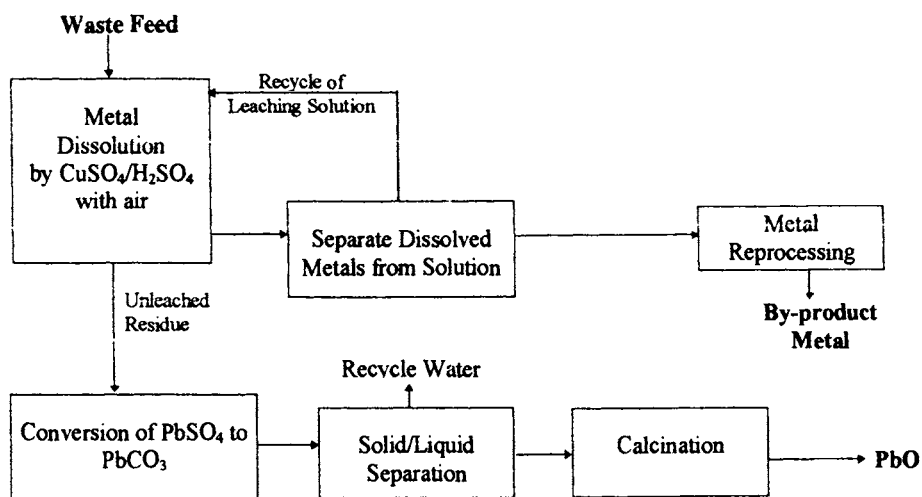


Figure 10.39. Flowsheet for the recovery of lead metal and compounds from lead-containing wastes (Xue and Nesbitt, 1996)

One such process developed to process lead-containing wastes, such as brass foundry waste is based on aqueous processing (Xue and Nesbitt, 1996). It consists of three stages: selective leaching, conversion, and calcinations; see Figure 10.39. Up to 91.5% of lead is recoverable in the leaching step. The sulfate system takes advantage of the low solubility of lead sulfate. The lead sulfate is converted into carbonate by treatment with 0.36 M sodium carbonate (pH 10.42), optimum concentration, to produce lead carbonate (cerussite). After solid/liquid separation, the lead carbonate is calcined to produce high quality litharge (yellow lead monoxide) at 400-450 °C or massicot, yellow lead monoxide

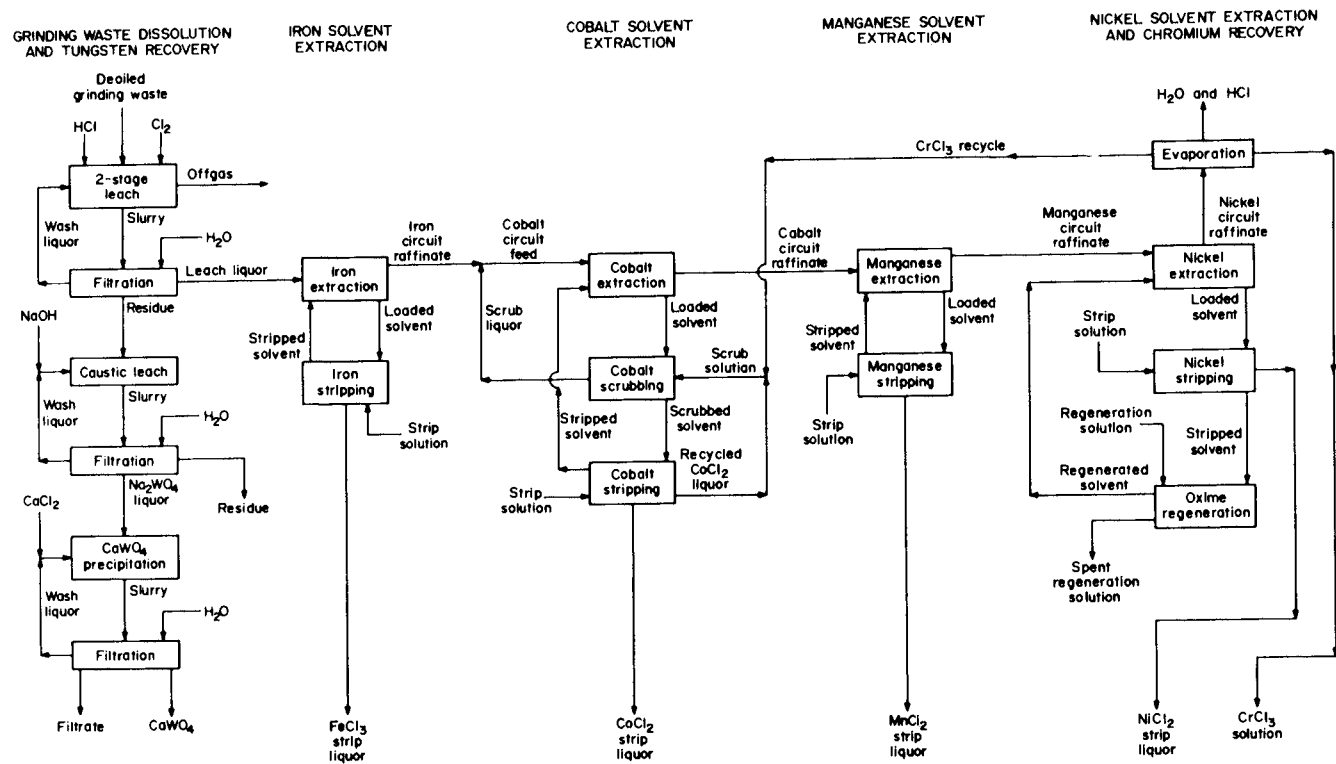


Figure 10.38. Generalized flowsheet for the recovery of metal products from grinding waste (Redden and Swarup, (1990)

at 500-550 °C. The process is very cost effective as the estimated cost for producing lead oxide is less than one dollar per kg.

10.5. Resource Recovery from Discarded Batteries

Besides lead batteries, which are a principal secondary source of lead, described in Chapter 5, there are a large variety of domestic batteries, in a range of composition. Various metals, including cobalt, nickel, cadmium, lithium are principal metallic components in batteries used in domestic appliances and industrial equipment. Discarded batteries, which would otherwise be a serious environmental liability, both by the solid waste generated as well as by the toxicity of the metals contained in them, are a rich potential source of these metals. The main kinds of batteries are described in Table 10.15.

Before recovering any metals, batteries have to be sorted and broken.. Some batteries, in particular, the mercury batteries are heated to volatilize the metal. Caution is required to control the internal pressure to prevent possible explosion.

Depending upon the physical nature and chemical composition of batteries, the recycling is done by physical processing (mineral processing techniques described in Chapter 1) pyrometallurgical or hydrometallurgical methods (Frenay and Feron, 1990).

Table 10.15. Principal Kinds of Batteries, Potential Secondary Sources of Metals

Battery	Anode	Cathode	Electrolyte
Zinc-Carbon	Zinc sheet	MnO ₂	NH ₄ Cl or ZnCl ₂
Alkaline-manganese	Zinc powder with lead and mercury as anti-corrosive agents	MnO-C-KOH (85-10-5)	KOH with 6 % ZnO
Mercury	Zinc powder with mercury	HgO with carbon	KOH + ZnO
Silver oxide	Zinc powder with mercury	AgO and MnO ₂	KOH or NaOH with ZnO
Zinc-air	Zinc powder with mercury	Activated carbon	KOH
Lithium	Lithium	Various oxides; e.g., MnO ₂ -Bi ₂ O ₃	Organic solvent
Nickel-cadmium	Cd, which transforms to Cd(OH) ₂	NiO(OH), which transforms to Ni(OH) ₂	Mixture of KOH and Li(OH) ₂

10.5.1. Techniques of Processing

Both hydro- and pyrometallurgical routes have been developed for the processing of batteries and recovery of metals. The choice depends upon the battery composition and economic considerations.

In many processes, the first step is to screen the ground cells to obtain a coarse material containing metal particles, papers and plastics and a finer fraction with powdered compounds and sludges. Soluble electrolytes are separated by washing in

water. The coarse fraction is air classified to separate the light materials, papers and plastics from the heavy metallic compounds, from which magnetic iron compounds are separated from the non-ferrous metals by magnetic separation.

Fine fraction contains mercury and can be processed by distilling the mercury or by hydrometallurgical process by oxidative leaching with hydrochloric acid and sodium hypochlorite (NaClO) producing a residue containing carbon and manganese dioxide and a solution containing zinc and mercury from which mercury is recovered by electrodeposition and zinc is precipitated by raising the pH.

Hydrometallurgical routes comprise leaching, followed by solvent extraction, precipitation and electrowinning. Nickel-cadmium batteries are processed by leaching in ammonium carbonate or hydrochloric acid. Where oxidation is required, leaching is done with hydrochloric acid and sodium hypochlorite as described before, followed by electrowinning to recover zinc.

In an example of pyrometallurgical processing, mercury distillation from broken or unbroken cells is done at about $600\text{ }^{\circ}\text{C}$. Volatile organic compounds are oxidized by burned the cells at $850\text{--}950\text{ }^{\circ}\text{C}$. They are then cooled close to $0\text{ }^{\circ}\text{C}$ to effectively condense the mercury. Exhaust gases are purified by carbon filters. One serious problem with this process is that the materials volatilized in the gas phase form with mercury a viscous compound, called mercury butter, which can clog the pipes leading to risks of explosion. Physical separation of the organic compounds is therefore much preferred.

Zinc and cadmium are volatilized at higher temperature than mercury. Depending on the kind of furnace, they can be condensed as metallic phase or recovered as oxides by cooling the oxidized gases. Zinc recovery is often done by hydrometallurgical processes

10.5.2. Metal Recycling from Used Nickel-Cadmium Batteries

The world production of household batteries amounts to several billions of units annually and the environmental risk associated with uncontrolled disposal of batteries is great as they contain several toxic metals; see Table 10.16.

Table 10.16. Composition of the Electrodes of Small Size Ni-Cd Batteries (Pietrelli, 1999)

Metal	Electrodes	Anode	Cathode
Nickel	28.9 %	21.8 %	26.4 %
Cadmium	30.7 %	51.9 %	110.8 %
Cobalt	0.081 %	0	0.02 %
Iron (from electrode support)	0.69	0.02 %	0.005 %
Others (graphite, K, etc.)	21.6	10.1 %	34.0 %
Stainless steel	18.1 %	16.2 %	110.8 %

The principal one in most widely used batteries is lead (see Section 7.5). Another class of widely used is nickel-cadmium batteries, which have found many applications in electronics communications, railways, emergency power supplies and domestic items. The disposal of these used batteries have serious potential hazard as both nickel and cadmium are toxic metals. The recycling of these metals is an absolute necessity.

A hydrometallurgical process for the recovery and recycling of metals from nickel-

cadmium exhaust batteries has been developed in Italy (Pietrelli, 1999). It comprises three steps: mechanical dismantling, leaching and metal separation by ion exchange; see Figure 10.40.

The ground electrodes are leached in 2 M sulfuric acid at 110° C for 6 hours. the pH of the leach solution is raised to 3-4 to precipitate iron as ferric hydroxide, which is separated from the solution containing nickel, cobalt and cadmium. The solution is then passed through an ion exchange column with aminomethyl phosphonic acid. This adsorbs cadmium. The solution with nickel and cobalt are processed for further separation. The cadmium is recovered by elution with sulfuric acid. The process is schematically presented in Figure 10.41

In an extended method to separate cobalt and nickel, after the separation of cadmium and iron by solvent extraction, the aqueous raffinate goes to selective extraction of cobalt by Cyanex 272. Alternatively, the raffinate is sent directly to produce a nickel-cobalt alloy by electrowinning (Cavallini *et al.*, 2000).

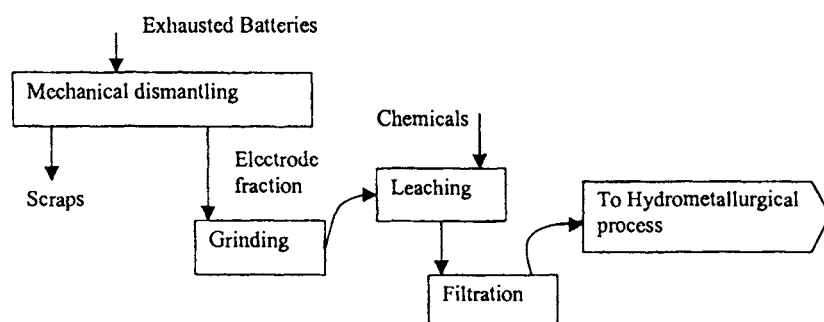


Figure 10.40. General process scheme to treat exhaust batteries (Pietrelli, 1999)

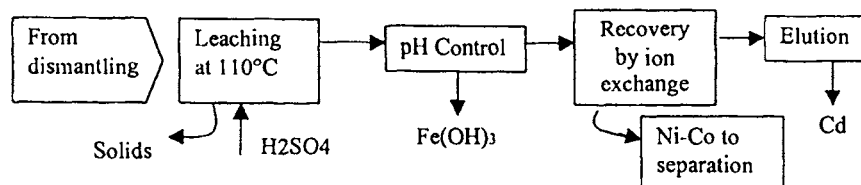


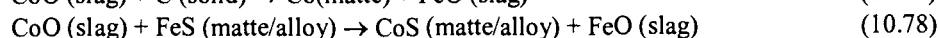
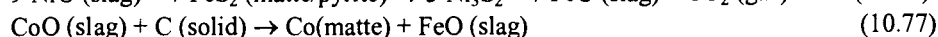
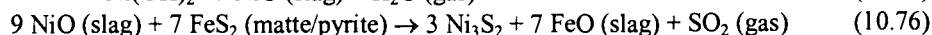
Figure 10.41. General layout of the process for the separation and recoveries of nickel, cobalt and cadmium from the leach solutions obtained from exhaust batteries (Pietrelli, 1999)

Cadmium can be removed from nickel and cobalt by selective electrolysis of the solution, as the redox potential for Cd^{2+}/Cd is -0.402 V, as compared to those of Ni^{2+}/Ni -0.250 V and Co^{2+}/Co -0.277 V. In a laboratory study de Oliveira and coworkers (2002) electrolysis under dynamic conditions is conducted using a rotating electrode reactor comprising an exterior cylinder made of carbon serving as anode and an interior cylinder made of stainless steel serving as the cathode. The rotation speed of the cathode is controlled by a motor within the set up. The results show that under dynamic conditions 100% extraction efficiency of cadmium can be achieved while the extraction of cobalt and nickel is below 20%.

10.5.3. Recoveries of Nickel and Cobalt by Ausmelt Process

Nickel cadmium batteries containing approximately 20 % nickel, 20 % cadmium, 35 % iron and 20 % plastic have been processed by Ausmelt converter (see Chapter 6 for description) to recover nickel. The batteries are processed at a temperature of 1250 °C with pyrite added as a sulfidizing agent, coal as a reductant, and lime stone (54 % CaO) and silica (99 %) as flux.

The principal reactions in the process are the decomposition of nickel hydroxide to oxide, the reaction of nickel oxide and iron sulfide (pyrite) and the carbothermic reduction of cobalt oxide:



Pyrite acts as both a reductant and a matte forming agent. It reacts with nickel oxide to produce nickel sulfide (Ni_3S_2 , which is a synthetic mineral called heazlewoodite). It is also the source of iron sulfide to form a matte with the nickel sulfide. Silica acts as a flux for the oxidation and deportment of iron to produce a slag with right thermal and viscous characteristics. Plastics and gaseous products (which include halogen compounds and some of the cadmium) are post combusted in the top space of the furnace.

Three principal products are matte, slag and fume. Most of the nickel and cobalt are carried in the matte. Its main components are 36.7 % nickel, 36.5 % iron, 1.7 % cobalt, with small concentrations of cadmium (< 0.1 %), zinc (50 ppm) and lead (250 ppm). It is sold to nickel smelters. The slag mainly consists of 35.6 % iron and 36.3 % silica and <1% toxic metals (Ni, Cd, Pb). It satisfies the toxicity leach test criteria and can be used as a building material. The cadmium fume is considered to be suitable for recycling.

Analysis of the off gases has shown that the concentration of organo-halides (produced by metal halides in the fed material) is very low, <0.04 mg/Nm³ of gas, which minimizes any potential environmental hazard. Most of the chlorine is soluble, which suggest that chlorides are released mainly as hydrogen chloride gas.

10.5.4. Recovery of Toxic Metals, Cadmium and Mercury

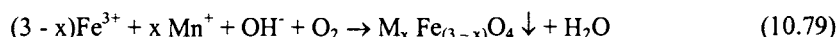
A bioleaching method using indigenous thiobacilli from sewage sludge to remove metals from nickel-cadmium batteries has been developed by Zhu and coworkers (2003). The operation is conducted at 30 °C in a reactor system, consisting of a bioreactor and a leaching reactor. Before the biochemical operation, acidified sludge is prepared by mixing elemental sulfur (1 % w/v) with sewage sludge and incubating for 17 days at 30 °C. This sludge is mixed with a second batch of sewage sludge and acclimating and incubating step are repeated under the same conditions. This operation is continued until the rate of pH reduction to 2.0 is maximized over two consecutive transfers. At this stage, the indigenous sulfur-oxidizing bacteria are assumed to be adapted. This is the final acidified sludge. In the bioreactor, indigenous thiobacilli are cultivated and sulfuric acid produced. A sludge sample at 4 °C is mixed with the final acidified sludge and 1 % (w/v) of elemental sulfur. A flow of fresh sewage sludge mixed with 1 % powdered sulfur is continuously fed to the bioreactor, and leaching and a flow of fresh air supplied. A high level of dissolved oxygen is maintained to ensure the proliferation and activity of

acidophilic thiobacilli. The acidified sludge from the bioreactor is thickened in a settling tank, and 20 % of it recycled to the bioreactor. The effluent from the settling tank flows into the leaching reactor, which contains anodic and cathodic material from nickel-cadmium batteries. The overflow from leaching reactor is collected and analyzed.

By this process all of the cadmium is released in 50 days of leaching, but the total nickel recovered is 75 % maximum. Sludge drained from the settling tank can be applied to agricultural land after neutralizing the acid by lime.

Another method described by Xia and Li (2004) applies vacuum distillation to separate mercury and cadmium. Mercury is distilled at 350-450 °C and vacuum of 740-750 mm Hg, while cadmium is recovered at 750-850 °C at the same vacuum pressure. Heating time is 2-3 h for mercury and 2-4 h for cadmium. The metals are condensed and the toxic gases are adsorbed by active carbon.

After the vacuum distillation step, the batteries are crushed and ground. The powdered scrap is leached in a mixture of sulfuric and nitric acids. The acid solution is filtered. The cake consists of manganese dioxide and carbon black. This could be marketed for producing ferromanganese. The filtrate contains manganese, mercury, iron, zinc, and other metal ions. This is converted to metal ferrite by adding an alkaline (Na or K) or ammonium hydroxide and ferrous sulfate in stoichiometric proportion. The corresponding metal ferrite (of sodium, potassium or ammonium) is formed by the reaction:



10.5.5. Cobalt Recovery from Lithium Batteries

Lithium and lithium-ion cells represent about a third of rechargeable battery world market and their use is still growing as they are found especially convenient for operating cell phones, computers and video cameras. Recycling of batteries is rapidly gaining importance both on environmental as well as economic considerations. Some components of the battery can be recovered to recycle them in the production of new ones.

In most batteries the active cathodic material is a lithium cobalt oxide, LiCoO_2 ; the anode is made of a carbonaceous materials. The electrolytic solution is made of a mix of different solvents: propylene carbonate (PC), ethylene carbonate (EC), diethylene carbonate (DEC), dimethyl carbonate (DMC) combined with LiPF_6 or LiClO_4 as solutes (Braun, 1996).

As cobalt is a strategic metal with limited natural sources its recovery from the discarded lithium batteries is of considerable economic significance. This has been done by solvent extraction.

An electrochemical method to recover cobalt has been proposed by Pasquali and Lupi (2001) based on their basic electrochemical measurements. The used batteries are dismantled and the cathode material is leached with sulfuric acid and hydrogen peroxide in the molar ratio $\text{Co}:\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 1:3:1$. The leach liquor at pH 4-4.2 contains 33 g/L Co, 1 g/L Mn and 15 g/L ammonium sulfate (additive to produce good deposit). It is fed into an electrowinning cell. At temperature 50°C and constant current density of 250 A/m², cobalt metal with a purity of 910.95 % is recovered at the cathode. Current efficiency is 96 % and specific energy consumption 2.8 kWh/kg metal produced.

The flowsheet is shown in Figure 10.42. It has two sub-schemes. Sub-scheme A is referred to electrolysis conducted using an aluminum foil cathode. Sub-scheme B uses an

aluminum net cathode. In the first case the cobalt deposit is brushed and then heated at 300°C in presence of oxygen to produce Co_3O_4 that is the precursor of cobaltite. In the second case cobalt deposit has to be re-dissolved and then crystallized as cobalt sulfate or acetate. The exhausted electrolyte is sent to a final electrochemical filter, in which a porous graphite cathode is used for a complete cobalt recovery. The metal content in the end solution is below the discharge limits.

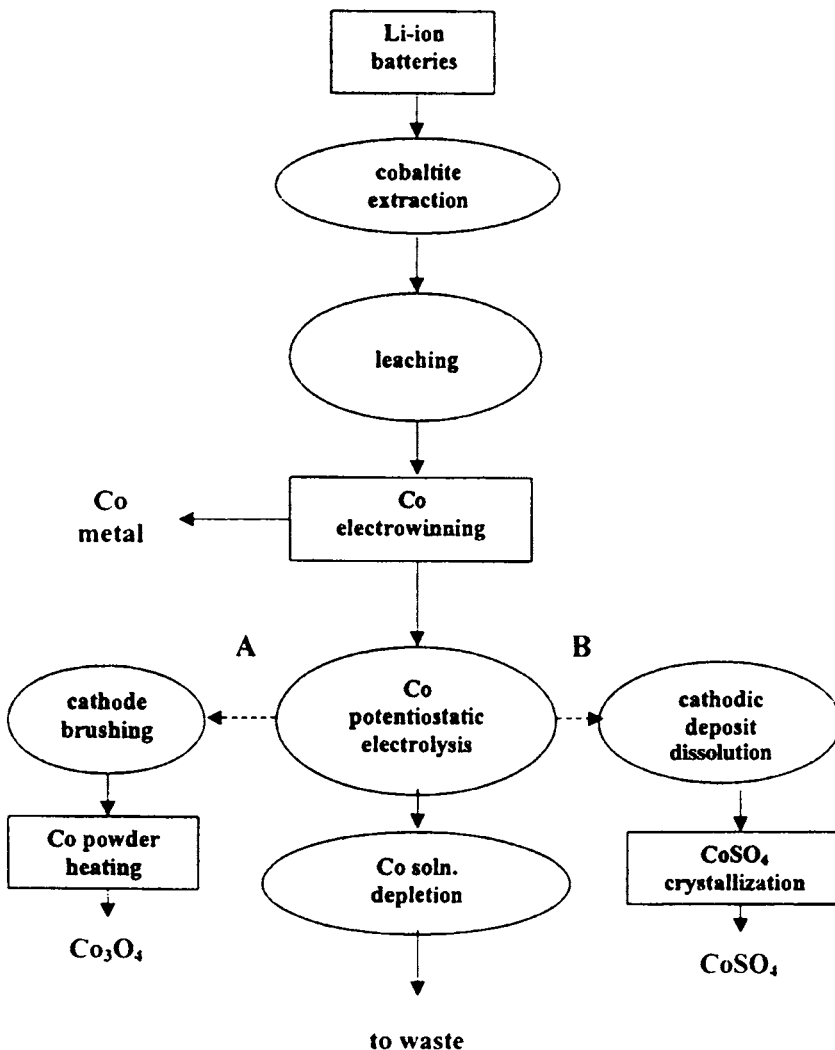


Figure 10.42. Flowsheet of the process for cobalt recovery from lithium batteries (Pasquali and Lupi, 2001). Sub-scheme A - Aluminum foil cathode and Sub-scheme B- Aluminum net cathode. Potentiostatic electrolysis refers to electrowinning at constant potential of -0.9 V vs. SCE

A similar process has been developed by Lupi and coworkers (2005) to recover nickel from lithium-ion batteries. Metallic nickel is produced at 250 A/m², at pH 3-3.2 and 50 °C, with 87% current efficiency and 2.96 kWh/kg energy consumption.

10.5.5.1. Recovery of Lithium and Cobalt by Hydrometallurgical Process

A hydrometallurgical process for the separation and recovery of both cobalt and lithium from spent lithium-ion secondary batteries has been developed (Zhang *et al.*, 1998a).

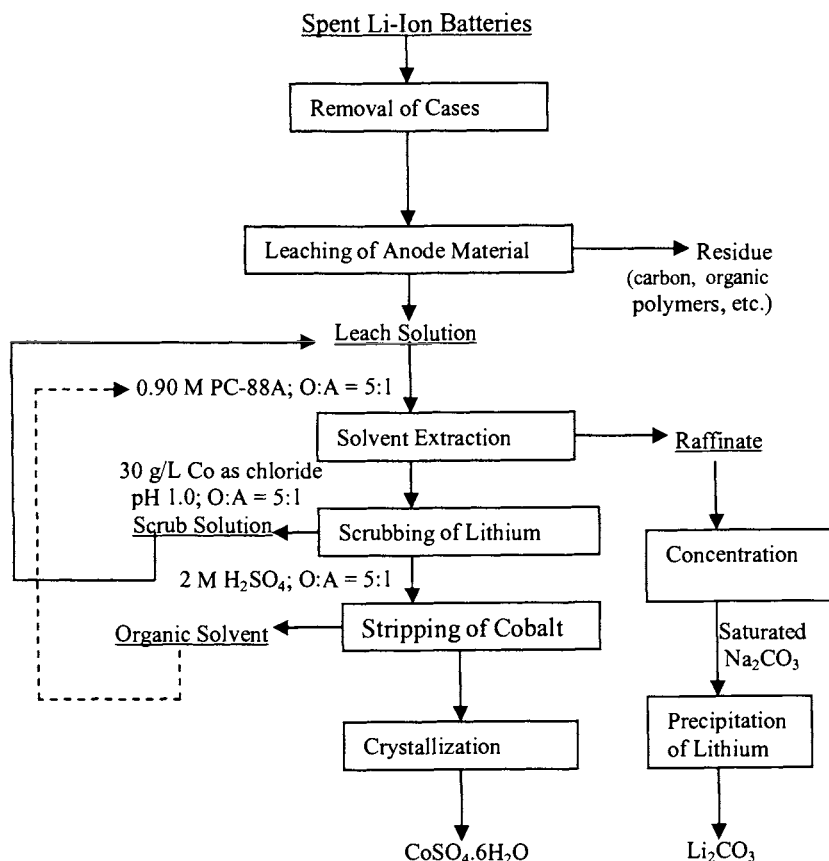


Figure 10.43. Flow sheet of the hydrometallurgical process for the recovery of cobalt and lithium from spent lithium-ion secondary batteries. The dotted line indicates that the organic phase is returned to the extraction step for reuse. (Zhang *et al.*, 1998a).

The process is relatively simple, consisting of three steps: (a) leaching of the anode materials of the lithium-ion batteries with hydrochloric acid; (b) separation of cobalt from lithium with solvent extraction; and (c) precipitation of lithium as carbonate. The best conditions for leaching are, hydrochloric acid 4 M at 80 °C for 1 hour and a solid to liquid ratio of 1 to 10. Under these conditions, over 99 % of cobalt and lithium are leached and a leach liquor of pH around 0.6 containing 17 g/L of cobalt and 17 g/L

lithium is produced. Cobalt and lithium are separated by solvent extraction with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A; see Chapter 2). Cobalt is quantitatively extracted with 0.90 M PC-88A) in kerosene at an O:A ratio (organic to aqueous phase ratio) of 0.65:1 and pH ~ 6.7 in a single stage. This is followed by a single stage scrubbing of lithium from the loaded solvent by a chloride solution containing 30 g/L of cobalt at an initial pH of 1.0 and O:A ratio of 10:1, and then by stripping with a 2 M sulfuric acid solution at an O:A ratio of 5:1.

The purity of the cobalt recovered is ≥ 910.99 %. Lithium is recovered by precipitating as lithium carbonate at a temperature close to 100 °C. Almost 80 % of lithium is recovered with very high purity, < 0.07 % cobalt. An overall process flow sheet is shown in Figure 10.43.

10.5.6. Metal Recoveries from Nickel-Metal Hydride Batteries

These batteries, denoted by Ni-MH, have been developed as a substitute for cadmium-containing electrodes. They are considered to be environmentally more acceptable as they eliminate the use of highly toxic cadmium. They also have greater electrochemical capacity and are strong candidates for electric vehicles. Several types of Ni-MH electrodes have been developed. One is based on an intermetallic compound LaNi_5 , which is a member of the family of alloys known as AB_5 . In the battery manufacture, LaNi_5 is used as the active material of the negative electrode and is converted into LaNi_5H_6 during the charge. In addition to lanthanum the intermetallic also contains cerium (Ce), praseodymium (Pr) and neodymium (Nd), all members of the rare earth lanthanide series, denoted by RE. Another type is made of a complex alloy of the composition $(\text{Ti}_{2-x}\text{Zr}_x\text{V}_{4-y}\text{Ni}_y)_{1-z}\text{Cr}_z$ where x varies from 0.00 to 1.5, y from 0.6 to 3.5 and $z < 0.20$. The designation AB_2 is given as the Ti-Zr atomic fraction and the Ni-V atomic fraction occurs in the ratio 1:2. The positive electrode is nickel and cobalt with small percentages of zinc and iron.

The discarded Ni-MH batteries are therefore a source of nickel, cobalt, and some rare earth metals. Hydrometallurgical routes to recover the metals have been described by Lyman and Palmer (1995) and Yoshida and coworkers (1995).

The used battery package in plastic case is first crushed and ground to separate the valuable components. The battery is then crushed and the crushed materials are separated by sizing. The fine fraction (-28 mesh) is primarily nickel hydroxide and hydrogen storage materials. The coarse fraction (+28 mesh) is further treated by a magnetic separator to separate resins, plastic paper. These are then subjected to a thermal treatment to burn the resins, plastics and papers encased in magnetic materials. The residue is crushed and screened into three parts: coarse (+16 mesh), intermediate (-16+24 mesh) and fine (-24 mesh). The flow diagram is schematically shown in Figure 10.44.

The valuable metals are concentrated in Products 1, 4 and 5. These constitute the material for leaching. Typical composition is 410.1 % Ni, 10.6 % Co, 21.6 % rare earth elements, 1.2 % Al, 0.6 % Zn and 0.3 % Fe. Sulfuric acid leaching dissolves 92-98 % of the metals. From the leach solution, rare earth elements (RE) are separated by crystallizing them as double salts by adding sodium sulfate. The double salts have the general composition, $\text{RE}(\text{SO}_4)_2 \cdot \text{Na} \cdot 2\text{H}_2\text{O}$. Zinc and copper are separated from cobalt and nickel by solvent extraction by di-2-ethylhexyl phosphoric acid (D2EHPA; see Chapter 4). Nickel and cobalt are recovered from the solution by electrowinning. Figure 10.45 shows complete flow sheet of the process to treat the batteries and recover metals.

The flowsheet developed by Lyman and Palmer (1994) differs from that of Yoshida and coworkers (1995) in some steps. They separate the plastic component of the crushed battery by coarse filtration. The rare earth metals from negative electrode leach extract are recovered by precipitating as phosphate. The nickel mesh substrate and the positive electrode materials are washed and separated by elutriation if desired. Approximately 17.5% of the nickel originally present in the scrap can be recovered as nickel mesh, and the positive electrode product contains 2.7% of the cobalt and 25.5% of the nickel originally present. This material can be recycled directly to metal scrap handlers or may be subjected to further chemical treatment steps.

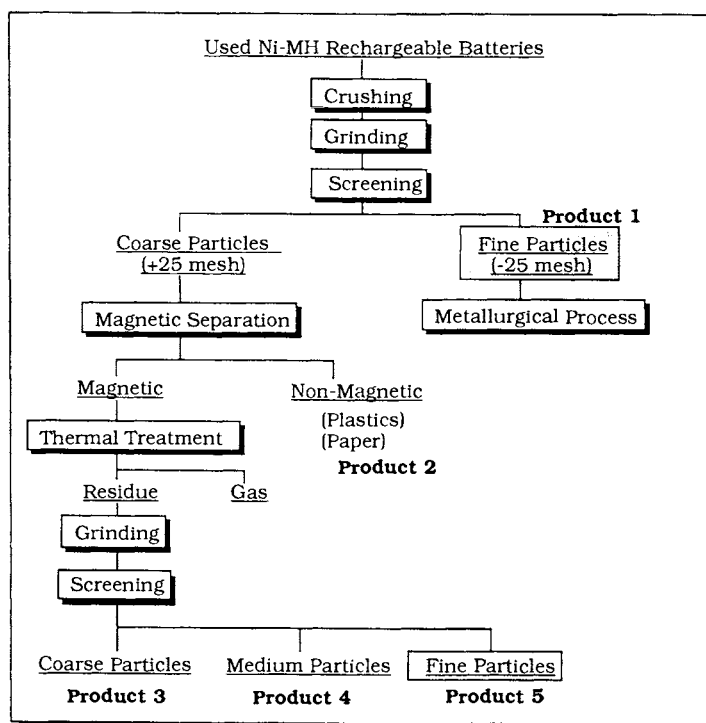


Figure 10.44. Flow diagram of mechanical processing of Ni-MH batteries (Yoshida *et al.*, 1995)

A slightly modified method, which enables selective separation of rare earth metals to be made has been described by Zhang and coworkers (1998b). The electrode materials are leached with hydrochloric acid. Rare earth metals, and cobalt and nickel are together separated by solvent extraction with 25 % D2EHPA in kerosene. At an equilibrium pH of 2.5, almost 100 % of the rare earths and cobalt and nickel are extracted along with about 80 % of the zinc and 40 % of the manganese present in the feed. Aluminum and iron are also nearly completely extracted. Extraction of manganese in organic phase is increased by multistage extraction. The rare earths and cobalt and nickel are stripped by hydrochloric acid. Rare earths are then selectively precipitated as oxalates and separated from impurities. Cobalt and nickel are extracted by trioctyl amine (TOA), stripped and

then selectively precipitated as oxalates. A conceptual flow diagram of the process is shown in Figure 10.46.

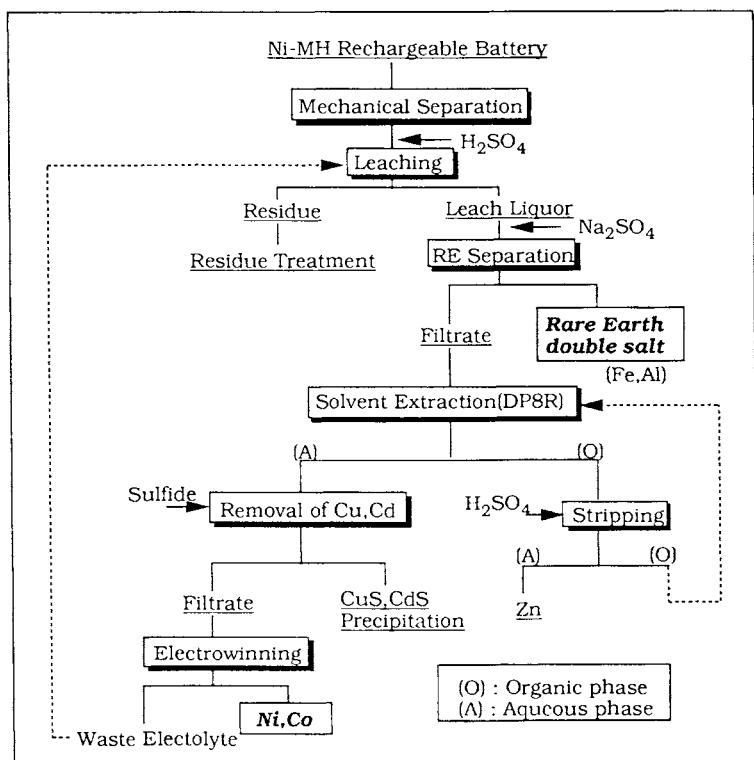


Figure 10.45. Total flow diagram of the recycling of metals from used Ni-MH batteries (Yoshida *et al.*, 1995)

A slightly modified method, which enables selective separation of rare earth metals to be made has been described by Zhang and coworkers (1998b). The electrode materials are leached with hydrochloric acid. Rare earth metals, and cobalt and nickel are together separated by solvent extraction with 25 % D2EHPA in kerosene. At an equilibrium pH of 2.5, almost 100 % of the rare earths and cobalt and nickel are extracted along with about 80 % of the zinc and 40 % of the manganese present in the feed. Aluminum and iron are also nearly completely extracted. Extraction of manganese in organic phase is increased by multistage extraction. The rare earths and cobalt and nickel are stripped by hydrochloric acid. Rare earths are then selectively precipitated as oxalates and separated from impurities. Cobalt and nickel are extracted by trioctyl amine (TOA), stripped and then selectively precipitated as oxalates. A conceptual flow diagram of the process is shown in Figure 10.46.

A more recent study on metal recoveries from nickel metal hydride batteries is that from Lupi and coworkers (2000). They separate metals out of plastics and recyclable plastics from nonrecyclable ones by physical process comprising shredding, screening and elutriation, followed by magnetic separation of steel chips. The metals are then recovered by hydrometallurgical process comprising leaching in sulfuric acid followed by

stage neutralization by potassium hydroxide to separate rare earths (precipitated in the 1st stage) from nickel and cobalt, which are separated by solvent extraction.

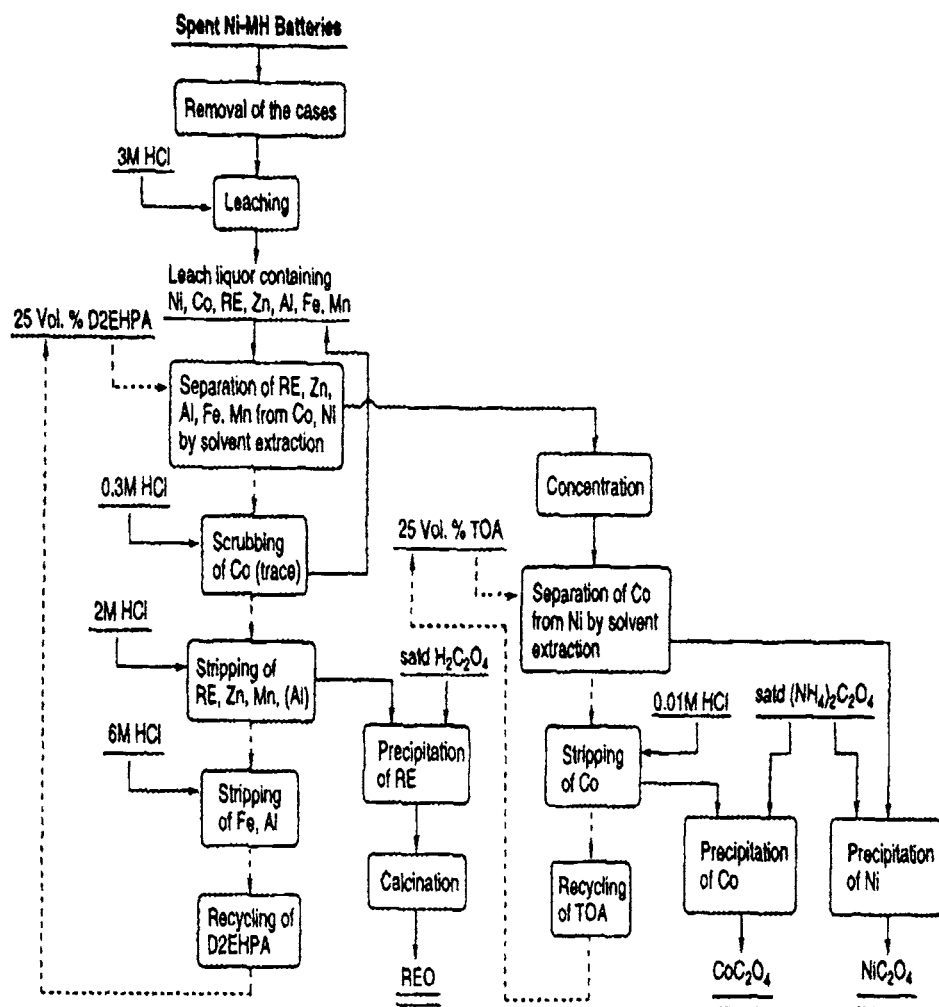


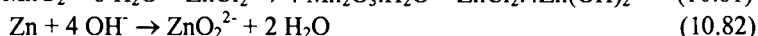
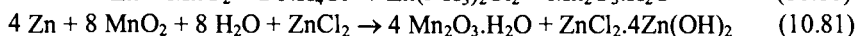
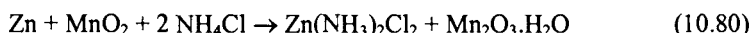
Figure 10.46. Conceptual flowsheet for the recovery of metal values from nickel-metal hydride secondary batteries. Dashed lines denote organic streams; solid lines denote aqueous streams (Zhang *et al.*, 1998b)

10.5.6.1. Recovery of Nickel by Ammonia Leaching

Dissolution of nickel hydroxide in ammonia to form nickel ammine complex (see Chapter 3) has been applied to develop a method to selectively recover nickel from nickel-metal hydride batteries (Miyake *et al.*, 2004). If zinc hydroxide is also present, that too will dissolve and the two metals will have to be separated from the ammine solution by electrodeposition.

10.5.7. Recovery of Zinc from Zinc-Manganese Batteries

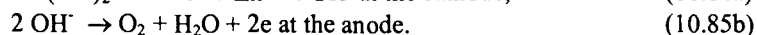
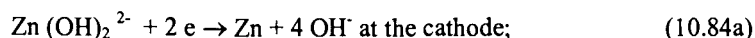
These secondary batteries contain primarily zinc and manganese dioxide. At the battery anode, zinc is oxidized to produce energy, and the zinc oxide is solubilized by potassium hydroxide. The reactions are as follows:



The batteries are crushed under a sprinkle of sodium hydroxide. The pulp is screened under alkali spray to separate fines and chunks. Iron is separated by a magnetic separator. The nonmagnetic fraction contains zinc in suspension and is taken to recover the metal. It is treated with an oxidant (sodium hypochlorite, hydrogen peroxide or manganese dioxide) in alkaline solution to oxidize zinc and convert it into zincate ions:



Mercury present in the pulp settles at the bottom. The redox potential has to be controlled to prevent the dissolution of other metals. The pulp is filtered and by pressure filter. The filter cake is used to recover manganese. Zinc is recovered from the solution by electrolysis. The reactions at the electrodes are:



On an industrial scale, with a current density of 1000 A/m² at 4 volts, 90 to 95 % of the metal is recovered from a solution containing 25 to 30 g/L zinc.

The filter cake is leached with 2 M sulfuric acid in presence of hydrogen peroxide to leach all remaining metals. The insoluble fraction (mainly plastics and carbon) is separated and the solution is mixed with a soluble sulfide (sodium or ammonium) at pH 2.5 to 3 to precipitate all metals except manganese. (Manganese is most soluble of the metal sulfides present because of its higher solubility product; see Chapter 4 for explanation of selective precipitation of metal sulfides). Manganese is recovered from the solution as manganese carbonate by bubbling in carbon dioxide.

This is known as Zimaval process, described by Ferlay (2000). It can also be applied to several other zinc-bearing metallurgical residues such as EAF dust, smelter residues and galvanization scraps.

10.6. Resource Recovery from Spent Petroleum Catalysts

Petroleum refining industry generates spent catalysts as a waste product, which contains several metals. A typical composition represents Al (15-25 %), Mo (3-10 %), Ni (0.2-3.0 %), V (4-8 %), Co (up to 3 %) besides Si (1-5 %), S (5-10 %) and oil (10-20 %) (Crnojević *et al.*, 1990). The resource recovery scheme is based on a two stage leach, one for a selective solubilization of molybdenum and vanadium, and the other for selective solubilization of aluminum. It converts the spent catalyst components into four products: molybdenum trisulfide, vanadium pentoxide, alumina trihydrate and nickel-cobalt concentrate. The spent catalyst is first fed to a ball mill, along with a sodium

hydroxide- sodium aluminate solution (which is recycled from the second stage of the process, described further). The resulting slurry is then pumped to an autoclave, where it is leached under oxidizing conditions at elevated temperature and pressure. This converts sulfur to sulfate, organic compounds are oxidized and molybdenum and vanadium are selectively dissolved. A liquid-solid separation of the autoclave product is done by thickening and filtration. The resultant solution forms the feed for molybdenum and vanadium recovery, and the solids are forwarded to the second stage alumina leach. Molybdenum sulfide is precipitated from the leach solution in presence of sulfuric acid. It is further processed into an oxide or other molybdenum compounds. Vanadium is precipitated from the molybdenum free solution as hydroxide by sodium carbonate or hydroxide. It is calcined into a granular vanadium pentoxide product, and sold to manufacturers of ferrovandium. Solids from the leach are high in alumina and are leached a second time at high temperature with strong caustic to solubilize aluminum. The solids are then separated by centrifuging and smelted into a nickel-cobalt matte from which nickel and cobalt are recovered. The sodium aluminate solution from the second leach goes through a series of alumina precipitators. Alumina trihydrate is precipitated by cooling. The sodium hydroxide-sodium aluminate solution, free of alumina, is recycled to the first and second stage leach. The process does not generate solid waste. The flowsheet is represented in Figure 10.48.

10.6.1. Recovery of Nickel Compounds from Spent Catalysts

Nickel is a major constituent in most catalysts. The metal recovery from spent catalyst by different processes was described in Chapter 7. Alternatively, it is possible to recover nickel compounds, which could be marketed with significant value. This has been demonstrated by Al-Mansi and Monem (2002), who applied a hydrometallurgical process to treat a spent catalyst from a fertilizer manufacturer leading to the production of nickel sulfate. The spent catalyst is crushed and screened to the desired particle size. The reaction takes place in a sealed container and the resulting slurry filtered on sinter glass to separate from the insoluble matter. The nickel sulfate is crystallized by evaporating the soluble fraction. The flow diagram is shown in Figure 10.47.

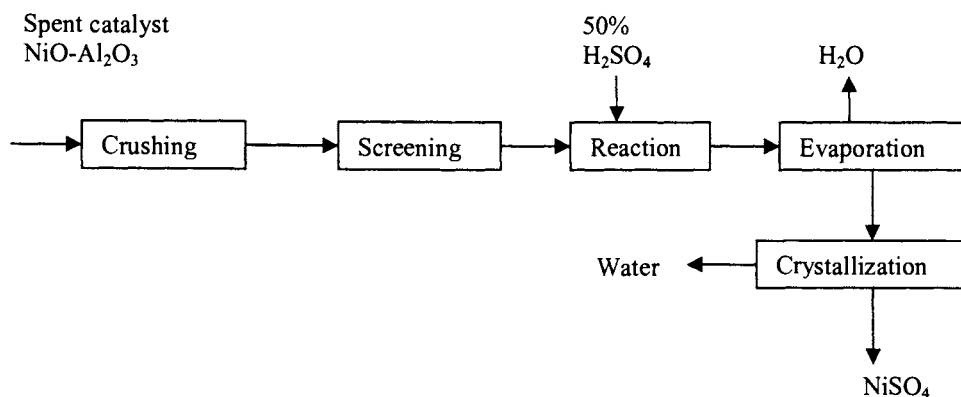


Figure 10.47. Processing of spent catalyst for nickel recovery

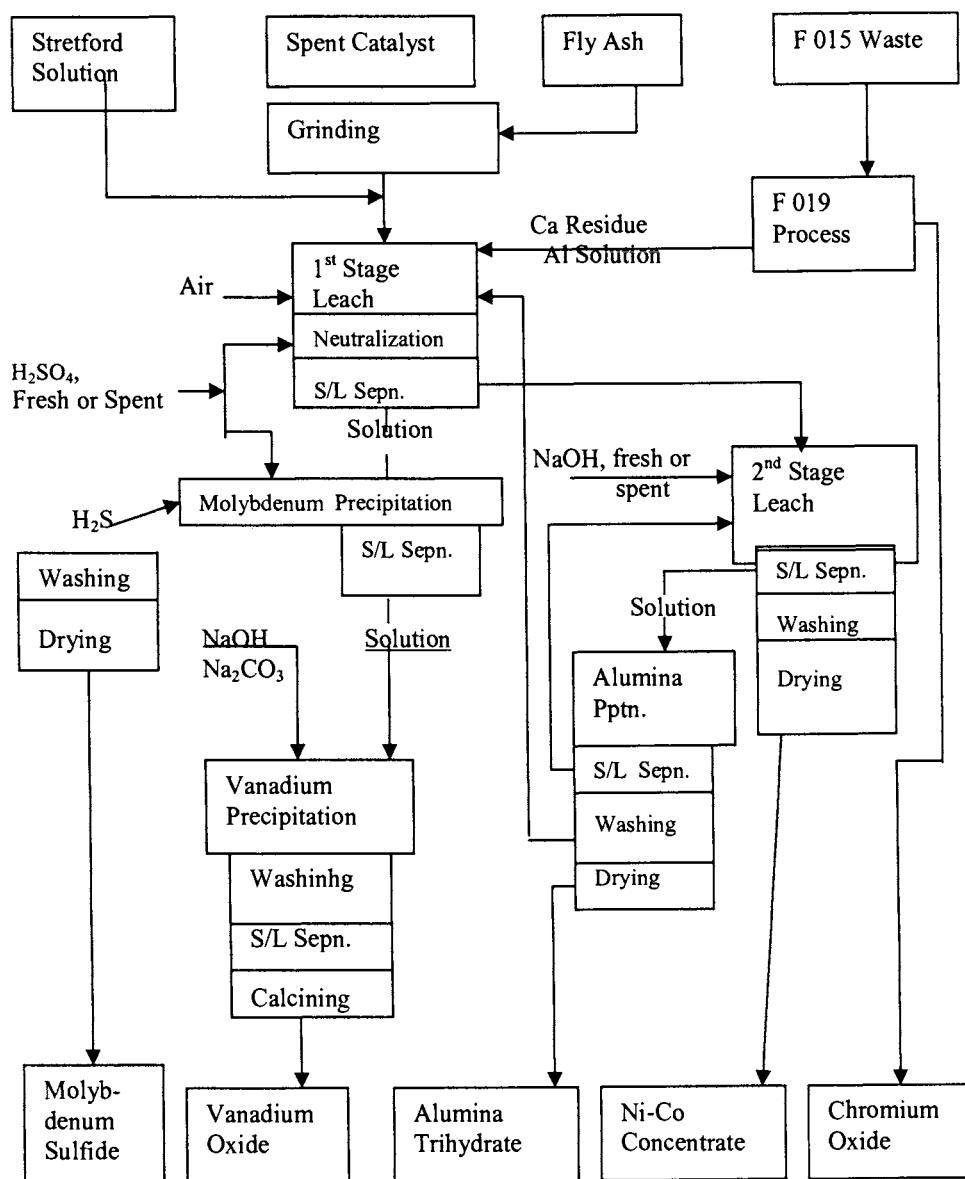


Figure 10.48. Recovery of Molybdenum, Vanadium, Nickel and Chromium from Spent Catalysts and Spent Etchant Solution (Crnojević *et al.*, 1990)

10.6.2. Chromium Recovery from Spent Etchants

Finished alumina products are etched for surface passivation using chromic acid. The spent etchant solution, saturated with impurities still carries 3-15 % chromium besides 5-

15 % aluminum, 5-20 % calcium and 2-15 % phosphorus. The material has been exploited as a secondary source of chromium.

The material is treated with sulfuric acid at temperature 20-60 °C to completely dissolve aluminum and chromium while calcium sulfate and some gangue material are left as insoluble residues. Iron present in ferrous state is oxidized to the ferric state by

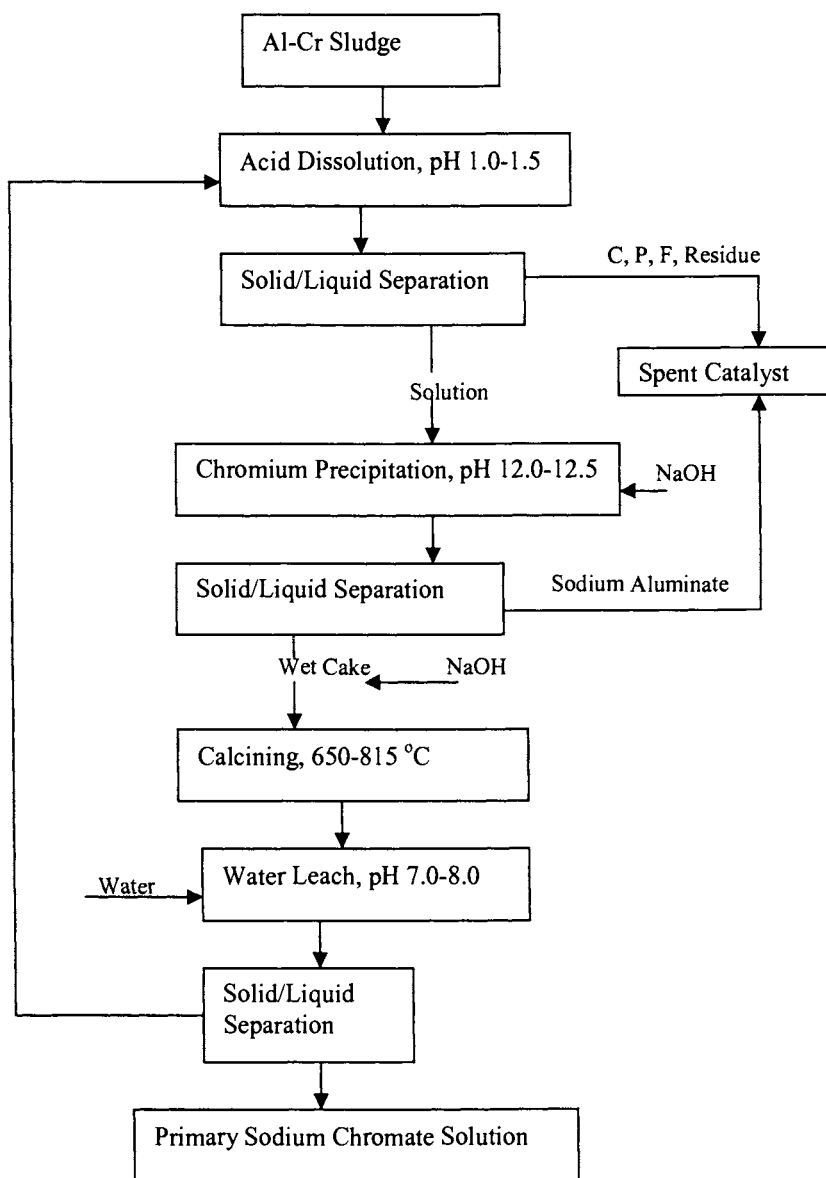


Figure 10.49. Process Flowsheet for Producing High Purity Chromium Compounds from Aluminum-Chromium Sludges (Crnojević *et al.*, 1990)

oxygen or any available mild oxidant. Chromium is precipitated by sodium hydroxide at a pH ~10 where aluminum remains in solution as aluminate. The lower pH also enhances phosphorus removal. Without further processing, the chromium hydroxide produced used to be a hazardous waste classified as F019 material. It is enriched with sodium hydroxide at a pH ~10 where aluminum remains in solution as aluminate. The lower pH also enhances phosphorus removal. It is enriched with sodium hydroxide to get Cr/Na₂O ratio of about 1 and calcined at 650°-870° C. The calcine is leached in water at pH 7.0-8.0 to produce a highly concentrated solution of chromate with 6-130 g/L Cr . The flowsheet is shown in Figure 10.49. The percentages of impurities (Fe, Al, Zn, P) are < 0.1 %. The alkaline solution after the precipitation of chromium is processed for the recoveries of molybdenum and vanadium by the process described in Section 10.6 and the flowsheet in Figure 10.48.

Selected Readings

- Aplin, C. L. and Argyll, Jr. G. O. (editors), 1973. *Tailing Disposal To-day*. Miller Freeman Publications, San Francisco, CA
- Chalkley, M. E., Lakshmanan, V. I., Conard, B. R. and Wheeland, K. G editors. 1989. *Tailings and Effluent Management*. Pergamon Press
- Ritcey, G. M., 1989. *Tailings Management*, Elsevier, Amsterdam.

Chapter 11

RECYCLING OF WATER AND REAGENTS

11.0. Introduction

Water has many vital functions in almost every mineral and metal processing operations as described in Chapters 3 and 4 (Mineral Processing and Hydrometallurgy). It is used as a carrier for fine solids, provides a column in which separation processes (jigging, flotation, classification) take place, is used in dust collection and cleaning systems, is employed in smelter refractory cooling systems and is a reagent in hydrometallurgical operations. The water inevitably picks up fine solid particles and soluble salts and organic materials in the course of this use necessitating purification treatment to make it suitable for recycling or before discharge to water courses is permitted. Water is a precious resource, essential for human, animal and plant life (in addition to its wide usage in process and construction industries), making conservation, purification and recycle of water is a necessity to ensure its constant availability wherever needed. This chapter describes some of the techniques used or proposed to permit re-use or recycling of water. Sometimes, particularly in arid areas the only water available for processing is from a saline aquifer or from the ocean except at the cost of installing very long pipelines to carry fresh water from distant sources. The treatment of this water to remove residual base metals, iron, anions such as cyanide and thiosulfate, oils and greases and suspended solids before reuse, recycle or discharge is required to a water course or return to the ocean.

Social Dimensions of Water Globally agriculture is the largest consumer of water predominantly for irrigation. Disagreements over access to water and contamination of water can result in local and international conflicts. Provision of ample clean water to local communities can also be a side benefit of the establishment of a mining or mineral/metal processing operation. Large-scale use of water can also have social implications if there is competition for limited surface water. The focus on water applies especially in a semi-arid or arid region or if extraction of underground water impacts on the depth at which water is available for other users of the underground water. The potential for contamination of aquifers and hence wells is another important issue. Mineral and metallurgical processing operations therefore seek to minimize the use of water, to recycle water and to process water to make it suitable for recycle or return to a water course.

Recycling of water is also connected with recycling of reagents dissolved in water. This applies specially to cyanide, which is used in many gold recovery operations. Very

high toxicity of this reagent and the cost are incentive for its recovery from process wastewater and recycling of the water.

11.1. Recycling Water

As water is an essential requirement for most process industries, including mineral and metallurgical industries, they are among major users of water. Both economic and environmental considerations make the recycling and re-use of water an absolute necessity. Use of water on such large scale can also have social implications if there is competition for limited surface water in a semi-arid or arid region or if extraction of underground water impacts on the depth at which water is available for other users of the underground water. Environmental, economic and social aspects of the sustainable development can be improved by recycling, depending upon the local circumstances. However, there are several technical aspects, which influence the extent to which the desirable practice of recycling water from plant practices is possible. As the chemistry of the system is altered, it could affect the process efficiency. This applies specially to flotation, which (as explained in Chapter 1), is principally governed by the chemistry of the ore pulp.

11.1.1. Recycling Water in Flotation Plants

Environmental, economic and social aspects of the sustainable development can be improved by recycling, depending upon the local circumstances. However, there are several technical aspects, which influence the extent to which the desirable practice of recycling water from plant practices is possible. As the chemistry of the system is altered, it could affect the process efficiency. This applies specially to flotation, which (as explained in Chapter 3), is principally governed by the chemistry of the ore pulp.

The quality of the external water can range from very high quality, soft water derived from melting snow, or poor quality, hard water (with high levels of dissolved calcium and magnesium) from underground aquifers, and to even lower quality sea water (with very high concentrations of dissolved salts). Some underground water may be more saline than the ocean water. Occasionally, a different source of water is used in the wet and dry seasons. Sewage water from cities is becoming a potential external source with sustainability implications. If the initial quality of the external water is high, the scope for recycling of water from all the products is maximized. Such reuse of recycle water from the products allows chemical species from the oxidation of the ore and from other inputs to the process such as reagents to increase in concentration in the water returned to the plant. Such accumulation of species often has negative effect on the performance of the process. There are, however, instances, where, depending upon the chemistry of the process, recycle water is found to have positive effect on the process.

The recycling of water from the various solid-liquid separations on the concentrate and tailing streams is called internal reuse. Reclamation of water from tailing pond areas, usually more distant from the concentrator, is called external reuse (Rao and Finch, 1989). The opportunities for recycling water from plant products (concentrate and tailing) are schematically shown in Figure 11.1.

The maximization of recycling of water is achieved when there is (I) maximum removal of water from each of the product streams; and (ii) return of water to the processing from all of the product streams.

Table 11.1. Selected Methods for Treatment of Recycle Water (from Rao and Finch, 1988).

Category	Method	Application
Chemical reaction	Precipitation	Removal of alkaline earth and heavy metal ions
	Oxidation, e.g., by ozone	Oxidation of most high molecular weight organics to simpler molecules
Adsorption on solid or at an interface	Adsorption on active carbon or coal	Removal of most organics
	Adsorption on mineral slimes	Removal of metal ions and some organics depending upon the slime composition
	Adsorption on bentonite clay	Removal of metal ions and slimes
	Adsorption at liquid-gas interface	Removal of highly surface-active organics (e.g., alkyl sulfates)
Other methods	Biological oxidation	Removal of biodegradable organics
	Ion exchange resins	Removal of ionic species
	Reverse osmosis	Removal of electrolytes
	Atmospheric freezing	Removal of electrolytes and organics

11.1.2.1. Removal of Metals by Modified Active Carbon.

Active carbon is an effective adsorbent for both inorganic as well as organic compounds. Industrial active carbon is prepared by degasifying charcoal. Several cheaper materials have been used to prepare active carbon. They are generally readily available and are often derived from agricultural waste. An example is that of peanut hull, a waste agricultural by-product. The active carbon prepared from this material has been shown to be superior to industrial active carbon for removing metal ions from dilute effluents. Using a product of particle size 0.575 mm, Periasamy and Namasivayan (1995) have shown effective removal of nickel ions from plating wastewater. With carbon dose of 3 g per liter of the effluent containing 12.5 mg/L in the pH range 4-10, about 75% nickel is removed in 3 hours of agitation. Increasing the carbon dosage to 8 g/L results in almost complete removal of the metal. The adsorbed metal can be desorbed by 0.2 M hydrochloric acid and nickel recovered in a concentrated solution. As the adsorbent is derived from a readily available waste product, the process is very economical. Other sources for preparing active carbon, also agricultural wastes, and employed for the removal of metals from dilute effluents are rice husk (Srinivasan *et al.*, 1988) and coconut shell (Arulanantham *et al.*, 1989).

Adsorption on active carbon does not involve chemical bonding. Most metals do not bind with carbon. It is possible to modify the carbon by introducing chemical functional groups, which would chemically bind the metal. Such modification enhances the effectiveness of the adsorption process as it now follows chemical binding. An example is that of the removal of copper, zinc and chromium by adsorption on active carbon modified with tetrabutyl ammonium iodide (TBAI), $(C_4H_9)_4NH_4^+ I^-$ and sodium diethyl dithiocarbamate (SDDC): $S=C-S^- Na^+$



As observed from their formulae, the molecular structures of these compounds consist of a polar functional group, which binds with the metal and a non-polar hydrocarbon group which attaches itself to the carbon. The carbon is impregnated in a solution of the modifying compound until it comes to equilibrium with the solution (Monser *et al.*, 1999). The capacity of the active carbon to remove metals is increased more than 3-fold as determined by adsorption measurements (Monser and Adhoum, 2002).

11.1.2.2. Removal of Heavy Metals by Clay Minerals

Some naturally occurring clay minerals possess adsorption capacity for cationic species. This has been exploited to remove some heavy metal ions from wastewater. A special class of clay minerals called zeolites are specially suited for this purpose. A natural zeolite mineral is clinoptilolite. In its simplest form, it is formulated $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]\cdot 24\text{H}_2\text{O}$ (Breck, 1974). However, many natural forms of zeolite contain calcium and potassium ions, partially replacing equivalents of sodium ions. In such cases, the mineral is exposed to 2 M solution of sodium chloride to get a homoionic zeolite. This is known to adsorb some heavy metals, in particular, lead, cadmium and zinc by ion exchange mechanism (Blanchard *et al.*, 1984; Curkovic *et al.*, 1997). The zeolite can be regenerated and the metal ions removed in concentrated form by stripping with a sodium chloride solution.

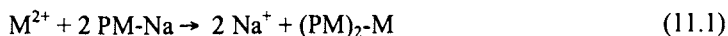
Attempts have been made to enhance the adsorption capacity of zeolites by chemical treatment with hydrochloric acid followed by neutralization with sodium hydroxide (Vengris *et al.*, 2001). Acidic treatment causes the dissolution of calcium, magnesium, iron and aluminum oxides. In the neutralization process, most of the dissolved metals except calcium, reprecipitate as hydroxides, leading to an increase in their amounts in the zeolite. While this has been successfully carried out in the laboratory, its industrial applications appear to be very limited. As yet, zeolites are used only in a few operations to remove dissolved metals. The principal factor, which limits their application, is the availability of natural zeolites in the mining region or in the neighborhood.

Another example of the use of natural zeolite in treating recycle water is found in the use of mordenite, $\text{Na}_8[\text{Al}_8\text{Si}_{40}\text{O}_{96}]\cdot 24\text{H}_2\text{O}$ to remove antimony, which is a toxic element and occurs in the discharge water from the production of electronic materials (Kato and Mita, 1999). Antimony ions are exchanged for sodium, calcium, magnesium and potassium ions in mordenite. By combining the zeolite with an anionic flocculant, up to 96 % antimony has been removed. The role of the flocculant has not been explained. It is possible, the anionic flocculant removes the fraction of antimony, which is present as antimoniate anion in highly alkaline solution. (Antimony oxide is amphoteric and therefore, depending upon the pH the antimony would occur as antimony cation or antimonite anion, the concentration of the anionic species increasing with increasing alkalinity).

11.1.2.3. Removal of Heavy Metals by Biosorptive Flotation

Metal binding capacities of various microorganisms (described in Chapter 5) are potentially useful to remove hazardous metals from wastewater and facilitate its reuse. Many biomasses, such as peat moss, often exist in small sponge flocs, which generally necessitates suitable solid-liquid separation downstream of the reaction tank. This has been attempted by flotation technique (see Chapter 3).

Metal uptake on the peat moss is a process of ion exchange at acidic sites, which can be expressed as



M and PM denoting metal and peat moss respectively. Peat moss is a complex material containing lignin and cellulose as its major constituents (Coupal and Lalancette, 1976). These constituents contain polar functional groups such as alcohols, aldehydes, ketones, acids and phenolic residues that can form chemical bonds or complex with the metal ions from solutions (Chen *et al.*, 1990). The adsorption capacities for the peat moss are in sequence of $\text{Pb} > \text{Ni} > \text{Cu} > \text{Cd}$, and the adsorption kinetics are in the same sequence, as shown by Aldrich and Feng (2000).

After the metal uptake the peat mass is floated using cetyl trimethyl ammonium bromide as collector with a dosage of 12.5 mg/L at pH 6.4 and a feed content of 0.5 g/L. Almost 100% peat moss floats in 3 minutes of flotation time. The metals are then desorbed by hydrochloric acid.

Biotechnological methods, which involve biosorption by organisms in naturally occurring substances like algae and fungi have been applied to remove several metals. Many examples have been described from time to time. An interesting and very economical method is based on the uptake of metal ions by the cell walls of organisms in green alga. The cell walls of *chlorella vulgaris*, a common green alga containing a complex mixture of sugars and proteins has a high sorptive capacity for a variety of metal ions. An interesting study by Greene and McPherson (1987) has shown that from a 0.1 mM solution at pH 5.0 the following metal ions are adsorbed with relative bond strength $\text{Ag(I)} > \text{Al(III)} > \text{Cu(II)} > \text{Pb(II)} > \text{Cd(II)} > \text{Ni(II)} > \text{Cr(III)} > \text{Co(II)}$. The less strongly bound metal ions are stripped by transferring to a medium of pH 2.0. This makes it possible to recover some of the metals. The metal uptake is, however, inhibited by chloride ions, which is a drawback limiting the application of this approach. Similar studies have been described on the uptake of nickel, copper, zinc and cadmium ions by fungal biomass (Bosecker, 1993).

Another example is the removal of manganese by a unique bacterial culture, which oxidizes dissolved Mn(II) to Mn(IV) , which then precipitates as manganese dioxide at neutral pH (Mita and Kato, 1999).

11.1.2.4. Removal of Toxic Metals

Wastewater generated in metal industries often contains toxic elements. They originate from the metal compounds, which are processed for the recovery of metals by chemical or electrochemical processing techniques. The removal of such elements require several steps of treatment to ensure, the final discharge water meets the environmental quality requirements. Another complication arises when the metal occurs as metal-chelate complexes. Such complexes are produced in electrowinning operations where chelating agents are added to enhance current efficiency of electrolytic process (see Chapter 4 for discussion of electrowinning techniques). Examples of such toxic metals are copper, nickel and zinc. A few examples will be described.

Separation of nickel from metal finishing industry wastes has been done by a multistage process (Brooks, 1987). The metals are first solubilized with 20% sulfuric acid and the insolubles separated. The metals iron, copper, zinc and nickel are precipitated by

raising the pH to near 6 by soda ash. The iron, copper and zinc are separated from nickel by solvent extraction by binary mixture of LIX64 and D2EHPA which selectively extracts these metals and nickel is separated in the aqueous phase. The organics and the trivalent chromium in the aqueous phase are oxidized by ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Nickel is then precipitated as oxalate by oxalic acid. The small amount of nickel still remaining is removed by chelate-type ion exchange resin. Other residual heavy metals are removed by precipitation as sulfides by mixing required amount of sodium sulfide. The separation stages are shown in Figure 11.2.

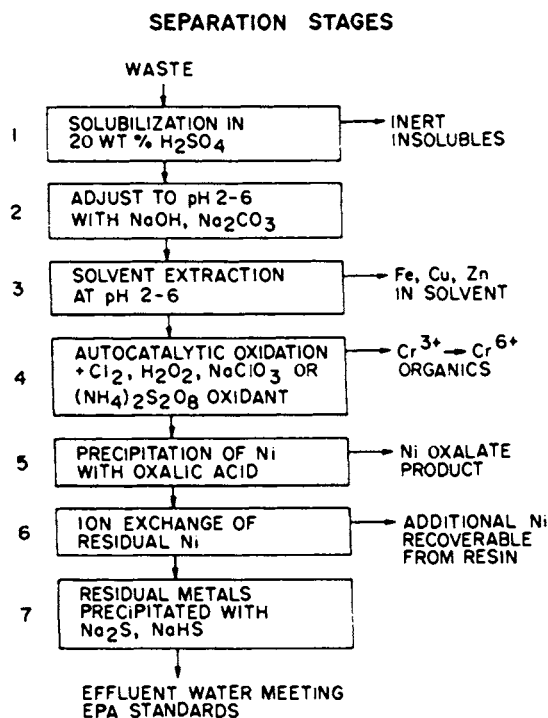


Figure 11.2. Stage of separation of toxic metals from wastewater from metal finishing process (Brooks, 1987)

Adsorption by activated carbon has been found effective to remove metals occurring as chelate complexes. The work of Shay and Etzell (1991) has shown that 30 to 60 minutes contact time is required for 90% removal of the metals. Other operating conditions have to be determined for different chelates. The principal one is pH. Increasing pH to near 9.0 increases removal of metal-citrate complexes. However, a more soluble complex like metal-EDTA (ethylene diamine tetra-acetate; formula is shown under Table 11.2) greater than 90% separation could be achieved even at pH 3.0, which is the usual pH of electroplating wastewaters.

Precipitation of toxic metals is also effective to remove some of them from wastewater. A reagent, which has been studied for this purpose is soluble xanthate. The xanthates are well known as flotation agents (described in Chapter 3). Alkali and alkaline earth xanthates and also starch xanthates are soluble whereas xanthates of heavy metals,

copper, lead, mercury are very insoluble. Addition of stoichiometric amount of xanthate completely precipitates these metals. In the case of mercury, however, although the X/M (xanthate to metal) is 2, molar ratio of 1 is found adequate for complete precipitation of mercury. It is likely, the precipitate produced is mainly mercurous xanthate as xanthate ions are reducing. The process has been investigated for the removal of mercury in wastewater using starch xanthate (Wing and Rayford, 1977). Mercury can be recovered by oxidizing the mercury xanthate precipitate using a suitable oxidant like sodium hypochlorite (NaClO). The xanthate is also decomposed (to carbon dioxide, sulfur dioxide and water) producing a non-toxic sludge.

Potassium ethyl xanthate as a precipitant has also been investigated for the removal of cupric ions from wastewater (Chang *et al.*, 2002). Cuprous ethyl xanthate formed as a sludge is found to be non-hazardous and can be disposed off in sanitary landfills. While using xanthates, however, it is necessary to state that xanthates themselves are toxic and should be used in exact amount required for metal precipitation and avoid excess, which would dissolve in water and cause its own toxicity.

A novel method of removing nickel from wastewater by reducing it to nickel metal by a strong reducing agent has been described by Ying and coworkers (1987). The reducing agent is sodium borohydride, which reduces the nickel ion at pH >12 by the following reaction:



Sodium borohydride is an expensive reagent. The cost of the process has to be evaluated against possible cost savings by the reduced volume of the sludge, which would be produced if the metal has to be removed by precipitation as hydroxide or sulfide.

11.1.2.5. Treatment of Wastewater by Selective Ion Exchangers

Laboratory investigations have been described on the removal of dissolved metals from wastewater using chelating ion exchange resins. An example is the use of amino-phosphonate and iminodiacetate resin to remove nickel and cadmium from metal-bearing rinsing baths (Lehto *et al.*, 1999). Following the removal of metals the metals are eluted from the resins with acids. This indicates the potential for the recovery of the metals. However, further development, especially for the selective separation of metals are required before the process can be considered on an industrial scale.

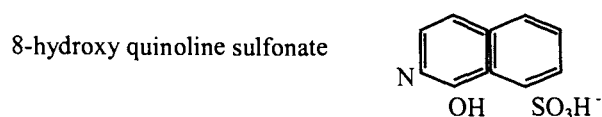
Note: Aminophosphonic acid is formed by replacing an H atom of the OR group in phosphonic acid (see Chapter 4 for the formula) by a NH₂ group. Imino group is represented by =NH. Imido group is (RCO)₂N-. When two CH₃CO groups are linked to -N-, the resultant compound is diacetylimine, also called iminodiacetate

In another procedure the wastewater is treated with a complexing agent to form anionic metal complex, which is then removed by adsorption by an anion exchange resin. The process is called chelation-assisted anion exchange (CAAE). By this procedure, nickel ions are removed by complexing with 8-hydroxyquinoline-5- sulfonic acid, followed by adsorption of the anionic complex by Amberlite anion exchange resin. Chromic ions are removed by complexing with 5-sulfosalicylic acid (Harris *et al.*, 1994). The metal binds to the complexing agent by co-ordinate bonding. As the complexing agent is anionic, with one negative charge for each, the four negative charges from the four binding chelating groups and two positive charges of nickel ion produce a complex

with two net negative charge in (hydroxyl-quinoline sulfonate; see structural formula below) it results in an anionic complex of the metal. The reaction may be represented by



where OHQSO_3^- denotes hydroxyl-quinoline sulfonate anion, represented by



Note: sulfonates are produced by the reaction of sulfuric acid on the aromatic benzene ring. The hydrogen atom from the benzene ring condenses with -OH group of the sulfuric acid. The resulting compound is called sulfonic acid, and possesses one negative charge, sulfonate. The reaction is represented by $\text{C}_6\text{H}_6 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{SO}_3\text{H} + \text{H}_2\text{O}$

Removal efficiencies of up to 95% have been achieved in batch tests with wastewater from a health care operation containing up to 4% Ni, 1% Cr and 9% Fe. Application of the process will, however, be limited to such low metal concentration wastewaters unless an additional step can be integrated to recycle the metal and regenerate the chelating agent.

11.1.2.6. Treatment of Wastewater by Membrane Processes

Membrane separation processes are coming into use in wastewater treatment. Originally used mainly for the desalination of brackish water, they have been applied to remove dissolved metals from wastewater from metallurgical industries. Two principal membrane based methods are reverse osmosis and electrodialysis. Both are based on the use of certain membranes made from high molecular weight polymers. The basic principles behind each of the two methods and their applications in wastewater treatment will be described.

Reverse osmosis is based on a simple concept explained in Figure 11.3. The two compartments of the process vessel (U shape tube in the Figure). In normal osmosis water diffuses through membrane to dilute the more concentrated of two solutions. If, however, pressure is applied to the concentrated solution the flow is reversed, which is the meaning of the term "reverse osmosis". As a result, dissolved salts, organics and colloidal solids are retained in the compartment where pressure is applied and the purified water is accumulated in the other compartment.

Reverse osmosis has been extensively applied for desalination of water and also to remove different salts and organic compounds from wastewater. The success of the operation depends upon the choice of the membranes for the desired operation. The water should be free of suspended matter to prevent fouling of the membrane. Economic considerations have thus far restricted the operation of the process.

In an **electrodialysis system**, cation and anion exchange membranes are formed into a multi-cell arrangement to form up to 100 cell pairs in a stack. The cation and anion exchange membranes are arranged in an alternating pattern between the anode and the cathode. Each set of anion and membranes forms a cell pair. Wastewater is pumped through the cells while an electrical potential is maintained across the electrodes. The positively charged cations in the wastewater migrate toward the cathode and the

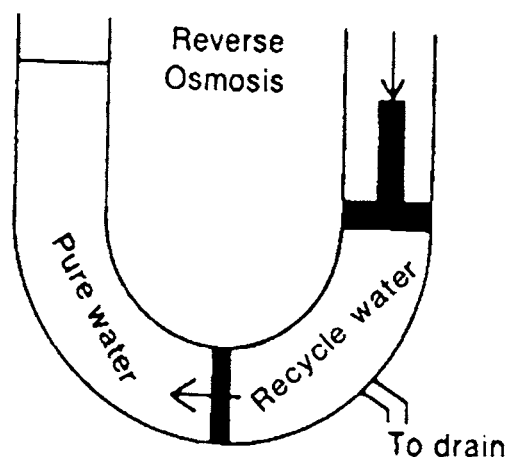


Figure 11.3. Principle of reverse osmosis

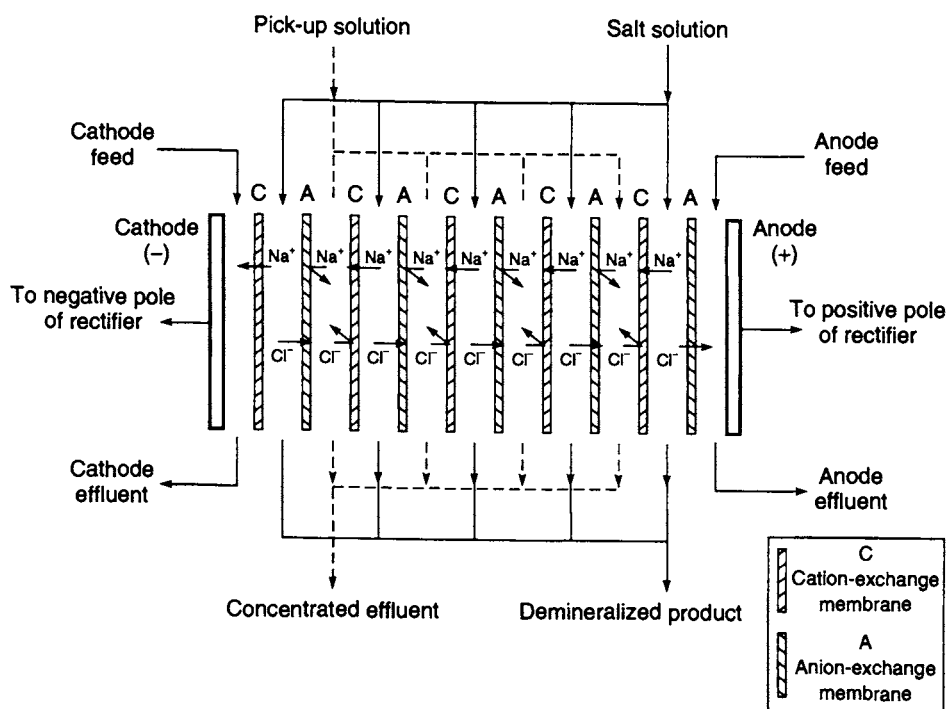


Figure 11.4. Schematic representation of an electrodialysis stack. Alternating cation- and anion-permeable membranes are arranged in a stack of up to 100 cell pairs. (Richard W. Baker, "Membrane Technology and Applications", 2004; p. 423. Copyright John Wiley & Sons; reproduced with permission).

negatively charged anions migrate toward the anode. Cations pass through the negatively charged cation exchange membrane, but are retained by the positively charged anion exchange membrane. Similarly, anions pass through the anion exchange membrane, but are retained by the cation exchange membrane. The whole process results in depletion of ions in one pair of the cell and enrichment in ions of the adjacent cell. The process is schematically illustrated in Figure 11.4.

The membrane separation methods have been applied to treat wastewater from electroplating bath, containing 10-20 mg/L copper and zinc with sulfate and chloride as the principal anionic species. Up to 96 % removal of the dissolved salts has been reported (Ujang and Anderson., 1998). Concentration of copper from a rinse stream and recovery of the metal as cupric sulfate and similar applications for the treatment of wastewater from metal refineries has been described by Eriksson and coworkers (1996). Another potential application is for the recovery of salt from aluminum salt cake waste brines produced in the processing of aluminum dross (described in Chapter 9) (Krumdick *et al.*, 2000).

11.1.2.7. Removal of Metals by Complexation with Natural Polyelectrolytes

Removal of metal ion by complexation with polyelectrolytes, which are polyacids or polybases, has been described by Jellinek and Sangal (1972). Metal ions form water soluble complexes with polyacids. On addition of a polybase an insoluble "sandwich" complex precipitates out of the solution. The metal ion "sandwiched" between the respective electrolytes can be dissolved by a mineral acid and the remaining polyelectrolyte dispersed in additional aqueous metal ion solutions for further complexation. The polybase is not required where the metal occurs fully as cation; however, if the metal is complexed as an anion (for example, chromium as chromate), polybase has to be added to precipitate the metal-polymer "sandwich".

The metal ion-polyelectrolyte complexation is characterized by complex stability constants. The equilibria are represented by the following equations:



$$\text{The stability constant } B_2 = \frac{[(\text{RCOO})_2\text{M}][\text{H}^+]^2}{[\text{M}^{2+}][\text{RCOOH}]_2} \quad (11.2)$$

The stability constants have been determined by titrating the polyacid with sodium hydroxide in presence and absence of the respective metal ion (Gregor *et al.*, 1955). Greater the magnitude of the stability constant, better is the removal of the metal ion. Jellinek and Sangal have applied this principle for the removal of cupric ion by polyglacturonic acid (PGA), which is a natural polyelectrolyte, but has to be purified. They have determined stability constant values for various metals with PGA. The values are Cu^{2+} 1.72, Cd^{2+} 0.59, Zn^{2+} 0.34 and Ni^{2+} 0.21. These metal ions can be removed by PGA. The PGA powder (about 2 g) is dispersed in the solution containing the metal ions in concentration range 50 mg/L to 100 mg/L in 1 liter solution. The metal complex precipitates formed are filtered and leached with 16 mL 1.5 N hydrochloric acid to produce a concentrated solution of the metal chlorides. The polymer is recovered and used for another batch. The loss of polymer is only 1%, which makes the process very economical. The extent of removal the various metal ions corresponds to the magnitude

of the stability constants. Cupric ion removal is highest with <2 mg/L residual cupric ion in solution. The respective values for zinc and cadmium are 3 mg/L and 2 mg/L. Nickel removal is the least with 8 mg/L remaining in solution after treatment with PGA.

The method has not so far been widely used for wastewater treatment in metal industry. The drawback seems to be that the method is not readily adaptable for higher metal concentrations as that would require large quantity of polyelectrolyte to be handled.

11.1.2.8. Metal Removal and Recovery by Precipitate Flotation

In precipitate flotation technique (described in chapter 3), metal ions in small concentrations are precipitated as hydroxides or sulfides, which are then floated after treatment with a surfactant. An example is the removal of copper, which is precipitated as sulfide by sodium sulfide and the cupric sulfide is floated using an amine collector at pH 2.0. Over 95% removal has been reported (Beitelshees *et al.*, 1979). In a modified process, the metal is precipitated by a chelating surfactant serving the dual function as a precipitant and as a collector to float the metal chelate precipitate (Allen *et al.*, 1979). Efficiency of the precipitate flotation can be enhanced by using finer bubbles as the precipitates are produced in particle size range < 5 μm . A microgas dispersion technique for this purpose has been described (Ciriello *et al.*, 1982).

As yet precipitate flotation technique has been done on bench scale and no large scale application of this technique has been described. The technique may still be considered where selective separation of metals can be achieved by varying operating parameters, in particular, pH. In industrial wastewater treatment to remove metal ions in low concentrations (<50 mg/L dissolved air flotation (see Chapter 3) is used in some places.

11.1.2.9. Anaerobic Processes.

In Chapter 10, mention was made of ecological engineering approach to treat acid mine drainage, using inexpensive organic material, which is mostly available as industrial or agricultural wastes (like hay, straw, etc.), and promoting the reduction of sulfate by sulfate reducing bacteria and simultaneously reducing the acidity of water (see Sections 10.1.1.5 and 10.1.1.6). While the principal objective is to reduce the acidity and toxicity of AMD, the process also leads to the reclamation of huge quantities of water from the tailing ponds. The ecological solution is currently attracting serious attention in mining industry because of its dual benefit: removing the toxic metals and lowering acidity and potentially making it possible to recycle millions of gallons of water resting currently staying idle in tailing ponds, and using relatively inexpensive technology.

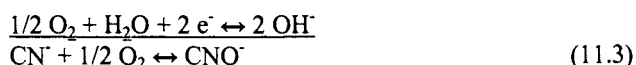
11.1.3 Removal of Cyanide

Sodium or potassium cyanide is commonly used in the extraction of gold and also in mineral processing operations where cyanide is a depressant for pyrite in the selective flotation of industrial sulfide minerals like galena, chalcopyrite and sphalerite (see Chapter 3). Cyanide is a lethal toxic and has to be removed from the wastewater. This is done either by chemical treatment or by physical process like adsorption.

11.1.3.1. Active Carbon Treatment

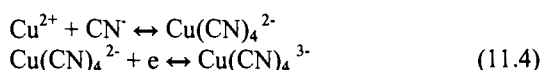
Activated carbon is known to be effective for catalyzing the oxidation of cyanide to cyanate (Adams, 1994):



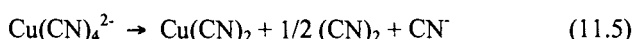


Activated carbon is also a strong adsorbent for many organic compounds, and it has a modest affinity for cyanide, but the adsorption capacity is too low for this to be a viable process for the removal of cyanide.

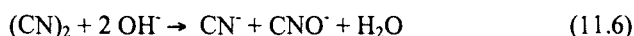
The adsorption of cyanide by activated carbon is greatly enhanced by impregnating the carbon with cupric chloride (Adams, 1994). The cupric ions react with cyanide forming cupricyanide complex ion, which is then reduced to cuprocyanide:



Typical activated carbons have a standard reduction potential of around +0.24 V (McDougall *et al.*, 1981), which provides the driving forces for this reaction. The cupricyanide species is also unstable in aqueous solution, and rapidly decomposes to form cyanogen:



The cyanogen thus produced decomposes producing cyanate:



The net result is that some of the cyanide in solution is adsorbed on the carbon and another portion is oxidized to cyanate, which remains in solution.

Activated carbon modified by treatment with tetrabutyl ammonium iodide (TBA) (see Section 9.1.1) has also been investigated for the removal of cyanide from waste solutions (Monser and Adhoum, 2002). The positively charged ammonium group of TBA promotes uptake of negatively charged cyanide by carbon. The investigators report the removal capacity of TBA-carbon column at 29.2 mg/g, which is almost five times that of plain carbon. The concentration of cyanide in a solution in 800 mL solution is reduced from 40 to 2 mg/L.

In another modification studies by the same investigators (Adhoum and Monser, 2002), active carbon is impregnated with silver or nickel salt solutions. The results show that silver-impregnated carbon has a cyanide removal capacity nearly twice that of nickel-impregnated carbon and four times that of untreated active carbon. The enhanced capacities of the metal treated carbon are explained by adsorption or by exchange with positively charged groups on the surface of active carbon. The cyanide is probably removed in the form of metal cyanide complexes, $\text{Ag}(\text{CN})_2^-$ or $\text{Ni}(\text{CN})_4^{2-}$. It is worth noting, nickel impregnation of the carbon represents only 0.4% of the mass of carbon, while the cyanide removal capacity is increased by a factor >2 by metal ion impregnation.

11.1.3.2. Anaerobic Treatment

Left to itself, cyanide in dilute solution degrades slowly producing ammonia and carbonate, by the reaction



The rate of reaction is very low, but it can be catalyzed by certain microorganism, which can be derived from the waste solids and cultivated in a medium of nutrients consisting of potassium hydrogen phosphate, magnesium sulfate, calcium chloride, ferrous sulfate, manganese chloride, sodium molybdate and beef extract. Biodegradation occurs at pH 10.5 dropping to 9.5 and is complete from 300 mg/L sodium cyanide in 35 days (Garcia *et al.*, 1994).

11.1.3.3. Chlorination

Chlorine oxidizes cyanide to cyanate. Chlorination may be done by addition of chlorine gas plus sodium hydroxide to pH 10 to produce sodium hypochlorite (NaClO). Chlorine gas treatment is about half as expensive as direct addition of sodium hypochlorite, but requires special handling equipment. Time of oxidation is usually 30 min to 2 hr (Crowle, 1971). The wastewater should be continuously agitated to avoid solid cyanide precipitates, which may resist chlorination. The process is controlled by redox potential and pH sensor and automatic chemical feed techniques for maximum reaction rate, minimum detention time and complete reaction.

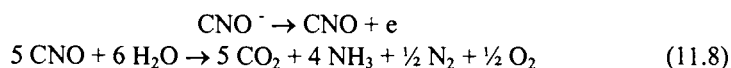
Complete oxidation of cyanide to nitrogen and carbon dioxide can be accomplished by chlorination for a longer time at the alkaline pH of 10. It can be completed within an hour if the pH is lowered to about 8.5.; however, excess chlorine is required to avoid the formation of highly toxic cyanogen chloride, which is intermediate product in the oxidation of cyanide to cyanate. It breaks down very rapidly at pH >10, but at lower pH excess chlorine is required to speed the breakdown.

11.1.3.4. Ozonation

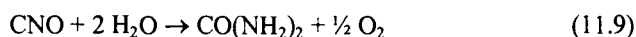
Cyanide can be oxidized to cyanate by ozonation. The oxidation is rapid (10-15 min) at pH 9-12 and is almost instantaneous in the presence of traces of copper acting as catalyst (Green and Smith, 1972). Oxidation of cyanide to final end products (carbon dioxide and nitrogen) is much slower, especially for complex cyanides other than copper and nickel. The reaction can be catalyzed by iron, copper or manganese. For iron and nickel cyanide complexes, elevated temperature or ultraviolet treatment is required (Green and Smith, 1972).

11.1.3.5. Electrolytic Decomposition of Cyanide and Possible Recovery of Gold

Electrolysis of cyanide solution leads to discharge of cyanide ion at the anode, where it is oxidized (anodic oxidation). Cyanide is completely broken down to carbon dioxide, nitrogen and ammonia, with cyanate as an intermediate product (Green and Smith, 1972). The probable anodic reactions are as follows:

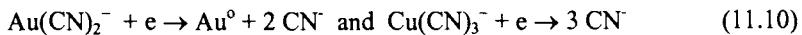


Urea may also be produced (Hillis, 1975) by the reaction,



The destruction of cyanide, however, is not complete; as the process continues, the waste electrolyte becomes less capable of conducting electricity. Typical anodic current density is around 200 A/m² for graphite electrodes. (Patterson, 1985). Low levels of residual cyanide, down to 0.1-0.4 mg/L, can be reached by electrolysis for sufficiently long time, 14-18 days. Final destruction of the residual cyanide may be done by chlorination.

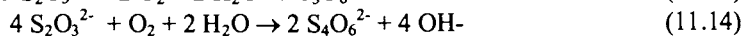
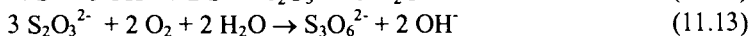
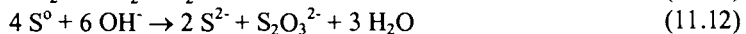
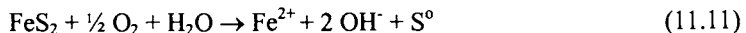
Electrochemical work on cyanide from gold recovery plants has been the subject of a laboratory study by Dutra and coworkers (2002) for recovering the residual gold and simultaneously the cyanide. A gold rotating disk electrode is used as cathode and a titanium gore covered with iridium dioxide as anode. Gold and copper occur as their cyanide complexes, aurocyanide $\text{Au}(\text{CN})_2^-$ and cuprocyanide $\text{Cu}(\text{CN})_3^-$ respectively. The electrochemical reactions are



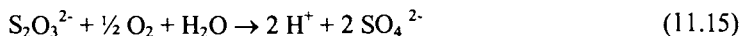
Although the study indicates a potentially useful method to recover both metals and cyanide, the experimental details of this laboratory study described by the investigators indicate the need for careful controls such as reagents of analytical grade. Any potential application using industrial effluents has not been demonstrated.

11.1.4. Removal of Thiosalts

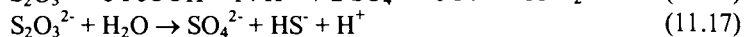
In the processing of sulfide ores, thiosalts are produced by the oxidation of sulfide (S^{2-}) group (e.g., pyrite- FeS_2 and pyrrhotite FeS) by oxygen. It is a slow process in the absence of a chemical or biological catalyst and particularly at or a little above neutral pH and produces several intermediate sulfur species, in the different oxidation states of sulfur, between sulfide and sulfate. They are collectively called thiosalts. They occur as sulfoxyl anions like thiosulfate ($\text{S}_2\text{O}_3^{2-}$), polythionates ($\text{S}_n\text{O}_6^{2-}$), and sulfite (SO_3^{2-}), as shown by the reactions:



These sulfoxy anions are metastable species and break down to more stable sulfate. For example, thiosulfate may be oxidized by oxygen and generate proton acidity as follows:



It may also be oxidized by iron oxyhydroxide (FeOOH) (Eq. 11.16), or simply disproportionate (Eq. 11.17).



Thiosalts represent a delayed acid generating capacity in mill effluents resulting in a drop in pH, and subsequently, an increase in metal and solid concentration, as seen from Equations 11.15)-(11.19). Studies have shown that 1 kg of thiosalts and a pH of 7 have a potential to release 0.67-1.33 kg sulfuric acid (Rolia and Tan, 1985). This could lead to

serious problem in the mill metallurgy when recycle water is used. In the short time period also, that is, before they are oxidized, thiosalt anions could have an adverse effect in flotation as they can act as depressants hindering the action of mineral collector (see Chapter 3). Even in situations where it is considered to have little effect, occurrence of thiosalts in discharge water can have serious negative environmental impact. Destruction of thiosalts by appropriate treatment methods is very desirable. Various treatment options for thiosalt removal have been investigated.

11.1.4.1. Natural Degradation.

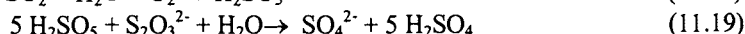
This is the most common method for reducing thiosalt content in process water. The thiosalts in tailings degrade over several days to weeks by exposure to air and sunlight. In Brunswick Mines in Canada the water is allowed to stand in a rock-packed pond called bio-pond. A combination of bacterial oxidation, sunlight and natural oxidation results in reduction of thiosalt concentration (Kuyucak *et al.*, 2001). At some sites, the decant pH is often increased to levels of 10 or more to remove metal ions. Carbon dioxide is bubbled into the effluent to lower the pH to meet regulatory limits (pH 5.5-9. the carbon dioxide enhances the buffering capacity of the effluent and helps to counteract the lowering of the pH from oxidation of thiosalts in the receiving environment.

11.1.4.2. Decomposition by Oxidation (Wasserlauf *et al.*, 1980)

Thiosalts can be oxidized to sulfate by oxidants such as hydrogen peroxide and ozone, which do not introduce a new species in the system. Oxidation kinetics with hydrogen peroxide can be enhanced by ferrous salts in the system. In many recycle water streams, ferrous ions may be present, derived from pyrite ore; otherwise, it is added as ferrous sulfate. When enough ferrous ions are present, oxidation reactions could be completed in 10 minutes (Kuyucak *et al.*, 2001).

Oxidation by ozone is similar to that by hydrogen peroxide. It requires an ozone generator on the site producing ozone from oxygen. A mixture of 2% ozone to 98% oxygen is adequate.

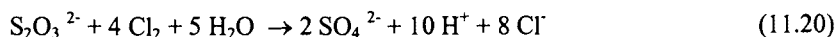
Oxidation by a mixture of sulfur dioxide and air has been applied for the oxidation of thiosalts. This gaseous oxidant forms permonosulfuric acid (also called Caro's acid), which is a powerful oxidant in water:



The wastewater is sparged with the gaseous mixture, SO_2 to air in the ratio 1:20. Cupric sulfate is used as catalyst and the pH set to 8.5-9.0 by lime, which neutralizes the acid produced forming gypsum and also precipitates cupric ions as cupric hydroxide.

It is worth noting that the sulfur dioxide oxygen combination has also been used as an oxidant for cyanide destruction.

The oxidation by chlorine is rapid and efficient; however, the chlorination process produces high chloride ion concentration in the water, which may cause other problems.



The reaction is carried out in stirred tank reactors, retention time 60 min. Also, removal of excess chlorine by active carbon would increase the process cost.

Biological oxidation of thiosalts is caused by the action of various *thiobacillei* species of sulfur oxidizing bacteria, especially *T. thiooxidans* and *T. ferrooxidans* (see Chapter 5). In summer months, 40-60% oxidation is possible. It is done in earthen rock-filled ponds with retention time of 3 days. Air is distributed using a plastic piping grid at the bottom. The rocks (5-10 cm diameter) provide surfaces for bacterial attachment and act as a diffusing medium for the air. Ammonia and phosphate nutrients are added for the microorganisms.

11.1.4.3. Other Methods for Thiosalt Removal

Active carbon adsorbs thiosalts (along with some organic compounds, which may be present in the wastewater. The carbon has to be regenerated and re-used. It is done by controlled heating, which releases sulfur dioxide formed by the decomposition of thiosalts. It is scrubbed and neutralized by lime (Wasserlauf *et al.*, 1980).

Reverse osmosis has been used to remove thiosalts. The wastewater is forced under 2000-10,000 kPa through a membrane (cellulose acetate or polyamide). The resultant water is allowed to settle in a pond and passed through a sand filter to remove suspended solids. It is a very effective method for almost complete removal of thiosalts and does not produce by-products (Subramanian *et al.*, 1980). However, the process cost is higher than the chemical or biological oxidation processes. Also, the residual liquid with >90% thiosalt requires additional treatment, like electrochemical oxidation or evaporation and eventual disposal of the solids.

11.1.5. Removal of Organic Species and Colloidal Matter.

Organic species are a common occurrence in the water used in mineral industry, especially flotation as it is driven by the interaction of heteropolar organic compounds on minerals. The composition of the residual organics varies depending upon the extent of decomposition of the organic molecules. This alters the chemistry of the system, often leading to unsatisfactory performance. Treatment with active carbon is effective to remove most organic species from recycle streams. This leads to significant improvement in the metallurgical performance as observed in the flotation of nickel mineral (Levay *et al.*, 2001.)

Wastewater with organic contaminants is frequently treated by biological processes by aerobic or anaerobic process. Most organic compounds occurring in mineral and metallurgical process waters go through one of the following processes:

- Biodegradation. The organic compound is mineralized into oxidized forms such as carbon dioxide and water, and cellular mass.
- Chemical conversion. The biological process transforms the organic compound into different a compound, which does not affect the metallurgical process, permitting the re-use of water.
- Sorption. The organic compound is removed by sorption onto soil particles, primary sludge, or mixed liquor particles.

Organic pollutants are also removed by oxidation by chlorination or ozonation. Oxone is used to break the chemical bonds in high molecular weight organic compounds. By oxidizing the carbon atoms (to CO₂) the high molecular weight compounds are

decomposed to form simpler molecules, which can be removed by adsorption methods described before.

More details on the treatment methods for toxic organics are described by Patterson (1985).

Colloidal species are often produced in the processing of minerals, released from the mineral surface when the ore is dispersed in water. Such colloidal species dispersed in recycle water. When they get smeared on the mineral surface they lower the hydrophobicity of the mineral as they cover the hydrophobic film and thus hinder its flotability. Chemical dispersants like polyphosphates (commercially available as calgon), sodium carbonate or polymeric dispersants can be used to disperse the colloidal particles from the mineral surface into water. Another method is by the shearing action of hydrocyclone, which effectively removes surface layers thereby helps to expose the hydrophobic mineral surface Levay *et al.*, 2001)

11.1.6. Recovery of Heavy Metals from Wastewaters

Stringent environmental regulations have made it necessary to treat the wastewaters to remove toxic metals before the water is discharged. This has led to opportunity and development of techniques to recover some of the useful metals from the wastewater.

Ion exchange resins are often used to recover metals from various kinds of wastewaters generated in manufacturing industry. Strong acid resins selectively favor the uptake of polyvalent cations from dilute solutions. Weak acid resins have still stronger affinity for heavy metal ions. Heavy metal ions can be selectively recovered from effluents using conventional resins of the sulfonic and the carboxylic type. Weak acid resins can be regenerated with stoichiometric quantity of mineral acid, as these resins have a strong affinity for hydrogen ions. They are therefore sensitive to the pH of the solution to be treated, and have no capacity to take up metals in highly acidic environment. Specific resins for the selective removal of ions are known. These are listed in Table 11.2. As their active groups are weakly acidic, they are also sensitive to pH of the environment. The choice of a resin, whether chelating or weak acid resin is dependent on the particular case. For example, weak acid Amberlite DP-1 is equivalent to the chelating resin Amberlite IRC-718 for the removal of zinc ions. But for regeneration with 10 % hydrochloric acid, the carboxylic acid gives a better result, as the concentration of the recovered solution is higher (Waitz, 1979). Similar results are obtained when an effluent containing lead or cadmium ions is treated with these resins. However, with an effluent containing copper ions in the presence of ammonium sulfate, chelating resins show better results.

When wastewater contains heavy metal ions in a complexed form, a chelating resin, such as the one containing imidodiacetic acid groups must be used as this resin is able to compete with the ligands in the wastewater provided the stability constant for the resin complex (e.g., for Ni^{2+} , $\text{pK} = 10.55$) is greater than that of complexes occurring in the wastewater (usually $\text{pK} = 9.2-9.9$) (Courdubvelis *et al.*, 1983).

When strong acid resins are applied to the recovery of metal ions from wastewater containing alkali metal ions in high concentration, further refinements are necessary. For example, in the recovery of zinc from wastewaters in the synthetic fiber industry the concentration of sodium ions is 5-times that of zinc ions. The ratio of ions taken up by the resin makes it impossible to recycle the regenerant effluent. In such cases a 2-step

regeneration may be conducted: elution with 1 % sulfuric acid for partial removal of sodium ions, followed by regeneration with 10 % sulfuric acid for elution of zinc ions.

Specific examples of selective metal recoveries from wastewaters have been described by Bolto and Pawlowski (1984).

Table 11.2. Ion exchangers containing specific group selective for particular ions (Calmon, 1979b)

Ion	Specific Exchanger or Group
Beryllium	Diallyl phosphate
Calcium	Iminodiacetic acid; Diallyl phosphate
Cobalt	8-hydroxyquinoline; β -diketone; Ethylene diamine tetraacetic acid
Copper	Diphenyl thiourea; 8-hydroxyquinoline Ethylene diamine tetraacetic acid
Iron	Alginic acid; Hydroxamic acid; Diallyl phosphate
Magnesium	Alginic acid; Phenyl diaminoacetic acid
Mercury	Pyrogallol; Dithiocarbamate
Nickel	Dimethyl dioxime; 8-hydroxyquinoline
Silver	Thiol
Zinc	Anthranilic acid; Phosphonic acid
Zirconium	Phosphonic

Notes: Allyl group is represented by $\text{CH}_2=\text{CH}-\text{CH}_2$. Two allyl groups replace two hydrogen atoms in phosphoric acid to make diallyl phosphate

Imino group is represented by $=\text{NH}$. (Imido group is $(\text{RCO})_2\text{N}$)..Imino diacetic acid is represented by $\text{N}-(\text{CH}_2\text{COOH})_2$

Thiol group, also referred to as mercaptan, is $-\text{SH}$ with an alkyl chain.

Diphenyl thiourea is $\text{CS}(\text{NR}_2)_2$, where R is $-\text{C}_6\text{H}_5$.

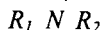
Alginic acid is a dibasic (two carboxyl groups) acid derived from algae and has a complex structure.

Anthranilic acid is amino benzoic acid, $\text{C}_6\text{H}_4\text{NH}_2\text{COOH}$

Ethylene diamine tetra-acetic acid (EDTA) is an amino derivative of acetic acid; represented by the formula, $(\text{HOOCCH}_2)_2-\text{NC}_2\text{H}_4\text{N}-(\text{CH}_2\text{COOH})_2$

Pyrogallol is trihydric phenol, $\text{C}_6\text{H}_3(\text{OH})_3$.

Dithiocarbamate is a derivative of dithiocarbonic acid (carbonic acid with 2 oxygen atoms replaced by sulfur), $\text{S}=\text{C}-\text{S}-$. It is monovalent anionic. Note that the third O atom is replaced by nitrogen atom.



Formulae of other chemical groups are described in Chapter 4.

11.2. Recycling Reagents

Both mineral process techniques, in particular, the technique of froth flotation, as well as hydrometallurgical processes consume a wide variety of reagents. In many instances, especially in hydrometallurgical operations, the reagents are consumed as they combine with dissolved metal ions to form a metal compound. In such case, the reagents are recovered and recycled in the same step where metal is recovered from the compounds formed in the process. For example, in the recycling of metals by solvent extraction, the

metal is recovered by stripping which, at the same time regenerates the solvent used for metal extraction. Similarly, in ion exchange process, the ion exchange is regenerated by stripping, which also releases the metal bound to the ion exchange resin; see Chapter 2 for examples and experimental procedures.

In some operations, however, additional recycling steps are required to ensure maximum possible recycling. This specially applies to those areas where the reagent has to be used in excess and good portion of it remains unreacted and could be used for another cycle. Such recycling step is specially necessary where the reagent is expensive or toxic and, therefore, hazardous for health and environment. Some examples will be described.

11.2.1. Recycling of Cyanide

Cyanide is widely used in the mineral industry to extract gold from ores. Typically, the ore is ground and agitated with a dilute cyanide solution for several hours in the presence of air or oxygen. The cyanide reacts with the finely disseminated gold particles to form a soluble gold-cyanide complex, $\text{Au}(\text{CN})_2^-$. Other metals, such as copper and zinc, which also form metal cyanide complexes are also dissolved. Gold is recovered from the gold-cyanide complex by adsorption on active carbon or by zinc cementation. A gold-free solution containing a significant amount of free cyanide and other dissolved metals remains.

Because of its high toxicity, the soluble cyanide must be destroyed before the solution is discharged to the environment. Usually, the cyanide content is decreased by exposing the cyanide solution to sunlight ponds, a process known as "natural degradation". The product of oxidation cyanate (CNO^-) is much less toxic. However, in many cases chemical oxidation processes are necessary for the complete destruction of cyanide. Such cyanide destruction processes suffer from economic and environmental drawbacks. In addition to the cost of the destruction process, fresh cyanide will be required to replace the lost reagent. Furthermore, the cyanate ion produced by the oxidation of cyanide has been found to generate ammonia, a highly toxic compound for fish. As well, copper and other metals contained in the barren solution end up in ponds and tailings, forming compounds of unknown stability (Riveros *et al.*, 1998).

11.2.1.1. AVR (Acidify, Volatilize, Reneutralize) Process

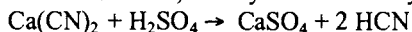
A method has been developed at CANMET laboratories (Ottawa, Canada) to recover and recycle cyanide from barren solutions. It comprises three steps, acidification, volatilization, and reneutralization and is therefore called AVR process (Riveros, 1997).

Typically, the AVR process consists of:

- acidifying the cyanide solution to about pH 2-3.5 with sulfuric acid;
- sparging air through the acidified solution to volatilize and remove the hydrocyanic acid, HCN, gas formed by acidification;
- reneutralization of the aerated solution to precipitate the excess sulfate and the last traces of metals.

Chemistry of the acidification process is summarized as follows:

1. On acidification, free cyanide is readily converted to HCN :



(calcium cyanide is produced as the cyanidation is usually done in the presence of lime to ensure high pH).

2. Metallo cyanides, such as $\text{CaCu}(\text{CN})_3$, $\text{CaZn}(\text{CN})_4$ and $\text{CaNi}(\text{CN})_4$ are decomposed and precipitate as simple cyanide salts, while more HCN is regenerated.
 $\text{CaCu}(\text{CN})_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CuCN} + 2 \text{HCN} + \text{CaSO}_4$
3. If thiocyanate occurs (by the combination of cyanide with sulfur of the sulfide minerals occurring in the ore), cupric thiocyanate is produced:
 $2 \text{CaCu}(\text{CN})_3 + \text{Ca}(\text{SCN})_2 + 3 \text{H}_2\text{SO}_4 \rightarrow 2 \text{CuSCN} + 6 \text{HCN} + 3 \text{CaSO}_4 \quad (11.20)$
 Iron complexes do not decompose, but they precipitate as double metal compounds:
 $4 \text{CaCu}(\text{CN})_3 + \text{Ca}_2\text{Fe}(\text{CN})_6 + 6 \text{H}_2\text{SO}_4 \rightarrow \text{Cu}_4\text{Fe}(\text{CN})_6 + 12 \text{HCN} + 6 \text{CaSO}_4 \quad (11.21)$

Hydrocyanic acid, HCN, can be volatilized by sparging air through the acidified solution. The resulting air/HCN mixture is then bubbled through a sodium hydroxide solution, where the hydrogen cyanide is readily absorbed and neutralized producing sodium cyanide solution. Lime can also be used, but the absorption is less efficient and special absorption towers are required.

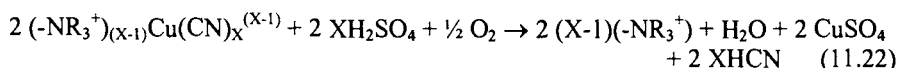
The main features of AVR process include:

- recovery of all free cyanide and about half of the complexed cyanides;
- no regeneration of toxic compounds like ammonia;
- recovery of copper from the barren solution as a precipitate. In some operations, the economic value of the precipitate may justify its reprocessing for copper recovery.

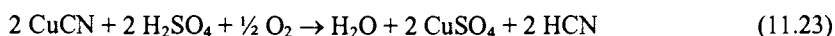
The AVR process for cyanide recovery presents both economic and environmental advantages over cyanide destruction methods. It is being applied to process waste cyanide solutions in several Canadian mineral process plants. One concern, which is sometimes expressed is about the evolution of hydrogen cyanide gas. However, this evolution can be easily controlled. Because of its high solubility in water and very low pressure, the gas is evolved very slowly from a quiescent solution especially if the ambient temperature is below 26° C. Volatilization of hydrogen cyanide requires intense aeration. In order to further reduce the risk of volatilization, only a fraction of the total barren solution is aerated, while the other fraction is recycled without aeration to the cyanidation circuit. This is a compromise between operating costs, water balance, and the elimination of excess impurities.

11.2.1.2. Recycling Cyanide by Ion Exchange Resins and Selective Oxidation

A process, which uses a strong base ion exchange resin to remove cyanide and complex metal cyanide ions from gold mining effluents has been described by Fernando and coworkers (2002, 2005). The process also enables most of the cyanide to be recovered by the oxidation of the cyanide adsorbed by the resin. Under suitable oxidizing acidic conditions, copper can be eluted from strong base resins, along with other base metals. The reaction leading to the removal of copper is shown by Equation 11.10, where X could take values 2, 3 or 4 depending on the copper cyanide ion.



Most base metal cyanide complexes decompose at low pH under non-oxidizing conditions. Copper cyanide species release all but one ligand of cyanide to form cuprous cyanide precipitate. Under mild oxidizing conditions, the cuprous cyanide decomposes, releasing cupric ions and hydrogen cyanide into the solution:



The hydrogen cyanide is neutralized by sodium hydroxide to produce sodium cyanide.

Cyanide complexes of gold, silver and iron, however, require stronger oxidizing conditions and are generally unaffected by the oxidizing conditions required to oxidize cuprous cyanide. This makes it possible to regulate the elution of metals from strong base resins loaded with a mixture of base and precious metal cyanide species by using an eluent whose redox potential is controlled as desired. This leads to an added benefit as the precious metal ions can be selectively recovered after removing all copper. Eluents with redox potentials between 350 and 550 (vs. saturated calomel electrode) can elute copper from strong base resins (Frey *et al.*, 1988). Fernando and coworkers (2002, 2005) have found 50% hydrogen peroxide suitable for this purpose. From equation 11.11, the stoichiometric ratio for copper to hydrogen peroxide is 2:1 (as $\frac{1}{2} \text{ O}_2$ is equivalent to 1 mole H_2O_2); however, excess hydrogen peroxide, is found necessary, which is attributed to the oxidation of cyanide to cyanate and the decomposition of peroxide under the conditions in the resin bed. The hydrogen peroxide efficiency ranges from 37% to 67%. A simplified flowchart of the process to treat a liquor containing approximately 50 mg/L copper, 10 mg/L silver and 0.68 mg/L gold and total cyanide concentration 45-65 mg/L is shown in Figure 11.5.

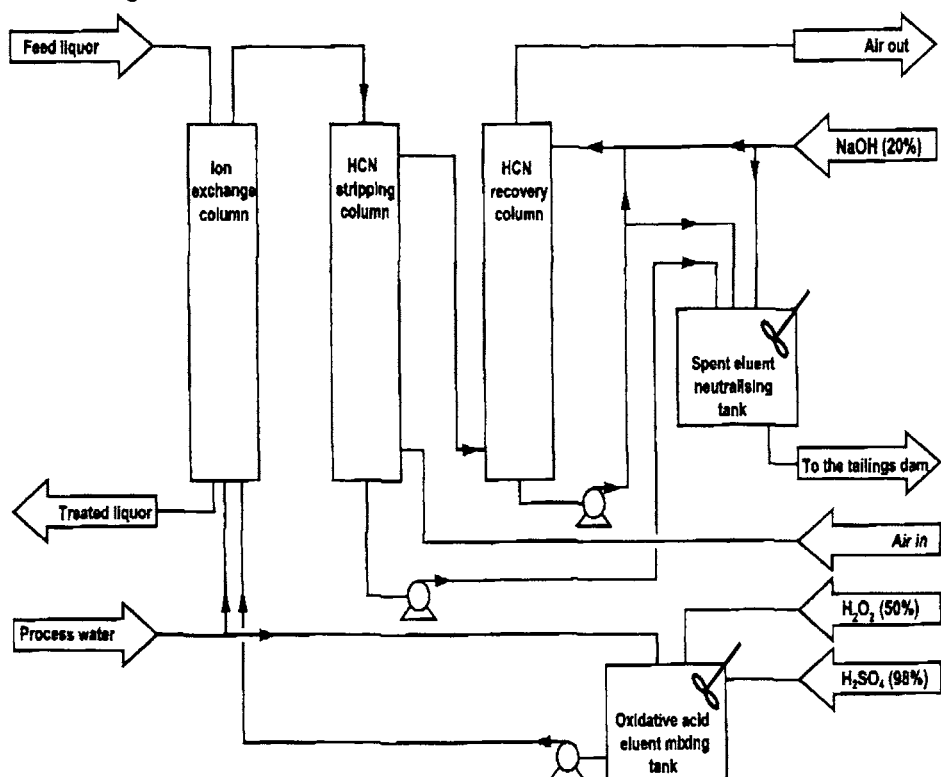


Figure 11.5. Simplified flowchart of the process to recover cyanide from effluents with metal cyanide complexes (Fernando *et al.*, 2005)

Adsorption is conducted by the downward flow through the resin bed. After adsorbing the feed liquor, the resin bed is washed with process water to remove any free feed liquor from the resin bed to prepare it for the base metal elution. The base metals are eluted by 50 g/L sulfuric acid. For elution of copper, the same concentration of sulfuric acid with 5 g/L hydrogen peroxide is used. Copper is recovered cupric sulfate in the spent eluant. After 6 cycles recovering most of the copper, the resin bed gets enriched with precious metals, which hinders the elution of copper. At this stage, the precious metals, gold and silver are eluted with a concentrated solution of sodium zinc tetracyanide. Gold and silver are recovered as concentrated complex cyanides. The metals are isolated by electrowinning.

Cyanide adsorbed on the resin as cuprocyanide is converted during the elution to hydrogen cyanide gas and liquid. This gas-liquid mixture leaving the resin bed is fed to a cyanide stripping column, where the hydrogen cyanide is recovered from the eluent using a counter current stream of air. The eluent stripped of hydrogen cyanide is discharged into an eluent neutralizing tank. The hydrogen cyanide air mixture from the stripping column is scrubbed with 20% sodium hydroxide in a packed column to produce sodium cyanide.

The process produces a discharge stream with total cyanide level less than 2.5 mg/L. This liquor is held in a detoxified liquor dam for natural degradation of the remaining cyanide. The overall process thus achieves dual purpose of prevention of environmental pollution and recycling of reagents with metal recovery as an added benefit.

Selected Readings

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- Patterson, J. W., 1985. *Industrial Wastewater Treatment Technology*, Butterworths, Boston.
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Chapter 12

EMERGING NEW TECHNOLOGIES

In the last 20 years several new innovative methods of separation have been introduced and are being developed for resource recovery from mineral and metallurgical wastes. Many of these techniques, based on physico-chemical principles originated and were applied in other separation processes such as separation of organic molecules and biochemicals of importance in pharmaceutical industry. The introduction of new technologies is driven by two main considerations. First is the constant search for improving the process efficiency, to maximize the recovery and selectivity. Secondly, the recovery of resources from complex materials and from dilute effluents where the concentrations of the desired compounds is below the limit recoverable by conventional techniques requires development of new technology, which can lead to their recovery also resulting in a cleaner effluent discharged in the environment. Some of these innovative developments in resource recovery will be discussed in this Chapter.

12.1. Magnetic Carrier Technology

Magnetic carriers are magnetic materials designed to bind selectively on a non-magnetic material to be able to separate using magnetic separation techniques (described in Chapter 2). By this approach, magnetic separation technology can be applied to the separation of materials that are otherwise non-magnetic. Magnetic carrier technology originated in 1940s, when magnetite was used to remove organic impurities from wastewater streams using electrostatic adsorption (Urbain and Steman, 1941). A generic term for this technology is magnetic support technology as it incorporates magnetic supports, which are materials, which have the property of selectively enhancing the magnetic properties of the target non-magnetic material that is desired to be separated. Magnetic support materials should fulfill two functions: first, provide highly selective attachment to the target species through appropriate surface properties; second, confer magnetic properties to those target species to be separated (Moffat *et al.*, 1994).

12.1.1. General Principles

A small amount of magnetic material is necessary to enhance the magnetic properties of a non-magnetic material until its magnetization approaches that of the same volume of a typical paramagnetic material. Ferro- or ferromagnetic materials such as ferrosilicon and magnetite (Fe_3O_4) have susceptibilities orders of magnitude greater than typical paramagnetic materials. A volume fraction of magnetic support material in the range of 0.1-1 % is usually sufficient to achieve magnetization of a non-magnetic material. The

principle of magnetic carrier separation is schematically illustrated in Figure 12.1. Magnetic supports are added to a mixture containing target species. The magnetic supports selectively bind to target, and the target species are separated from the undesired ones by magnetic separation.

Magnetic support materials are classified in two groups, carriers and tags (Moffat *et al.*, 1994). The carriers are usually 10-1000 times larger than the target species. Selective recovery of colloidal or ionic species is achieved by varying the surface characteristics of the carrier. This is illustrated in Figure 12.2. It shows the case where the target coats the surface of the magnetic carrier (i), and the case where the targets are entrapped within a porous magnetic carrier (ii). In magnetic tagging, the tags are usually smaller than particles to be separated. Tags can be either ions (for example, yttrium, Y^{3+}) or fine magnetic particles like magnetite that coat or cluster around non-magnetic species, which are then manipulated using external magnetic fields (Moffat *et al.*, 1994). The tagging can occur through specific coupling mechanisms or through electrostatic adsorption. This is shown by Figure (iii).

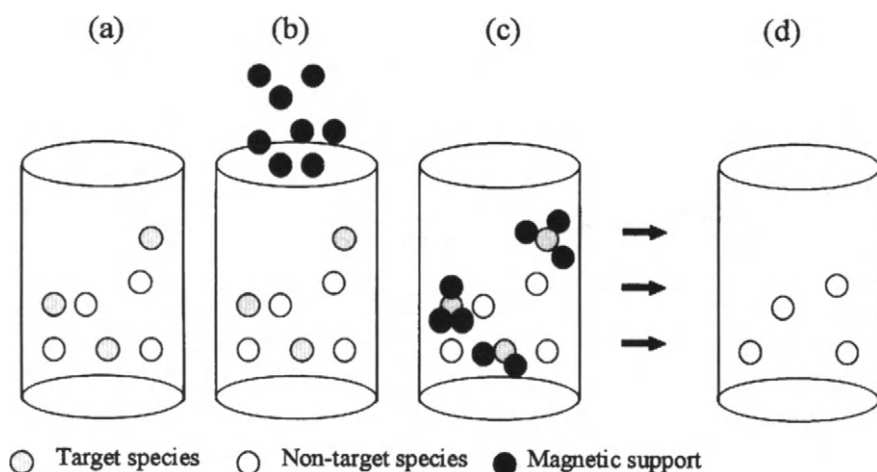


Figure 12.1. Principle of magnetic carrier separation. A mixture to be treated contains target and non-target species (a). Magnetic support material is added to the mixture (b). the magnetic carriers selectively bind to the target species (c). After magnetic separation, the target species are separated from non-target species (d), and the carriers are recycled to (b). (Broomberg *et al.*, 1994).

Generally, a probing molecule or reactive functional group on magnetic carriers has a specific affinity to targeted biological cells or metal ions as shown in Figure 12.3. The interaction between fabricated magnetic particles and target molecules can be described by a key and lock relationship. Such specific interactions as antibody-antigen and ligand-metal have been incorporated in magnetic carrier technology for selectively removing the target cells from biological systems and metal ions from industrial effluents (Spinke *et al.*, 1993; Nunez *et al.*, 1995).

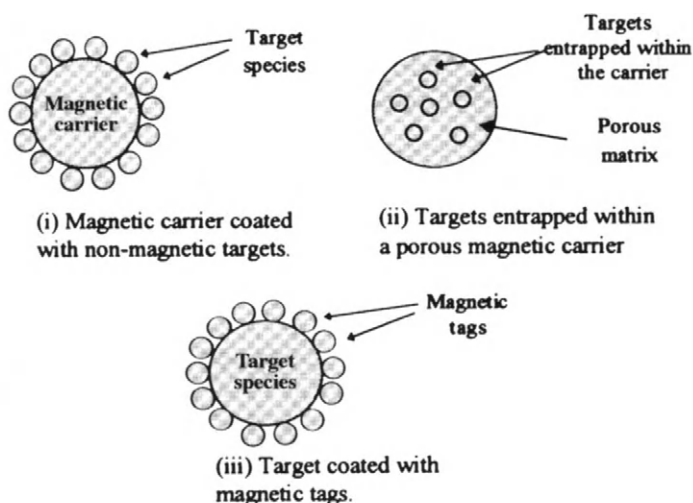


Figure 12.2 Schematic representation of magnetic carrier (i) and (ii), and magnetic tagging (iii). (Broomberg *et al.*, 1994).

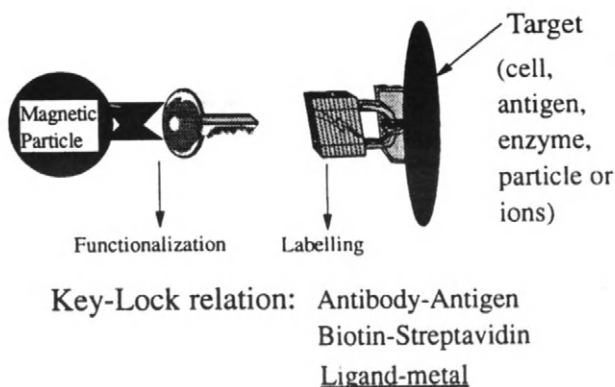


Figure 12.3. Schematic representation describing the design of magnetic carriers for target species (from Q. Liu, Ph.D. thesis, McGill University, with author's permission).

12.1.2. Methods for the Preparation of Magnetic Carriers

Many methods have been developed to prepare magnetic carriers. They include polymer adsorption and polymerization (Ugelstad, 1992) and ligand complexation on magnetic particle (Briggs *et al.*, 1977). Either a single reaction or several steps are required to prepare desirable magnetic carriers. The process is called **functionalization**.

12.1.2.1. Polymer Adsorption and Polymerization

Co-precipitation of Fe^{2+} and Fe^{3+} with polymers under similar conditions to those used in the production of synthetic magnetite has been used to prepare magnetic resins (Yen *et al.*, 1981; Molday and Mackenzie, 1982; Molday, 1984; Qi, 1996). The density of

functional groups on polymer-coated magnetic particles is, in general, lower than those prepared by molecular bilayer assembly (described in the following paragraph). As a result, the subsequent uptake of target cells or particles will be retarded (Albert *et al.*, 1989).

12.1.2.2. Molecular Bilayer Assembly Using Amphiphiles

In this method, a magnetic carrier is prepared by building two layers of surfactants on colloidal magnetite as shown in Figure 12.4a (Huang, 1990). The inner layer surfactant has a functional group with an affinity for magnetite. The outer layer of surfactant can be built on top of the inner layer through hydrophobic association between hydrocarbon chains. The functional group of the outer layer orients outwards from magnetite and provides the capability for coupling with the target species. The functional group of the outer layer can be tailored so as to control the selectivity of the coupling. The main drawback of magnetic carriers prepared by this method is that the outer layer can be unstable when in contact with metal ions in application, resulting in the loss of capacity and functionality. This is overcome by self-assembling a monolayer using a bolaamphiphile with two functional groups at both ends of an alkyl chain. By controlling the relative reactivity of the two functional groups with the surface, one functional group can anchor chemically on the magnetic particles and the other remains reactive as shown in Figure 12.4b.

Note. Amphiphile, also called amphipatic molecule, consists of an oil-soluble (lipophilic, oleophilic or hydrophobic) and one water-soluble (hydrophilic) group. The hydrophobic part is non-polar group. They are also called heteropolar molecules; see Chapter 3 under Froth Flotation. A bolaamphiphile is an amphiphile with two functional hydrophilic groups.

12.1.2.3. Silanation by Silane Coupling Agents

The most widely used technique for covalently placing reactive organic groups on inorganic species is through the reaction of inorganic surface with silane coupling agents with dual functionalities, inorganic group at one end and organic group at the other (Plueddemann, 1982). The inorganic functional group is silanol (SiH_3OH) condenses with surface hydroxyl groups on the substrate through chemical bonding, and the organic functional group at the other end reacts with the target species in solution.

12.1.3. Some Applications of Magnetic Carrier Technology

As yet, the technology has been successfully applied in wastewater treatment and some resource recovery processes. Many laboratory studies have been reported, some of which may well find industrial applications. Examples of some applications and the potential ones will be discussed.

12.1.3.1. Adsorption of Metal Ions by Functionalized Magnetic Ferric Oxide

Functionalization of nanosized maghemite ($\gamma\text{-Fe}_2\text{O}_3$) particles by coating them with a monolayer of bolaamphiphile surfactant was investigated by Liu and Xu (1995, 1996). The bolaamphiphile used is 16-mercaptohexadecanoic acid, $\text{HS}-(\text{CH}_2)_{15}\text{-COOH}$. Maghemite powder (50 mg) is gently mixed with a 3 mM solution of the surfactant in chloroform and the mixture shaken for 24 hours. The treated particles are separated from solution by a hand magnet and rinsed with chloroform, followed by dry hexane to remove

unbound surfactant. The particles are then dried in a vacuum at 400 C and stored under nitrogen. The magnetization characteristics of the product show that nano-sized maghemite particles do not become permanently magnetized after exposure to external magnetic field. This property permits the particles to be redispersed without magnetic aggregation. The magnetic carrier thus prepared can be reused or recycled in practical applications. The functionalization procedure has also been used to prepare magnetic carriers with amine groups using surfactants with these groups, for example, diethylenetriamine, $(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2, \text{DETA})$, which is known to bind transition metals like copper and nickel by co-ordinate bonding Gelin *et al.*, 2000).

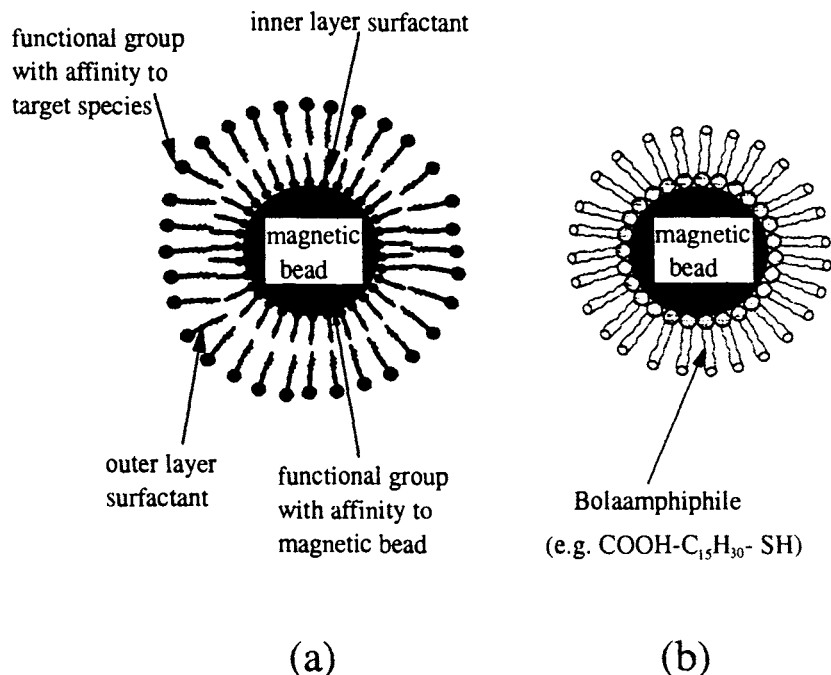


Figure 12.4. Schematic pictures for (a) bilayer assembly using amphiphiles on magnetic particles; (b) monolayer assembly using bolaamphiphiles on magnetic particles (from Q. Liu, Ph.D. thesis, McGill University, with author's permission).

A second method investigated by Liu and Xu to prepare magnetic carriers is to deposit a thin, densely packed layer on magnetic particles and silanating the surface by reaction with silane reagent, while maintaining the maximum magnetization required for applications. Magnetic particles (nano-sized maghemite) are mixed with ethanol, followed by tetraethoxy silane (TEOS). A 30 % ammonium hydroxide is added as a catalyst. After 5 hours reaction time, the treated particles are separated from solution by a hand magnet, rinsed with ethanol and dried.

Other silanating agents with specific functional groups have been used. A reagent, with an amino group, which has been used for silanation is 3-aminopropylethoxy silane $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si-(OCH}_2\text{-CH}_3)_3$, APTES. It is used mainly due to the interest of making magnetic carriers with reactive amino groups, which can remove and potentially recover heavy metals in effluents. Silanation by this reagent is done by first coating

maghemite particles with a thin silica layer. This procedure ensures greater stability of silanized maghemite in acid and neutral solutions. In alkaline solutions, however, significant degradation has been observed. That may not be a serious drawback as most metallurgical effluents are acidic.

The functionalized magnetic carriers have so far been found useful in removing dissolved metals from relatively dilute solutions, in the concentration range, 10-20 mg/L. Almost 100 % copper and zinc are extracted by amine-type magnetic carriers (Liu, 1996, pp. 134-5). After separating the carrier by magnet, the adsorbed metal is stripped by 0.01 N nitric acid, which results in 100 % detachment. The recycled magnetic carrier has reduced loading capacity (by about 20 %) due to the loss of surface film. More systematic work is required to optimize conditions for best separation process. One area of interest is selectivity. When electrostatic adsorption is the main mechanism, selectivity can be monitored by controlling the zeta potential of the species and is usually achieved by adjusting the pH, ionic strength, or by surfactant addition. Another factor determining selectivity is the ability to prepare functionalized particles, that is, functional groups with selectivity for specific metals.

12.1.3.2. Wastewater Treatment by Magnetic Resins

Work on magnetic polymer resins, also called magnetic polymeric beads, was initiated in Australia by Bolto and coworkers, who used them for wastewater treatment (1977). Two principal types, homogeneous and heterogeneous have been developed. Homogeneous resins consist either of a magnetic material uniformly distributed within an inert cross-linked ion exchange resin, or of magnetic material and microion exchangers (e.g., activated carbon), uniformly distributed within an inert cross-linked polymer (Bolto, 1990). Selectivity is governed by allowing the permeability of the resin to vary by the nature and degree of cross-linking of the polymer backbone, to limit the size of the molecules able to penetrate the resin matrix (Dixon, 1980). Regeneration of such resins is not easy after they are used to treat wastewater (Dixon, 1980).

The second type, heterogeneous, consist of active polymeric chains grafted onto a core of magnetic polymer of the homogeneous type described before. The advantage claimed for heterogeneity type is that grafting of a precursor or monomer followed by chemical modification enables a wide range of exchange resins to be produced (Bolto *et al.*, 1978). The selectivity can be tailored by choosing the appropriate type of active polymers to be grafted on the surface. This is another kind of functionalization.

Magnetic resin beads do not settle to a close-packed bed, but form loose flocs containing large volumes of void water. This property makes it possible for the resins to be pumped without attrition, and also enables suspended solids in the feed stream to pass through the resin bed without blinding it. The beads are readily dispersed by mild shear, but aggregate strongly under quiescent conditions. They can be made very fine (down to about 5 μm), with very high reaction rates. As a result, high upflow rates (30-40 m/hr) can be used in countercurrent fluid bed plant. A continuous moving bed pilot plant is schematically illustrated in Figure 12.5 (Becker *et al.*, 1983). The adsorption and regeneration columns are divided into four adsorber or 13 regenerator contacting stages. An agitator shaft in each column allows each stage to be agitated by a small turbine. Feed enters the base of the adsorber at rates of 10-40 L/min and rises through the falling resin, exchanging divalent cations for sodium ions. Product overflows at the top. Loaded resin is transferred to the regenerator by an airlift, where it is stripped with sulfuric acid,

rinsed, and converted partially to the sodium form with sodium hydroxide. Regenerated resin flows back to the adsorber under gravity, driven by the difference in head between the regenerator and adsorber.

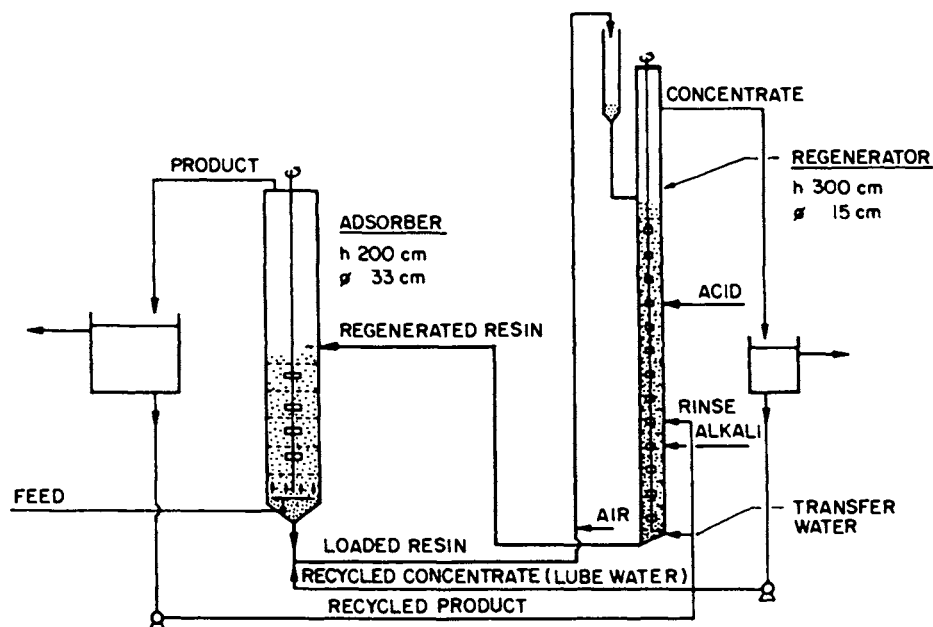


Figure 12.5. Moving-bed ion exchange pilot plant (Becker *et al.*, 1989)

The process has been applied to remove bivalent metal ions (e.g., Ni^{2+} , Cu^{2+}) from nickel plating rinse water containing about 50 mg/L Ni. Almost 90 % nickel is removed producing a reusable water with 6.4 mg/L Ni (Becker *et al.*, 1989). The resins can be effectively separated from gelatinous suspensions using a magnetic drum separator. The magnetic technique largely overcomes the fouling problem, which often plagues the operation of conventional ion exchange resin. That results in cost savings as prior clarification (to prevent fouling) is not required (Bolto, 1990).

A prototype of moving bed ion exchange apparatus for bench scale studies has been described by Tokuyama and coworkers (2003). They applied it to study the recovery of nickel from electroplating wastewater using a strong acid type cation exchange resin. A schematic diagram is shown in Figure 12.6.

The bed column is made of glass pipe of inside diameter 1.3 cm and variable bed height. Teflon plate with a hole in the center is installed at the bottom of resin bed of height 1.0 cm. The diameters of hole, D_h , vary from 0.31 cm to 0.41 cm. The resin is stocked at the top of the column, falling down through the bed and the hole by gravity and is exhausted into the resin tank. Liquid is fed by a pump to the bottom of the column and overflows from the top of the column. Another pump (no. 3 in the Figure) is installed for liquid pulse, which prevents the resin from clogging at the hole. The pulse frequency and the amplitude of the pump are 0.8 s^{-1} and 0.15 cm^3 , respectively. The flow rate of resin, Q_R is measured at the outlet by the volume of resin discharged during a fixed time and that of liquid, Q_L , is determined by an orifice manometer.

Details of methods of preparing magnetic resins for wastewater treatment and specific case studies of their applications are found in the book by Bolto and Pawlowski (1987).

In place of synthetic polymers, natural zeolite (see Chapter 11 for description of zeolite clay minerals) has been used to produce magnetic beads for wastewater treatment. Zeolite magnetic beads are produced by encapsulating technique, by sticking ground magnetite epoxy resin mixture onto zeolite surface. A study described by Gaydardjiev and Pramatarova (1999) with effluents containing copper and arsenic has shown rapid removal of the toxic metals, (up to 80% arsenic and 60% copper).

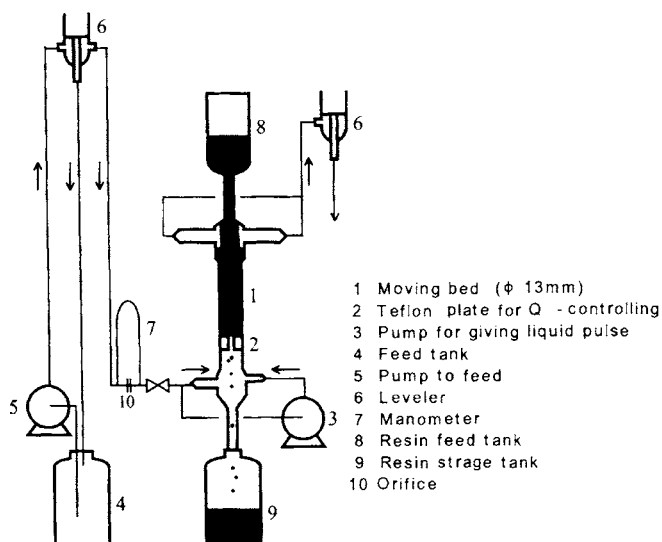
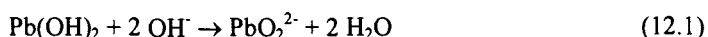


Figure 12.6. Schematic diagram of moving bed ion exchange unit for laboratory studies (Tokuyama *et al.*, 2003)

12.1.3.3. Treatment of Acid Mine Water by Magnetic Seeds

Carrier magnetic separation has been proposed for more effective separation of water and solids from acid mine water to generate very pure water (Feng *et al.*, 2000). As discussed in Chapter 10, dissolved heavy metals like zinc and copper can be recovered from acid mine drainage (AMD) by selective precipitation controlling the pH for the precipitation of specific metals. Following this recovery step, the remaining solution is treated with lime to a pH ~12 to precipitate the residual metal ions. The water thus produced is satisfactory for recycling in mineral processing, but not of the quality for domestic use as it still contains some heavy metal ions. That is because, some of the metal hydroxides are amphoteric and their hydroxides re-dissolve at very high pH. For example, the concentration of lead ion increases from nearly zero at pH 9 to 0.12 mg/L at pH 12 as the precipitated lead hydroxide dissolves producing plumbate:



Magnetic filtration has been applied in place of lime treatment by Feng and coworkers (2000). Ultrafine magnetic particles are used as magnetic seeds. At a dosage of 0.5 g/L

magnetite, all fine precipitate flocs can be rendered strongly magnetic. The mine water is treated with hydrogen peroxide (to oxidize ferrous iron and manganese), followed by the addition of lime and magnetite to raise the pH to 5. Sodium sulfide and more lime are then added to raise the pH to 8. The heavy metal sulfide precipitates are filtered magnetically using a high gradient magnetic separator with a permanent magnetic assembly. This produces an effluent with heavy metal ion (Cu, Zn, Pb, Cd, Cr, Mn, Ti,) well below the discharge limits. The effluent thus freed from heavy metals is then passed to an ion exchange step, where the calcium ion is removed by a cationic resin and sulfate ions by an anion exchange resin. In the elution step, the cation resin is treated with sulfuric acid and the anion resin is treated with sodium hydroxide and lime. High quality gypsum (calcium sulfate) is produced by both elutions. This is a useful byproduct, which helps to offset the cost of the process for the effective removal of toxic metal ions.

A similar process to separate various metal ions in acid mine water by magnetic seeds has been described by Choung and coworkers (2000). In their laboratory study the metal ions are precipitated as hydroxides and magnetite is added as a magnetic seed. The metal hydroxide precipitates are thought to be locked by the magnetic seed, which is then separated by a hand magnet.

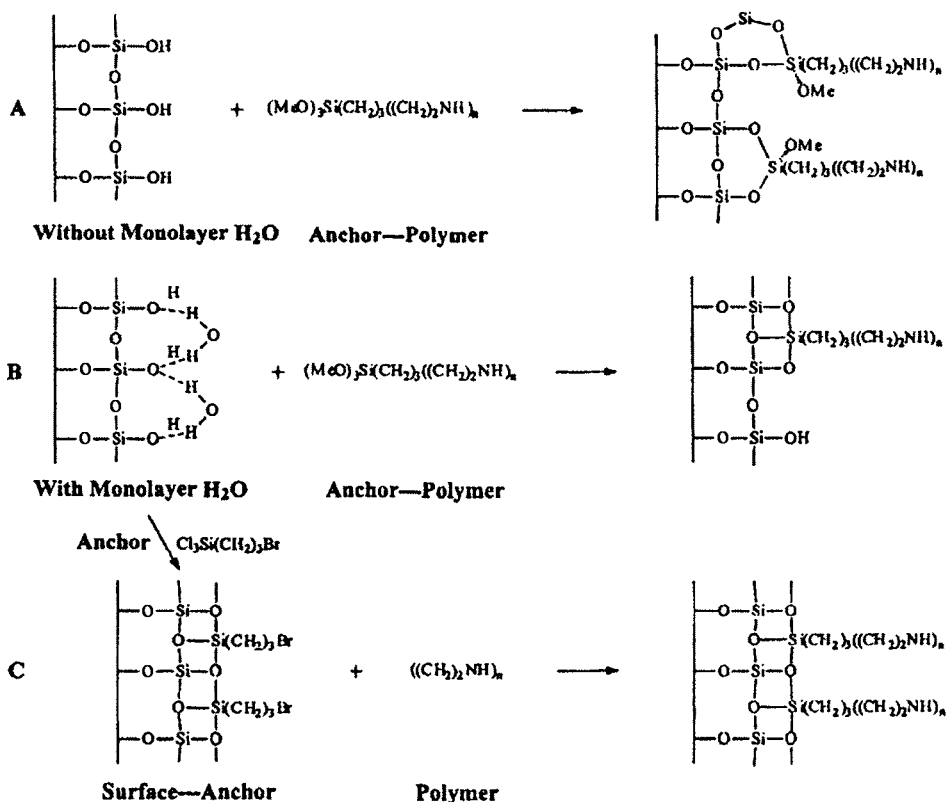
The technique has so far been demonstrated only on a laboratory scale. While it may have considerable potential in removing toxic metals from relatively dilute streams of acid mine water, it has not been applied on a pilot plant scale. Economic factors, in particular, the quantity of magnetite required for large scale treatment is an important factor to be considered.

12.2. Separation by Silica-Polyamine Complexes

This new class of reagents are also based on the principle of functionalization. The functional group, an amine or amine derivative, is grafted on silica. The compounds are therefore not magnetic; but they form insoluble complexes with specific transition metals, which are thus separated. Such materials have been synthesized and details described in the papers by Beatty and coworkers (1999) and Fischer and coworkers (1999). The basic steps comprise preparation of clean hydrated silica gel, mixing it with $\text{Br}(\text{CH}_2)_3\text{Cl}_3$, which serves as anchor to react with polyethyleneimine (PEI), $(\text{CH}_2)_2\text{NH})_n$. The PEI is added from a methanol solution. The gel is then filtered, washed and air dried. The resultant compound is named silica gel-Si-propyl-PEI by the reaction represented by Equation 12.2. This compound is given the name WP-1.

The compound has been found effective for removing aluminum, copper and zinc from mine water. The iron is first precipitated by raising the pH to 4.7. The remaining effluent water containing copper (132 mg/L), aluminum (41 mg/L), manganese (214 mg/L) and zinc (549 mg/L). After one pass through a column of WP-1 compound, copper and aluminum are almost completely removed while the manganese and zinc concentrations are unchanged. After the second cycle the concentration of zinc is reduced to half while the manganese remains unchanged. After three cycles, zinc is completely removed while the manganese is unchanged. The results show the potential for selective separation, which is based on the bond strength of the individual metals to the PEI functional group. Highly concentrated eluant solutions can be produced by eluting the metals bound to PEI by an acid. The principal objective, however, has been removal of metal ions in low concentrations while recovery is a secondary objective.

Several modified structures in which the H atom of the imine group is replaced by a thiol functional group, $-(\text{CH}_2\text{CH}_2\text{S})_n\text{H}$ or a carboxyl group, $-\text{CH}_2\text{COOH}$ have been described by the same investigators and tested for metal separations from dilute effluents.



(12.2)

12.3. Molecular Recognition Technology

This is a relatively new innovation applied for separation processes, largely due to the pioneering work of R. M. Izatt in 1970s and '80s, which followed developments in the synthesis of very large molecular species, supramolecules. They are also called macrocycles as they have a cyclical molecular structure. One of the three main classes of such macrocycle compounds, of importance in metal separation, is called crown ether. The name is related to the molecular structure consisting of $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$ units bridged through nitrogen atoms. When this is chemically attached to a substrate molecule silica gel it acts like a ligand, and with a large cavity of specific dimension depending upon the number of ether groups in the 'crown'. A metal ions of radius matching with the cavity radius gets bound to the ligand. This is called host-guest principle. Binding of a substrate into the cavity yields an inclusion complex called cryptate. Understanding of the host-guest principle has led to designing and synthesis of molecules with

predetermined cation complexation properties. An example is shown in Figure 12.7 for the binding of chromium atom. Macrocyclic ligands with sulfur atom in place of oxygen have also been synthesized. They have been found effective for binding platinum group metal anions as well as silver and mercury.

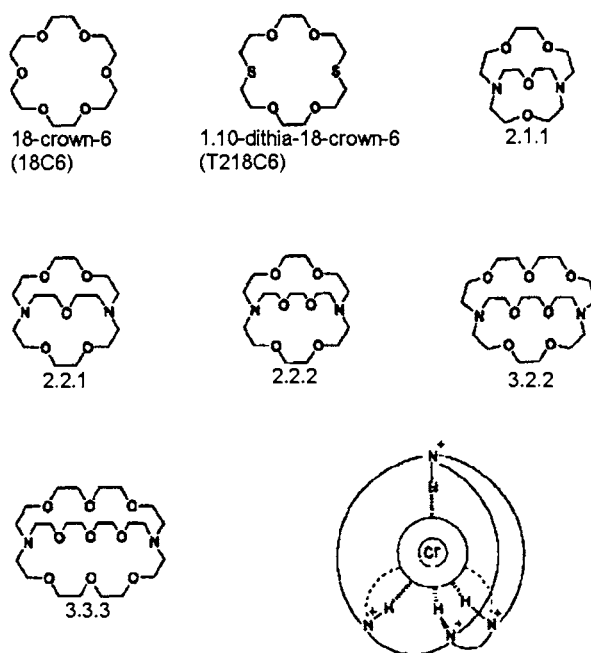


Figure 12.7. Spherical crown ether containing bound chromium. (Izatt *et al.*, 2000)

The other two classes are natural macrocycles some of which have antibiotic properties and synthetic macropolycyclic ligands. They have various applications, but, so far are not applied in metal separation systems. Details are described by Lehn (1995).

The procedure for the synthesis of these compounds is very complex and is described in reviews and monographs on the subject of supramolecular chemistry (Christensen *et al.*, 1974; Busch and Cairns, 1979; Lehn, 1995).

As may be noted, the principle of molecular recognition technology (MRT) bears resemblance to functionalization described before. The major difference is that in MRT very high molecular weight species constitute the ligand and the binding of the metal is governed by compatibility of atomic radii of the cations with the radius of cavity of the ligand crown. In sulfur species, chemical binding of metal to sulfur could also have a role. Collectively, such macrocycle compounds specifically designed for metal separations have been named SuperLig by Izatt. The method of their application resembles that of ion exchange resins. The effluent is passed through a column or a series of columns with SuperLig and in the second step an eluant is passed to recover the metal and recycle the SuperLig. The eluant is usually an acid for base metals and for precious metals such as gold, hot water is elution serves the purpose.

An example of the application of molecular recognition technology (MRT) is in the removal of mercury from concentrated sulfuric acid streams (Izatt *et al.*, 2003). When it

is used to remove mercury in high concentration, the MRT system maximizes the quantity removal of mercury from the feed stream, reducing the mercury concentration to a few ppm. Up to five MRT columns are employed in series. Another series of five columns in the polishing mode results in an effluent discharge with less than 0.1 ppm mercury. The mercury bound to the SuperLig compound is recovered by elution with 0.5 M thiourea, $\text{CS}(\text{NH}_2)_2$ in 0.1 M sulfuric acid, which releases mercury ions captured by the SuperLig by exchange mechanism. Virtually complete elution of mercury is achieved in less than six bed volumes. The first third of the elution is sent to metal recovery. The second two sections of the elution are sent to recycle, to be used as the first and second thirds of the next elution. The eluent product is neutralized with sodium hydroxide to produce sulfide and urea. The probable reaction is as follows:



The sulfide then precipitates the mercury sulfide, which can be disposed of or used as a secondary source to extract mercury. Urea is a useful byproduct.

SuperLig compounds tailor made to recover different metals by the host-guest principle have been synthesized. Their potential applications for a number of metal separations have been described (Dale *et al.*, 1999; Izatt *et al.*, 1999; Amos *et al.*, 2000; Ichiishi *et al.*, 2000; Ezawa *et al.*, 2000); but details of their structure, mechanism and the nature of the metal ion binding are not well described in literature on the subject. The technology, however, is very attractive to achieve high selectivity and a very high degree of separation of metals from effluent streams. The system does not demand large, high capital cost and it can be added to an existing plant or designed into a new plant where the plant area is restricted.

12.4. Separation in Magnetic Fluids (Svoboda, 1998)

This is an extension of heavy media separation (described in chapter 3), where in addition to the conventional force of gravity, a magnetically induced force acts on the fluid. This additional magnetic pull creates a magnetically induced buoyancy force on a particle immersed in the fluid. The separation medium is called ferrofluid, which is a stable colloidal suspension of sub-domain magnetic particles in a carrier fluid. Magnetite is the most common magnetic material; ferrosilicon is also used. Ferrofluids are usually based in kerosene; water-based fluids are also used in some application. Volume concentration of the magnetic material is usually about 10 %. A non-magnetic particle suspended in a ferrofluid is, acted upon by two buoyancy forces. The first is the classical Archimedes gravity-related force, and the other is the magnetically induced buoyancy force due to magnetic "weight" of the ferrofluid. As a result, the loss of weight experienced by a particle suspended in a ferrofluid is determined by a generalized Archimedes law in which the force of gravity is aided by the magnetic induction force. Particles whose densities are smaller than the apparent density of the ferrofluid float and those with density greater than the apparent density of the ferrofluid sink.

The most commonly used separation process is called ferrohydrostatic separation (FHS), in which the force of gravity is the main competing force. It can be designed in such a way that the density of separation is practically constant throughout the entire separation volume. With kerosene-based ferrofluid the FHS technique can distinguish a density difference of at least 0.03 g/cm^3 for 2 mm particles. The separation of weakly and

medium magnetic particles is not affected by the modest magnetic field. The technology is amenable to scale-up, to high throughputs and to automation. Industrial grade kerosene can be produced at modest cost and can be recycled or recovered relatively easily.

The FHS technology is currently used for the recovery of gold. Up to 93 % recovery of free gold has been reported. Separation of platinum group metals and electronic and automobile scrap and slags has been conducted on pilot plant scale. (Svoboda, 1998)

12.5. Mesoporous Adsorbents

In the past few years, the discovery of a new type of silica-based molecular sieve materials with ordered pore channels in the diameter range of 1-10 nm has attracted wide attention for many industrial and environmental applications. The synthesis of nanoporous materials and preparation of highly effective heavy metal ion adsorbents by the incorporation of thiol moieties into the pore channels of mesoporous silica molecular sieves have been the subject of many research investigations (Brown *et al.*, 2000). The thiol functionalized adsorbent, were shown to exhibit high affinity towards the binding of chalcophilic ions such as Hg(II), and had unprecedentedly high loading capacities for these metals (up to 500 mg/g).

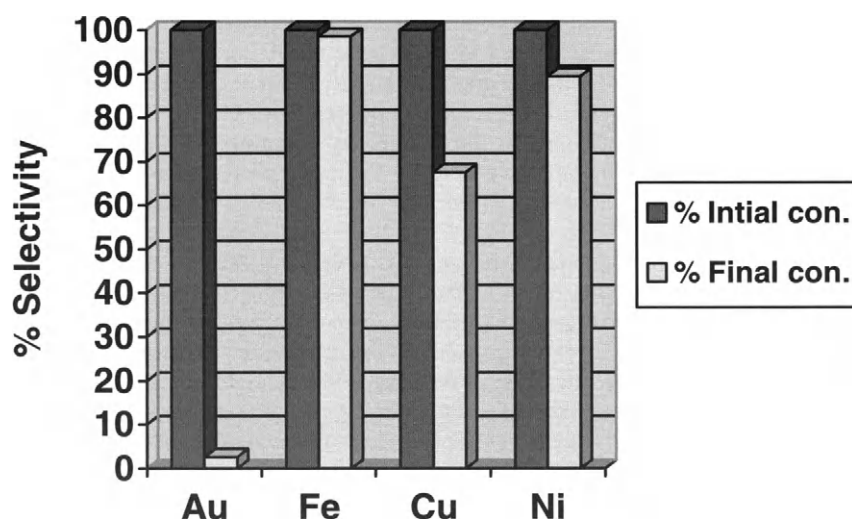


Figure 12.8. Gold recovery from a simulated mine tailing by meso porous adsorbent (El-Hsaeri *et al.*, 2004)

Mesostructure HMS silica (hexagonal mesoporous structure) molecular sieves were synthesized by a S¹T⁰ assembly process using neutral amines surfactants as framework structure directors and subsequently removing the neutral surfactant by solvent extraction. HMS silica is obtained by first dissolving dodecylamine in ethanol, adding water to obtain a fine emulsion, then adding tetraethyl orthosilicate (TEOS) under vigorous stirring. 1,3,5- Trimethylbenzene (TMB) is added and the reaction mixture is stirred vigorously for 20 hours at room temperature. The molar ratio of reagents is 1.0 TEOS: 0.23 amine: 0.23 TMB:160 water. The precipitated product is filtered, washed

with water and allowed to dry at room temperature for 24 hours. The powder is then washed free of the surfactant by soxhlet extraction over ethanol for 72 hours.

The mesostructure is then functionalized with appropriate functional groups to bind the desired metals. In a laboratory study by E-Hsaeri and coworkers (2004), a functionalized meso-adsorbent was used to remove and recover gold present in mine tailings. The procedure for functionalization is as follows. 1 g quantity of each surfactant-free mesostructure is dried under vacuum at 110 °C and refluxed in 25 ml of dry toluene containing 3-mercaptopropyltrimethoxy-silane for 24 hours. The dried materials are then recovered by filtration and washed with toluene followed by soxhlet extraction over ethanol. Any residual organosilane is removed by soxhlet extraction over ethanol for 24 hours. The mercaptopropylsilyl-functionalized mesostructures are denoted as MP-HMS.

The functionalized mesoporous adsorbent selectively binds gold from a solution containing several other metal ions. The selectivity is shown by the results in Figure 12.8.

Another noteworthy feature of mesoporous adsorbents is their large surface area, which results in very high uptake of the metal (318 mg/g or 31.8 % of the weight of the adsorbent) as compared to conventional adsorbent like active carbon.

12.6. Liquid Membrane Processes

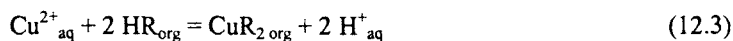
Since it was first patented in 1968 for separating hydrocarbons (Li, 1968) this technology has been successfully applied in the separation of many organic compounds (Edwards, 1972). In the last 20 years its applications have been extended to the removal of contaminants from wastewater and for metal recovery from effluents. In the area of resource recovery from industrial waste, the technology is rapidly developing. It is also referred to as liquid emulsion membrane process as the liquid phase is emulsified.

Liquid membrane process is based on principle similar to solvent extraction explained in Chapter 4. In solvent extraction (sometimes referred to as liquid ion exchange), there are three distinct phases: an aqueous phase as the source of metal ion, an organic phase consisting of a metal complexing agent in the form of anion exchanger dispersed in an organic solvent, and an aqueous eluant or stripping solution to recover metal ion from the organic phase. The process of recovering metal ion thus comprises two consecutive steps. In the first, extraction step, the metal ion in the source aqueous phase reacts with the ion exchanger in the organic phase to form a metal complex. The metal complex is soluble in the solvent but not in the aqueous phase. The organic phase now containing the metal complex is referred to as the loaded organic. In the subsequent stripping step, the metal ion is stripped from the metal complex in the loaded organic phase and recovered as an ion in the eluant aqueous phase.

In the liquid membrane metal extraction (LMME) process, the eluant is emulsified into the organic (membrane) phase, which contains the ion exchanger, and the transfer of metal ion is accomplished in a single simultaneous extraction, that is, stripping process.

12.6.1. Extraction of Copper

As an example, to extract a metal like copper, the extraction step from the source aqueous phase, the first step is the reaction,



where HR_{org} is the hydrogen form of the copper extraction reagent R dissolved in the organic phase and $\text{CuR}_{2\text{org}}$ is the copper complex in the organic phase. The intermediate step in the membrane process consists of the diffusion of $\text{CuR}_{2\text{org}}$ within the membrane phase from one side of the membrane to the other side. In the stripping step, copper is transferred to the eluant phase by the reverse of the reaction above:



The overall transport of copper in the liquid membrane process is illustrated in Figure 12.9. In practice, the internal phase consists of many thousands of droplets within the organic membrane phase. This leads to emulsion stability and assists the mass transfer rate by increasing the availability of the stripping solution.

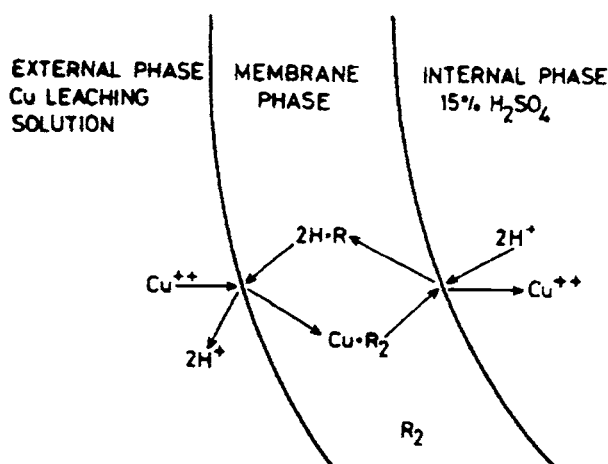


Figure 12.9. Mechanism of copper extraction by liquid membrane process. R denotes organic phase extraction reagent (Li *et al.*, 1983)

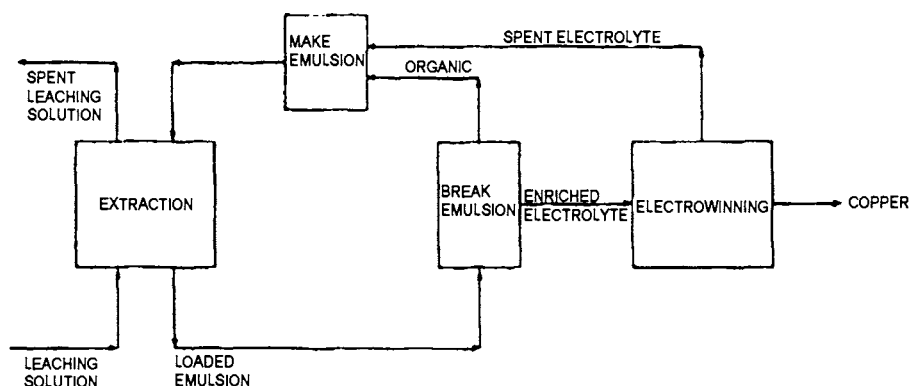
The two equations (12.2) and (12.4) and Figure 12.9 explicitly indicate that the transfer of copper from an external aqueous phase depend on the copper concentration gradient in the membrane phase. This gradient is a function of the square of the hydrogen ion concentration in the aqueous phases and the equilibrium constant of the ion exchanger in the particular solvent at a given temperature.

In the application of the LMME process to copper recovery, the first step is to extract the copper ion from the external aqueous phase (for example, mine water or leach effluent) and store it in internal aqueous phase, for example, sulfuric acid. The ion selectivity is controlled by using a commercial chelating agent dispersed in the membrane phase.

There are two basic methods of recovering the copper from the dispersed internal aqueous phase as illustrated in Figure 12.10. In one, the extracted copper is recovered directly from the internal aqueous phase by breaking the emulsion into an organic phase and a copper-rich aqueous phase, as shown in Figure 12.9 (I). The breaking of emulsion can be accomplished by mechanical means, by electrical coalescence (Martin and Davies, 1976), or the addition of an emulsion breakers, which can be separated from the organic

and aqueous phases, usually by distillation, and can be re-used. The aqueous phase, loaded with the metal, goes to electrowinning and the spent electrolyte is re-emulsified with the organic phase and recycled to the extraction unit.

(1) WITH EMULSION BRAKING



(11) WITHOUT EMULSION BRAKING

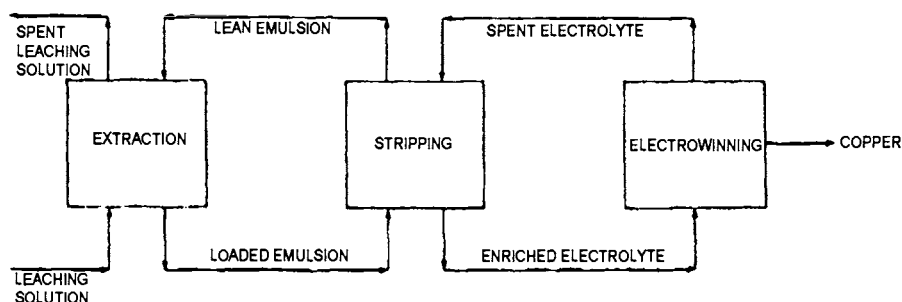


Figure 12.10. Two possible copper extraction processes by liquid membrane process (Li and Cahn, 1983)

The second recovery process, shown in Figure 12.8 (II) follows the same sequences as in conventional solvent extraction, but does not involve breaking of emulsion. Instead, the copper is recovered in a separate reverse liquid membrane extraction step to transfer copper from the internal aqueous to a new external aqueous phase, that is, spent electrolyte, which thus becomes loaded electrolyte. The step is referred to as re-extraction.

The membrane phase used is a mixture of surfactant, solvent and extractant. Surfactants used are polyamines, solvents are basically isoparaffin hydrocarbons. The system is therefore known as liquid surfactant membrane (LSM). The organic phase copper extractant can be any of the available reagents, which should be soluble in the membrane phase solvent. LIX 64N (see Chapter 4) meets this requirement. Emulsions are made by extensive mixing of the organic membrane phase with the internal aqueous

phase in a blender. In continuous extraction process emulsions are made continuously in a non-scaleable shear pump.

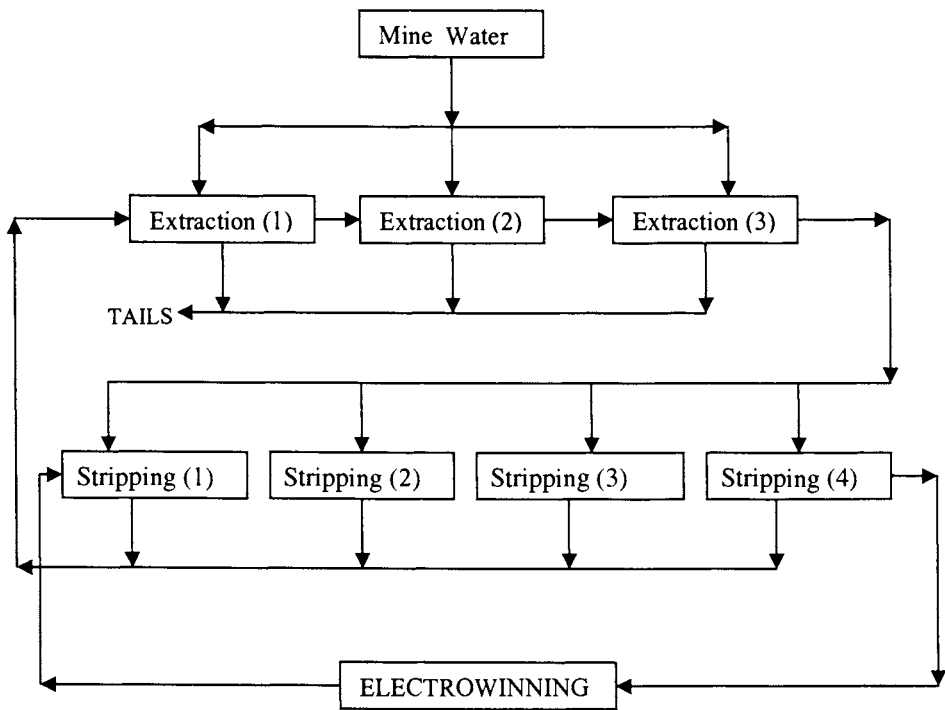


Figure 12.11. Flowsheet for copper extraction from mine water by crossflow extraction (dashed lines). Emulsion flow is indicated by continuous lines (Li and Cahn, 1983)

The emulsion has the advantage of a high loading capacity per unit weight of extractant used in recovery from dilute solutions. This is illustrated by bench scale evaluation of copper recovery from mine water containing 0.5 g/L copper at pH 2.5. (Li and Cahn, 1983). The membrane phase of the emulsion is made up of 2.5 % surfactant, 83 % hydrocarbon and 15 % LIX 64N containing 50 % active extractant. The ratio of membrane to internal phase is 2/1. The emulsion (40 g) and mine water (160 g) are charged into a separatory funnel. After the equilibrium temperature is established, the mixture is tumbled for 3 minutes at the rate of 1 turn per second. After the tumble mixing, the dispersion is allowed to settle into two layers. From the analysis of the spent mine water, the change in the copper content of the internal phase, the total copper concentration after the extraction and the percentage of copper extracted is calculated, assuming that the copper retained in the membrane phase is negligible compared with the total copper extracted. The extraction is conducted in 3 stages, as shown in Figure 12.11. The percent copper extracted decreases from 92 % in the second step down to 56.8 % in the third step.

12.6.2. Separation of Cobalt from Nickel

A new emulsion liquid membrane (ELM) system comprising a tri-alkyl-amine chloride (TAAHCl), $\text{CH}_3-(\text{CH}_2)_{6-10}-(\text{CH}_2)_3\text{N}$, as carrier has been studied for the separation of cobalt from nickel in hydrometallurgical effluents (Fang *et al.*, 2003). A polyamine with an average molecular weight of 9150 (designated as LMA) is used as emulsifier for water in oil (W/O) emulsion. Kerosene (boiling range 200-400 °C) is used as the organic phase of the membrane. It is sulfonated by treating with sulfuric acid and neutralizing with sodium bicarbonate. The membrane phase is prepared by dissolving tri-alkyl-amine in the sulfonated kerosene. The resultant organic solution is treated with 3 M solution of hydrochloric acid to convert the amine to hydrochloride, TAAHCl. The surfactant LMA is then dissolved in the organic solution. The mixture is then emulsified by mechanical mixing to produce a water in oil (W/O) emulsion. After the extraction step, the spent emulsion is phase-separated from the mixture. The separated water in oil (W/O) emulsion is demulsified by an electrostatic emulsion breaker.

The selective extraction of cobalt is based on its complexation with hydrochloric acid to form CoCl_4^{2-} in feed solutions. This complex anionic species is effectively extracted by ion exchange with chloride ions in TAAHCl carrier, forming oil-soluble $\text{CoCl}_4^{2-}-(\text{TAAH})_2$, which by diffusion migrates to the interface of the membrane and internal aqueous stripping phases, where it is converted back to water-soluble CoCl_4^{2-} . A concentration of 7 M hydrochloric acid is found to be optimum for this complex formation leading to the extraction of cobalt in the organic phase. At higher acid concentration, CoCl_4^{2-} starts to be converted to HCoCl_4^- , which is less effective for ion exchange with chloride ions of TAAHCl. Nickel ions do not form such chloro complexes and are not transferred to the organic phase, leading to an excellent separation of the two recoverable metals from effluents.

The potential advantages of LMME process are that (i) the extraction and stripping of metal ion can be accomplished in a single-stage operation, (ii) the ion exchange molecule can be repeatedly used in a multicycle transfer of metal ion between the two sides of the membrane during the single stage operation. The working capacity of the ion exchange molecule is thus increased accordingly, resulting in some cases to lower concentration and consequently, lower losses of the expensive extraction reagent. Liquid membrane extraction may be carried out in a single stage, or co-current multistage operation (as illustrated by the preceding example).

A problem that is encountered in the application of liquid membrane systems is membrane rupture. The membrane should be strong enough so as not to allow leakage of the encapsulated phase into the continuous phase by membrane rupture. Surfactants are added to the membrane phase to strengthen it. Even so, the encapsulated phase leakage may not be completely prevented. The mechanism of encapsulated phase leakage needs to be thoroughly investigated in order to be able to design stable systems ((Borwankar *et al.*, 1987).

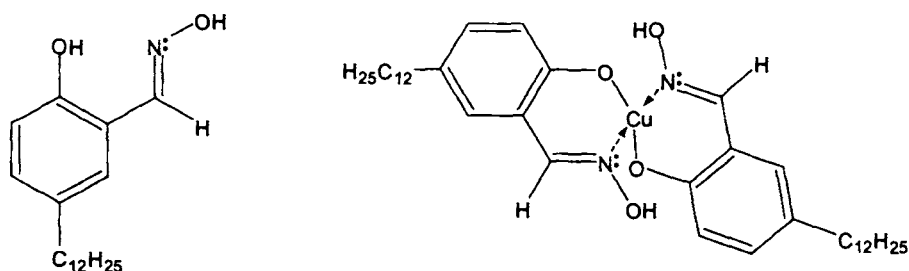
12.6.3. Metal Recovery from Acid Mine Water

The emulsion membrane process has been applied to treat acid mine waters and recover metal values, in particular, copper and zinc. Nilsen and Hundley (2000) have described an unsupported liquid emulsion membrane (LEM), which is made by forming an emulsion from two immiscible phases and then dispersing that solution into a third phase, which is feed solution. The process is largely similar to the one described before

(Li and Cahn, 1983). The emulsions used are water-in-oil type. The internal solution, the stripping solution is emulsified into the organic phase forming an emulsion of extremely fine droplets of the internal solution dispersed in the organic phase. Kerosene is the principal component of the organic phase. It also contains a surfactant to stabilize the emulsion. A conventional solvent extraction reagent is added to the organic phase to facilitate the transport of metal ions through the organic membrane. The emulsion is then dispersed into the feed solution, forming globules of the emulsion. Metal is extracted at the outside surface of the globule by the extractant, transported across the membrane as a metal-organic complex, then stripped and stored in the internal solution. A strong acid solution is used as the internal solution. Extraction and stripping are thus combined in the overall process.

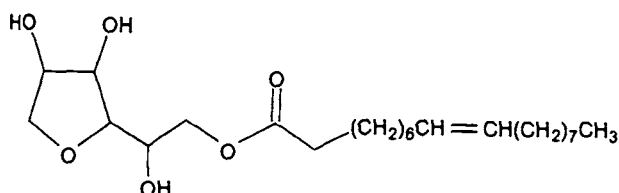
The flow rate of the feed solution range from 1.0 to 3.8 L/min. A 4-stage co-current flow unit with a superficial residence time of 20 minutes is used. The loaded emulsion is broken by an electrical coalescer, fitted with two horizontal electrodes. A 60-hertz ac potential (5000-8000 volt) is applied across the electrodes. The recovered internal solution from the coalescer contains the extracted metal and is sent to a metal recovery unit, which, in the present case is an electrowinning cell. Nilsen and Hundley have obtained very high recoveries (86-99 %) of copper and zinc. As in the treatment of acid rock drainage (see Chapter 10), the mine water is first treated with lime to a pH of 3.5 to selectively precipitate iron as ferric hydroxide and copper and zinc are separated by pH control.

A similar method using LIX-860 N-IC (5-nonyl salicylaldoxine) as extractant together with a surfactant of trade name Span-80, which is monoleate of sorbitan0 and industrial kerosene as a diluent has been applied for the removal of copper ions from mine water (Valenzuela *et al.*, 2005).

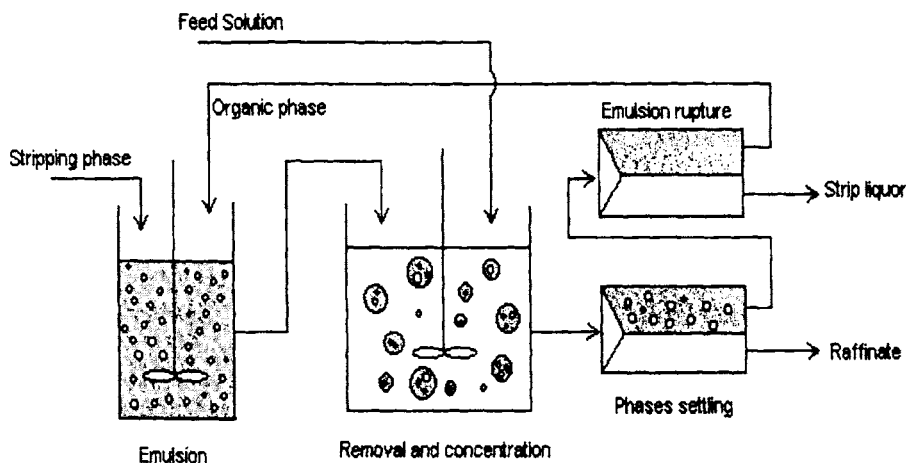


Molecular structure of extractant and metal-extractant complex

The surfactant liquid membrane corresponds to a double emulsion W/O/W. In the first stage, the metal solution with low pH (2.5) is dispersed by vigorous stirring inside an organic phase (the membrane), which is primary emulsion, prepared by dissolving the carrier extractant and a surfactant in a diluent. The extractant selectively transports the metal and the surfactant is added in low concentration to stabilize the system. In the next step, the primary emulsion formed is mixed with a third phase corresponding to the external aqueous phase containing the metal ions to be removed. This generates a double emulsion membrane; see Figure 12.12. The copper ions are transported from the external aqueous phase and get concentrated at the inner strip aqueous phase. The metal-extractant complex is then stripped by an acid carrier transported in a reverse direction.



Molecular structure of surfactant compound

Figure 12.12. Schematic representation of double emulsion liquid membrane process (Valenzuela *et al.*, 2005)

12.6.4. Supported Impregnated Membrane

In a related process called supported impregnated membrane (SLM), the ion exchange material is emulsified in an organic solvent. This has been applied for the separation of rhenium from a hydrometallurgical effluent (Verhaege and Wettick, 2001). Cyanex 921 Tri-octyl-phosphine-oxide, TOPO (trade name, Cyanex 92; see Chapter 4) is used in combination with an aliphatic amine. The reagents are supported on a cross-linked aromatic polymer. Solvent mixtures containing 0.1 M TOPO plus 10 volume % of a primary or secondary amine at pH 10. Di-(2-ethyl-hexyl)-amine (D2EHA) is found most effective. This is found to have high selectivity for rhenium. Exact chemical reactions are given, but the reaction is probably related to complex compound of rhenium with amine. The strip solution is 1 M ammonium hydroxide, which forms soluble ammonium rhenate, NH_4ReO_4 . Rhenium has been selectively extracted from a molybdenum-rhenium roaster flue gas effluent.

Pilot plant work on application of this technology to recover copper from dilute effluents (~500 mg/L Cu) has been described by Vander Linden and coworkers (2000). A LIX reagent (see Chapter 4 for description of the chemistry) is used to extract copper in a pilot plant consisting of two modules, one operating with a membrane containing 30 volume percent of LIX to remove the bulk of the copper while the other operating with a membrane containing a lower LIX concentration of 10 volume percent to remove the

final copper content. The strip solution is 3 M sulfuric acid and is operated in a recycling mode. In the strip circuit, a bleed to an electrolysis cell is provided. In this cell, comprising copper cathode sheets and lead anode, copper is plated from the strip solution. The copper concentration in the strip is kept to a level $\sim 5\text{--}8$ g/L. At this level, copper can be plated with $\sim 80\%$ current efficiency. And a good metal flux is maintained across the membrane. The results show that bulk of the copper is removed from copper acid plating rinse containing 500 ppm copper, but is not reduced to ppm level. A membrane of larger surface area will be required to reduce the metal concentration to that level. This is not considered feasible on an industrial scale. The system is a good alternative to common precipitation treatment as no metal containing sludge is produced and pure copper metal or cupric sulfate solution containing 10 g/L Cu can be recovered, which can be recycled. However, fungi crud is found in the system, probably due to degradation of the polymeric material of the modules. Ultraviolet treatment has been suggested to prevent this undesired product.

12.7. Nanofiltration

Nanofiltration is a crossflow filtration process, using a membrane filter with a pore size of about one nm (nanometer). Molecules larger than 1 nm cannot pass through the membrane because of their size. Almost all nanofiltration membranes have a relatively high charge density. This causes like charge ions to be repelled by the membrane, even though the ions are small to otherwise pass through the pores. The higher the charge of the like charge ion, the higher is the repulsive force. Electrical neutrality is maintained, as oppositely charged ions are also rejected when like charges are rejected. Nanofiltration occurs between reverse osmosis (see Chapter 11) and ultrafiltration. Reverse osmosis membranes have smaller pores, causing even monovalent ions to be mostly rejected. Ultrafiltration membranes have pore sizes from a few nm, up to 50 nm. A pore size of 3 nm is too large to reject even closely charged ions.

A solution is concentrated by nanofiltration until either the osmotic pressure difference between the concentrate and the permeate (filtrate) becomes very high, or the solubility limit of dissolved species is reached. The osmotic pressure of a solution is a function of the molar concentration of the dissolved species, ions and molecules. Small monovalent ions and small molecules pass through a nanofiltration membrane without significantly contributing to the osmotic pressure between the concentrate and the permeate. This makes it possible to concentrate most solutions to at least 20 % dissolved solids level by nanofiltration at a feed pressure not exceeding 1000 psig (6890 kPa), as long as there is no precipitation from a supersaturated solution. In applications to natural water systems, the solubility limit of sulfates is often the limiting factor in the concentration of the water by nanofiltration. Precipitation of carbonate does not present serious problem as it can be easily treated by lowering the pH of the feed solution. If sulfate precipitates on the membrane, it forms scales blocking the water transport through the membrane. Extensive cleaning will then be required to restore the membrane performance. The precipitation can be sometimes delayed by adding organic polymers, which function as scale inhibitors or antiscalants. They prevent formation of large crystals for a limited time by interfering with the crystal growth.

The feed solution has to flow tangentially over the membrane surface, in order to remove dissolved and suspended solids, which are left behind on the membrane surface when the water passes through it. This operation is called crossflow filtration, illustrated

in Figure 12.13 Without crossflow, the dissolved species would accumulate fast at the membrane surface, causing a high osmotic pressure and inorganic precipitation, which would stop the permeate flow.

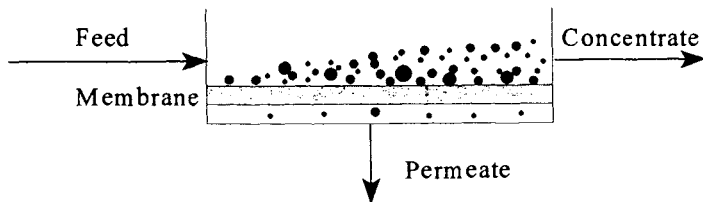


Figure 12.13. Flow scheme of crossflow filtration

The following terms are used in membrane filtration:

Permeate flux = permeate flow rate per unit active membrane area and unit time

Permeate recovery = permeate flow rate/feed flow rate

Solute rejection = $1 - (\text{solute concentration in permeate}) / (\text{solute concentration in feed})$

The solute rejection may also be based "average concentration on the feed side", or the "estimated average solute concentration at the membrane surface".

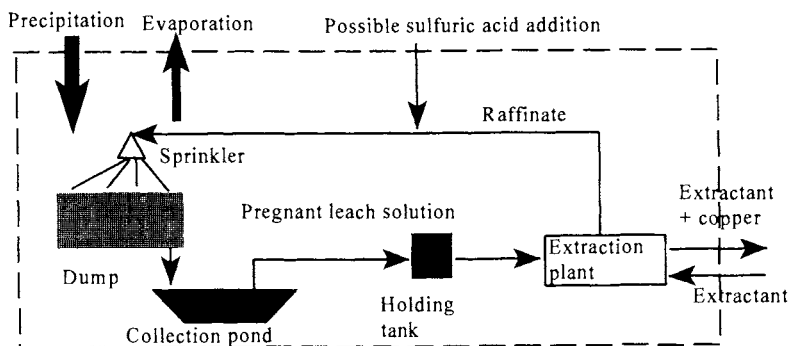


Figure 12.14. Schematic of the pilot plant for treating a copper leach solution from waste dump (Eriksson and Lien, 1996)

An example of the application of this technique for the recovery of copper from pregnant leach solution from a copper dump waste has been described by Eriksson and Lien (1996). In this recovery process, the leach solution first goes through a filter medium to remove suspended solids. As the solution is saturated with several species, the major one being calcium sulfate, an antiscalant is added and the solution passed through nanofiltration unit at a feed pressure of 2200 kPa (300 psig). About 50 % permeate recovery is obtained, leading to an increase in copper concentration by a factor of 2. The rejection of sodium is only 50 % and there is practically no rejection of silica., but this is of no concern for meeting the discharge regulations. The concentrate goes to a holding tank and becomes feedstock for extraction plant. The permeate goes through a filter media, then through a biomass adsorption unit where the remaining metals are adsorbed to produce water for internal use or discharge.

Approximate cost estimates indicate the technology will result in significant pay back.

12.8. Double Membrane Electrolytic Cell (DMEC)

This novel design of electrolytic cell developed by the U.S. Bureau of Mines has some unique features (Atwood *et al.*, 1995), which enhances the capability to recycle contaminated metals and metal alloys. It is based on integrating separation by ion exchange with electrowinning. The cell incorporates two anionic ion exchange membranes, separating anodic and cathodic regions of the cell. The ion exchange membranes prevent significant transport of unwanted cationic impurities to the catholyte from the anolyte while the anion/cation balance in the cell compartments is maintained through the free movement of anions between compartments. The membrane barrier makes it possible to electrorefine highly contaminated materials or to electrowin from solution by alternate anode reactions. The elimination of cross contamination between anolyte and catholyte leads to cathode products of very high purity.

A schematic diagram of DMEC is shown in Figure 12.15. It consists of an anode compartment and cathode compartment separated by two industrial anionic membranes. The separation between the two membranes forms a third compartment, which is referred to as the membrane compartment. This makes it possible to electrorefine highly contaminated metals or to electrowin from solution by using alternate anode currents.

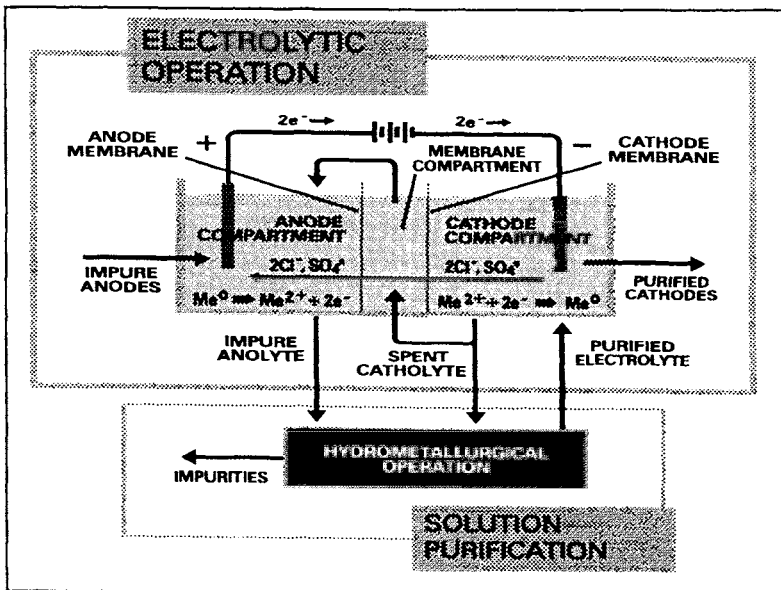


Figure 12.15. Schematic of double membrane electrolytic cell (Atwood *et al.*, 1995)

The DMEC membranes separate the impure electrolyte from the purified catholyte solution while maintaining current flow with anions passing from catholyte to anolyte. An electrolyte solution (called “flush” solution) flows through the membrane compartment. This sweeps away cations, which penetrate through either the anode or

cathode membranes and nearly eliminates the cross-contamination of anolyte and catholyte.

The DMEC process has been applied for a number of metal recovery operations. An example is a metal recycling application, where cobalt is recovered from an industrial effluent. The anodes are made from solid copper sheets. The anodic dissolution the metallic scrap anode produces a concentrated cupric sulfate solution. The membrane compartment flush solution is 20 g/L sulfuric acid. Cobalt is deposited on the cathode as a high quality metal. Average cathode current efficiency is about 80 % and the overall voltage average 5.5 volts with a power consumption of 5.9 kWh per kg cobalt.

Another application described by Atwood and coworkers (1995) is for recycling of superalloy scrap (SAS). The SAS solid anodes are electrochemically dissolved in each of two separate DMEC units. The anolytes produced are combined and subjected to a number of solution purification and extraction steps (see Figure 12.16) to produce separate, purified and concentrated and nickel electrolytes. Nickel metal is deposited at the cathode of one DMEC unit while cobalt metal is produced at the cathode of the other DMEC unit. Cobalt is deposited at a current density of 430 A/m². Energy consumption is 4.4 kWh per kg metal with a cathode current efficiency of 94 %. This is considered to be significantly better than that for some conventional cobalt electrowinning industrial operations (Atwood *et al.*, 1995). For nickel deposition current efficiencies are in the range 97-98 % with energy consumptions 15-2.6 kWh per g metal.

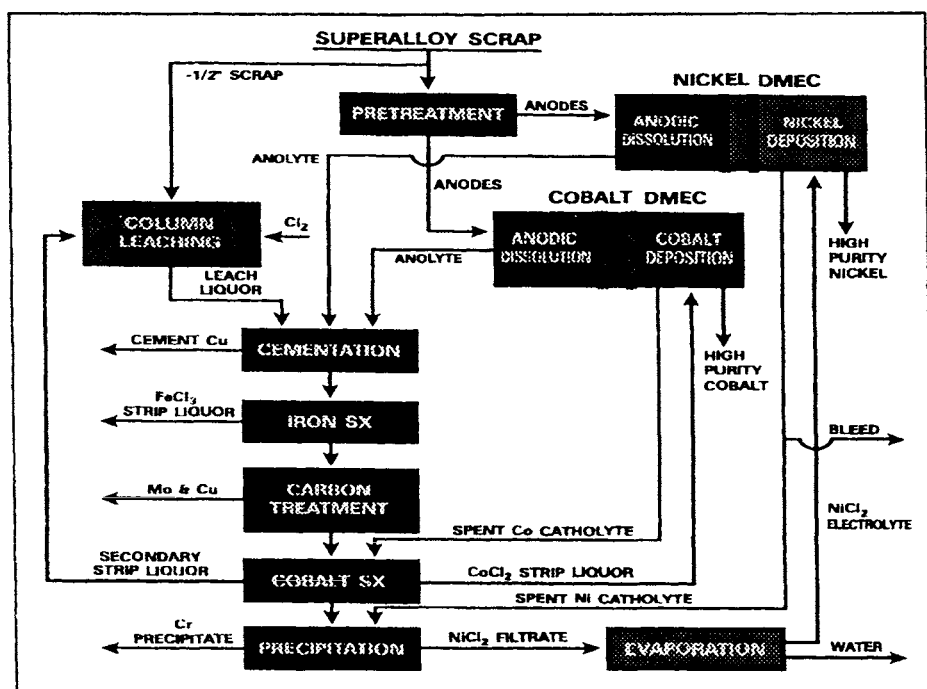


Figure 12.16. Flowsheet to recover cobalt and nickel from superalloy scrap (Atwood *et al.*, 1995)

12.9. Air Assisted Solvent Extraction

This novel technique, still in early stages of development, integrates the principle of flotation (explained in Chapter 3) and solvent extraction (Chapter 4). The method comprises coating of an air bubble by an organic solvent, which is selected to serve as extractant of metal ions to be separated from aqueous solution, on the same principle as in solvent extraction. A laboratory set up to do this has been described by Tarkan and Finch (2005); see Figure 12.17. Solvent is placed in A and air bubbled through it to produce foam. The foam passes through a capillary of diameter 2.5 m. The bubbles released at the orifice carry a thin coating ($\sim 3 \mu\text{m}$) of solvent into aqueous phase. The air readily disengages at the surface of the solution producing a layer of solvent, from where the solvent is recycled.

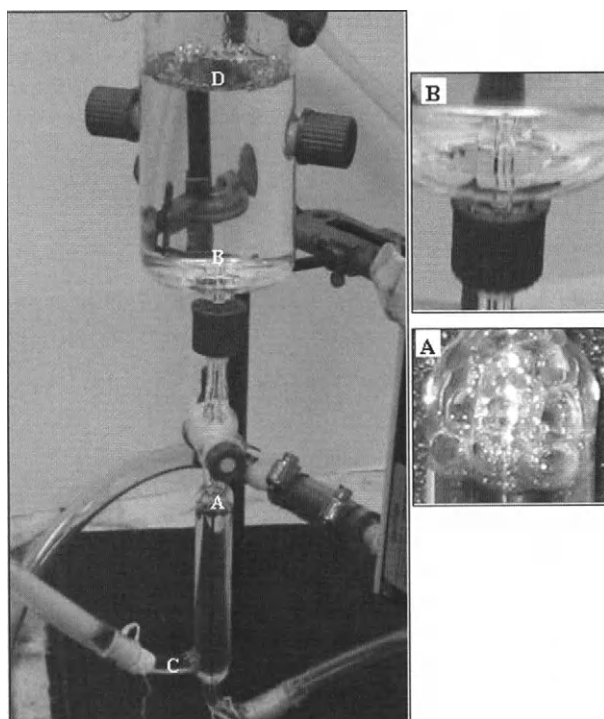


Figure 12.17. Laboratory set up for air assisted solvent extraction. A, solvent placed in a column; B, C, fresh solvent input regulated by an autoburette; D, layer of solvent after the air disengages at the surface (Tarkan and Finch, 2005)

Solvent coated bubbles present a high contact area per unit volume of solvent and rapid phase disengagement. It leads to a rapid separation of dissolved metal ions from the solution and recovery in the organic phase.

The technique has been tested for the separation of cupric ions from a 0.001 M solution using chelating extractants, LIX and D2EHPA, same as the ones used for conventional solvent extraction described in Chapter 4. the results indicate potential application for removing and recovering metal ions form dilute effluent streams.

12.10. Concluding Statement

Metallurgical waste processing, with the twin objectives of resource recovery, recycling and environmental reclamation for health and general well being of peoples round the world has made great strides in the last 50 years. It is now evident, these objectives have to be pursued continuously for sustainable development, to ensure adequate availability of resources for healthy living standards. Continuing intense activities, reflected by conferences held in many centers and applications of new innovations point to ongoing progress. The eleven chapters in the book have surveyed the principal technologies in the area and the present chapter has described some of the new technologies. This represents a fraction of the recent advances. Developments of new innovations and technologies and more effective ways of using the existing ones are constantly taking place. Advances in hydro- and pyrometallurgy and various physical separation techniques applying sensitive instruments of detection and monitoring will play important roles in the development of recycling technology. The next 50 years promise to be even more exciting as mineral and metallurgical industry strive towards the goal of eliminating waste using all technological resources and innovations.

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TMS, The Minerals, Metals and Materials Society, Warrendale, PA, U.S.A.

CIM, Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada

EPD Congress 1995, Ed. G. W. Warren, TMS.

EPD Congress 1997, Ed. B. Mishra, TMS

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