Fathi Habashi **TEXTBOOK OF HYDROMETALLURGY**

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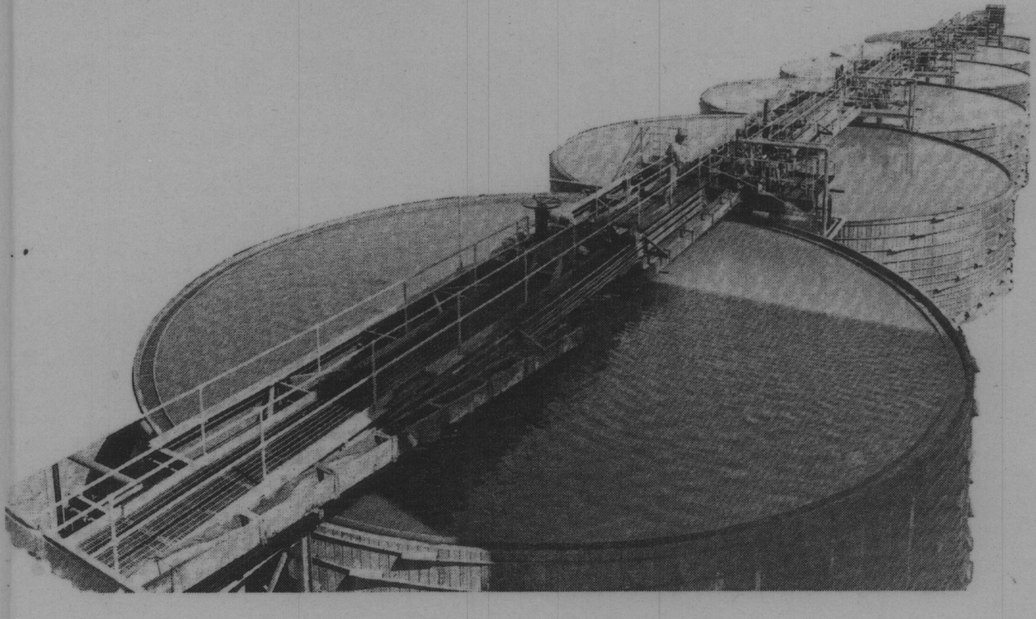
Of
HYDROMETALLURGY

Fathi Habashi
Laval University, Quebec City, Canada



Second Edition

A Textbook of Hydrometallurgy

Fathi Habashi

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To
Nadia, Hani, and
Hatem with love

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- F. Habashi (editor), ***Handbook of Extractive Metallurgy,*** 4 volumes, 2500 pages, ISBN 3-527-287-92-2, WILEY–VCH, P.O. Box 10 11 61, D69451 Weinheim, Germany, Fax: +49 (0) 6201 606-184. Price US$1200.
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Preface to the First Edition

Hydrometallurgy is a specialized branch of extractive metallurgy dealing with metal recovery from ores, concentrates, and other metallurgical intermediate products by wet methods. The other branches are pyrometallurgy (treatment by thermal methods) and electrometallurgy (treatment by using an electric current). This book covers the elementary theoretical basis of solution chemistry, the engineering aspects, and the technical applications for a large variety of raw materials, e.g., metals, oxides, sulfides, phosphates, silicates, and others. It also covers the purification-concentration steps such as adsorption on activated charcoal, ion exchange, and solvent extraction. Finally, the general aspects of precipitation from aqueous solutions are covered with numerous examples.

Volume Two of *Principles of Extractive Metallurgy* by the author published in 1970 and reprinted in 1980 was devoted to hydrometallurgy. Since then, hydrometallurgy has greatly advanced. Leaching of gold ores has expanded, in-situ and dump leaching became wide spread, pressure leaching was applied industrially to sulfides with elemental sulfur recovery, treatment of the so-called refractory gold ores was industrialized, activated charcoal became an important hydrometallurgical reagent, numerous new organic solvents became known and new applications were found. Further, the literature on hydrometallurgy increased greatly as a result of the numerous conferences held on this topic, new journals, and many review articles. All this led to the decision that a new edition of *Hydrometallurgy* was warranted.

The present volume is an expanded and completely revised version of the original volume. It is composed of five parts as follows:

Part One: Introduction. This part covers the history and scope of hydrometallurgy, and a chapter devoted to solution chemistry. In this chapter, the structure of minerals and water, elementary concepts of acids and bases, oxidation and reduction, complex formation and precipitation is introduced. It was found necessary to bring these concepts because many metallurgy students do not have this chemistry background.

Part Two: Leaching — General. This part is devoted to the general aspects of leaching of ores and concentrates, the reagents used, methods and equipment, the engineering aspects, and the role of microorganisms.

Part Three: Leaching Processes. In this part, a systematic description of the different leaching processes is given. It follows the nature of the material to be leached whether metals, oxides, sulfides, etc.

Part Four: Treatment of Leach Solution — Purification, Concentration. In this part, the methods used to purify and/or concentrate the leach solutions are given. This includes adsorption on activated charcoal, ion exchange, and solvent extraction.

Part Five: Treatment of Leach Solution Precipitation. In this part, the methods of recovery of metal values from leach solution are outlined. These are divided into physical and chemical methods. Physical methods are based on crystallization while chemical methods are based on hydrolysis, ionic precipitation, and reduction. Electrolytic methods, i.e., those based on the use of electric current, are only briefly outlined since these are usually discussed in electrometallurgy books.

The characteristics of this book are the clear and simplified flowsheets, numerous chemical equations written mainly in ionic form, many illustrations for equipment and plants, and finally a lucid style presenting the facts point by point as concise as possible. To make the book of a reasonable size, detailed theory of hydrometallurgical processes is covered in the author's companion volume "Kinetics of Heterogeneous Processes", which is an enlarged and revised version of Volume One of *Principles of Extractive Metallurgy.* Contrary to the previous edition, the present edition contains only key references to the original literature to save space. Nevertheless, many of the references cited earlier are still useful.

The present work forms the basis of lectures to first year students at the Department of Mining and Metallurgy at Laval University. It is hoped that it will be useful to other students of metallurgy, chemistry, chemical engineering, mineral dressing, geology, as well as to the practicing engineer in industry.

The book has been partially subsidized by the Faculty of Science and Engineering of Laval University. Special thanks are due to the

Dean Louis Cloutier, the Vice-Dean Andrt Duval, and to Jacques Giguère and Jean-Franqois Morin, of the Pedagogical Resources.

April 1993
Qutbec City

Fathi Habashi

Preface to the Second Edition

Hydrometallurgy is a rapidly expanding field. A second edition was prepared after six years from the publication of the ***Textbook*** to incorporate some new material and because the stock of the first edition was exhausted. The new edition has been revised along the following lines:

- Titles of recent monographs and conference proceeding volumes dealing with hydrometallurgy were updated in Chapter 2
- Oxyhydrolysis was added to Chapter 3
- Ferric salts were put under oxidizing agents and not under leaching agents (Chapter 4)
- Expansion in pressure leaching technology since major advances were made recently (Chapters 6 and 9)
- More importance was given to pyrite and arsenopyrite. This resulted in changing the title of Chapter 12 to Sulfides and Disulfides
- More details were added to the treatment of phosphate rock (Chapter 15)
- Minor additions were incorporated in the sections dealing with nitric acid, zinc, gold, and nickel metallurgy and correcting minor typographical errors
- An appendix entitled "Laboratory Autoclaves for Hydrometallurgical Research" was added to help those interested in entering the field of pressure hydrometallurgy

May 1999
Sainte-Foy

Fathi Habashi

Table of Contents

Part One — Introduction 1

1. History 3
2. Scope 13
3. Solution Chemistry 31

Part Two — Leaching — General 65

4. Leaching Agents 67
5. Theory 101
6. Methods and Equipment 123
7. Engineering Aspects 163
8. The Role of Microorganisms 195

Part Three — Leaching Processes 201

9. Metals 203
10. Oxides and Hydroxides 241
11. Complex Oxides 275
12. Sulfides and Disulfides 287
13. Selenides and Tellurides 327
14. Arsenides 335
15. Phosphates 341
16. Silicates 357
17. Chlorides and Sulfates 375

Part Four —Treatment of Leach Solutions: Concentration, Purification 379

18. General Aspects 381
19. Adsorption on Activated Charcoal 385
20. Ion Exchange 405
21. Solvent Extraction 437

Part Five — Treatment of Leach Solutions: Precipitation 529

22. General Aspects 531
23. Physical Precipitation: Crystallization 543
24. Hydrolytic and Ionic Precipitation 593
25. Reduction 631

Appendix — Laboratory Autoclaves for Hydrometallurgical Research 667

Questions and Problems 705

Acknowledgements 717

Index 721

Part One

Introduction

Chapter One

History

Early Period. 3
The Modern Era. 5
  The cyanidation process 5
  The Bayer Process 7
  Other processes 8
Recent Developments 9

"Hydro" means water and "hydrometallurgy" is therefore the art and science of aqueous methods of extracting metals from their ores. It is a relatively recent subject when compared with pyrometallurgy — the ancient art of metal production. Man has learned thousands of years ago how to build furnaces and use fire to melt rocks and produce metals but the use of water and aqueous solutions for ore processing came much later, mainly at the time of the alchemists when acids and alkalies became known and used. Modern hydrometallurgy, however, can be traced back to the end of the Nineteenth Century when two major operations were discovered: the cyanidation process for gold and silver and the Bayer Process for bauxite. Later, in the 1940s, a breakthrough came during the Manhattan Project in USA in connection with uranium extraction. Since then, it has been advancing progressively and even replacing some pyrometallurgical processes.

EARLY PERIOD

The roots of hydrometallurgy may be traced back to the period of alchemists when the transmutation of base metals into gold was their prime occupation. Some of these operations involved wet, i.e., hydrometallurgical methods. For example, when an alchemist dipped a piece of iron into a solution of blue vitriol, i.e., copper sulfate, the iron was immediately covered by a layer of metallic copper. This apparent transmutation of iron into copper is represented in modern terms by the equation: $Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$, but it was not known at that time that blue vitriol contained copper. The major question, however, that remained unanswered was: how can the transmutation of iron or copper into gold be affected? Gold, the most noble of all metals dissolved in mercury forming an amalgam but was insoluble in all acids or alkalies known at that time. The discovery of aqua regia by Jabir Ibn Hayyan (720–813 A.D.), the Arab alchemist, may be considered as a milestone marking the beginning of hydrometallurgy. Aqua regia, i.e., royal water, is a mixture of HCI and HNO_3 that dissolves gold; neither of the acids alone has any dissolving action. Aqua regia is still used today for gold refining, and chlorine one of its active ingredients: $3HCl + HNO_3 \rightarrow Cl_2 + NOCl + 2H_2O$ was utilized extensively for extracting gold from its ores till the 1890s.

In the Middle Ages, certain soils containing putrefied organic matter were leached to extract saltpeter, a necessary ingredient for the manufacture of gunpowder. The process was fully described by Vannoccio Biringuccio (1480–1539) in his *Pirotechnia* published in 1540.

In the Sixteenth century, the extraction of copper by wet methods received some attention. Heap leaching was practiced in the Harz mountains area in Germany and in Río Tinto mines in Spain. In these operations, pyrite containing some copper sulfide minerals was piled in the open air and left for months to the action of rain and air whereby oxidation and dissolution of copper took place. **A** solution containing copper sulfate was drained from the heap and collected in a basin. Metallic copper was then precipitated from this solution by scrap iron, a process that became known as “cementation process”, which is apparently derived from the Spanish “cementacicin”meaning precipitation. This is the same process that was already known to the alchemists and is still in operation today to an appreciable extent.

In the Eighteenth century, one of the most important industries in Quebec was the production of potash for export to France to satisfy the needs of the soap and glass industries. Before the invention of Leblanc Process for the manufacture of Na_2CO_3 from NaCl, the main source of Na_2CO_3 was from ashes of seashore vegetation, and that of potash was from ashes produced by burning wood in areas where the clearing of forests was in progress on large scale. The importance of this process to hydrometallurgy lies in the fact that leaching was extensively practiced. During the period 1767–1867, wood ash was collected from domestic stoves and fireplaces, and from lime kilns, then agitated with water, filtered, then evaporated to dryness to yield potash. One ton potash required the burning of 400 tons of hardwood, which is equivalent to the cutting of about 10 acres of forest.

THE MODERN ERA

The birth of modern hydrometallurgy dates back to 1887 when two important processes were invented. The first, the cyanidation process for treating gold ores, and the second, the Bayer Process for the production of alumina.

The cyanidation process

The dissolving action of cyanide solution on metallic gold was known as early as 1783 by the Swedish chemist Carl Wilhelm Scheele (1742–1786). Elsner in Germany in 1846 studied this reaction and noted that atmospheric oxygen played an important role during dissolution. The application of this knowledge to extract gold from its ores was proposed and patented much later in England by John Stewart MacArthur (1871–1908) (Figure 1.1), Robert Forrest, and William Forrest in 1887 and became known as the cyanidation process. Bodlander in 1896 made the important discovery that hydrogen peroxide was formed as an intermediate product during the dissolution of gold. The cyanidation process had already been applied to each mining district in the world and still its chemistry was very obscure. Its impact on hydrometallurgy had been tremendous. Extremely large reactors known as ***Dorr agitators*** in which the finely ground ore was agitated with the cyanide leaching agent and equipped with compressed air injection in the pulp have been designed and built by the metallurgical engineer John Dorr. Huge filtration plants designed to obtain clear leach solutions for metals recovery were similarly constructed. The ancient process known as cementation which was applied only for precipitating copper from solution by scrap iron was applied to gold solutions, iron being replaced by zinc. In spite of all these advances in engineering and the wide application of the process, the theory still remained lagging behind. As a result of introducing the cyanidation process worldwide, gold production increased greatly during the period 1900–1910 (Figure 1.2).

Figure 1.1: The founders of hydrometallurgy. Left: Karl Josef Bayer (1847–1904) Right: John Stewart MacArthur (1871–1908).

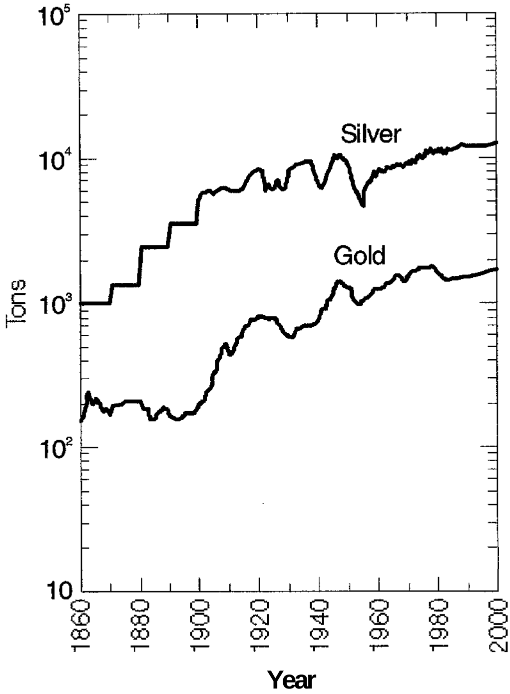

Figure 1.2: Increase in world gold and silver production between 1900 and 1910 as a result of introducing the cyanidation process.

The Bayer Process

The second major hydrometallurgical process of this era was the process invented by Karl Josef Bayer (1847–1904) (Figure 1.1) for the preparation of pure Al_2O_3 and known as the *Bayer Process.* This process was concerned with leaching bauxite, discovered in 1821 in France in a small village called Les Baux, near Marseille, with sodium hydroxide solution above its boiling point in a pressure reactor. After separating the insoluble material, the pure solution was then seeded to precipitate pure crystalline aluminum hydroxide which was filtered, washed, dried, and calcined to pure Al_2O_3 suitable for charging to the electrolytic reduction cell invented two years earlier. Bayer was an Austrian chemist working in Saint Petersburg, in Russia; his process is used at present in its original version with practically no change. It is interesting to point out the following:

- The process was originally developed to satisfy the needs of the textile industry and not for metallurgical application; Al_2O_3 was used as a mordant in dyeing cotton. It was only after the invention of the electrolytic aluminum process by Paul Héroult (1863–1914) in France and Charles Martin Hall (1863–1914) in USA that Bayer turned his attention to metallurgy.

- Bayer's first contribution was in 1887 when he discovered that $Al(OH)_3$ precipitated from alkaline solution was *crystalline* easy to filter and wash free from impurities while that precipitated from acid medium by neutralization was gelatinous difficult to filter and wash.

- Few years earlier to Bayer's invention, Louis Le Chatelier (1815–1873) in France described a method for making Al_2O_3 by heating bauxite with Na_2CO_3 at 1200 °C, leaching the sodium aluminate formed with water, then precipitating $Al(OH)_3$ by CO_2 which was then filtered, dried, and ignited to pure Al_2O_3. In spite of the numerous improvements introduced to this process by later investigators, it was abandoned in favor of the Bayer Process.

Other processes

At the beginning of the Twentieth Century numerous leaching and recovery processes were proposed, some of them were put into practice, others had to wait for about half a century until they were applied, while other never developed beyond a pilot plant. When examining the patent literature at the beginning of this century it is remarkable to see the large variety of leaching agents proposed. In 1903, M. Malzac in France proposed the use of ammonia solutions for leaching sulfides of copper, nickel, and cobalt. At that time NH_3 was an expensive reagent obtained exclusively as a by-product of the coal industry. It became a cheap commercial reagent only after its synthesis ten years later by Fritz Haber in Germany. Nitric acid was proposed by Kingsley in 1909 for leaching sulfide ores. Also, at that time HNO_3 was an expensive reagent obtained exclusively from the sodium nitrate deposits in Chile by treatment with concentrated H_2SO_4. It became relatively cheap only after the invention of Haber's process since nitric acid is made now exclusively by the oxidation of ammonia.

Friedrich August Henglein (1893–1968) in Germany proposed in 1927 the use of oxygen under pressure to dissolve ZnS with water: $ZnS + 2O_{2(aq)} \rightarrow ZnSO_{4(aq)}$. This invention was made in the chemical and not in the metallurgical industry as a method for regenerating ZnS formed during the absorption of H_2S from coke oven gas by an ammoniacal solution of $ZnSO_4$. Here again oxygen was an expensive gas since the air liquefaction process was not yet perfected. Vladimir Ipatieff (1867–1952) and his son in Russia in 1904–1920 used hydrogen under pressure to precipitate metals from solution; hydrogen at that time was an expensive gas; it became cheap only after the discovery of reforming processes for petroleum gases. In the hydrometallurgy of copper, instead of precipitating copper from leach solution by scrap iron in the usual way, electrowinning was used in Chile in 1912.

The First World War (1914–1918) created a demand for the zinc for the manufacture of cartridge brass. Zinc for this purpose used to be obtained by the distillation of commercially available metal in Belgium and Germany from ore supplied by Australia. This situation inspired industry in North America to supply additional metal from ores that were not amenable to standard methods. At Trail in British Columbia and Anaconda in Montana, the processes for electrolytic zinc and the leaching of a large tonnage of ZnO by H_2SO_4 was introduced. The process is mainly based on a patent by L. Létrange in France issued in 1881. Cadmium gradually emerged as an important by-product of this process.

RECENT DEVELOPMENTS

In the 1940s, the technology of uranium production was introduced in connection with the *Manhattan* ***Project*** — a US project aimed at producing an atomic bomb. Numerous new techniques became suddenly used on large scale. Some of these are, for example, the use of Na_2CO_3 as a leaching agent, ion exchange, solvent extraction, and many processes for precipitation from aqueous solutions. A large number of synthetic resins for use as ion exchangers and, similarly, a large number of organic solvents were specially synthesized for use as extractants for uranium. In the 1950s, pressure hydrometallurgy was introduced for leaching sulfide concentrates, for laterites, for tungsten ores, as well as for the direct precipitation of metals from solution. Also, during this period, the recovery of uranium as a by-product of phosphate fertilizers was achieved. Although this process was abandoned few years later when important uranium deposits were discovered, now it has been revived in view of the expansion in nuclear energy programs. In the 1960s, the role of bacteria in leaching became known and the wide spread use of heap and in situ leaching for extracting copper was practiced. The same technique was later adopted for leaching low-grade uranium and gold ores. In the same period the application of organic solvents mainly oximes for extracting copper from solution was realized.

In the 1970s, the mechanism of dissolution of sulfides was well established and the pressure leaching of zinc sulfide concentrates was applied industrially in Canada. In the 1980s, the hydrometallurgy of gold dominated the scene: Widespread application of activated charcoal for gold adsorption and the aqueous oxidation of gold refractory ores was industrialized. Table 1.1 gives a summary of the historical development in hydrometallurgy.

Table **1.1:** Summary of historical development in hydrometallurgy.

	Early period
7th century	The apparent transmutation of iron into copper by alchemists ($Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$)
8th century	The discovery of aqua regia by the Arab alchemist Jabir Ibn Hayyan (720–813 A.D.). This was the only known solvent for gold. Still used today in gold refining.
16th century	Heap leaching of copper-containing pyrite in the Harz mountains in Germany and in Río Tinto in Spain, and the precipitation of copper from the solutions by iron.
18th century	Production of potash for soap and glass industries by leaching ashes left after burning wood, e.g., in Québec, where the clearing of forests was in progress on large scale.
	Modern Era
1887	The invention of the cyanidation process, i.e., dissolution of gold from ores by a dilute sodium cyanide solution and the precipitation of gold from the solutions by zinc. The invention of Bayer's Process: precipitation of crystalline $Al(OH)_3$ from sodium aluminate solution by seeding, followed in 1892 by his invention of pressure leaching of bauxite by NaOH solution.
1912	Recovery of copper from leach solution in Chile by electrolysis.

1916	The use of ammonium hydroxide for leaching native copper ore in Lake Superior District, and for malachite–azurite ore in Alaska. Development of the hydrometallurgical–electrowinning zinc process at Trail and Anaconda. The recovery of cadmium as a by-product of the zinc hydrometallurgical process.
	Recent Development
1940s	Development of the uranium technology in connection with the US Manhattan Project aimed at producing an atomic bomb. Introduction of sodium carbonate as a leaching agent for uranium, the widespread use of ion exchange and solvent extraction for uranium recovery, and the separation of the lanthanides by ion exchange.
1950s	The application of pressure hydrometallurgy for leaching nickel sulfide ores and the precipitation of pure nickel from solution by hydrogen under pressure.
1960s	Discovery of the role played by microorganisms in leaching processes and the widespread use of heap and in-situ leaching for extracting copper from low-grade material. The application of pressure leaching to a variety of raw materials, e.g., laterites, tungsten ores, uranium ores. The application of solvent extraction for copper.
1970s	Discovery of galvanic action in leaching sulfide minerals. Recovery of traces of uranium from waste leach solutions after copper precipitation with scrap iron. Pressure leaching of zinc sulfide concentrate in dilute H_2SO_4 at Trail and Timmins in Canada.
1980s	The hydrometallurgy of gold greatly advanced: widespread application of activated charcoal technology, and aqueous oxidation of gold refractory ores.

Chapter Two

Scope

Hydrometallurgy as a Branch of Extractive Metallurgy. 13
Hydro- versus Pyrometallurgy 16
    Sulfur dioxide generation 17
    Material handling. 17
    Energy consumption 18
    Dust formation. 18
    Treatment of complex ores 18
    Treatment of low-grade ores. 19
    Waste disposal 19
    Economics. 19
Sources of Information. 19
Selected References 20
    Monographs 20
    Conferences and Symposia. 21
    Journal Articles. 26

HYDROMETALLURGY AS A BRANCH OF EXTRACTIVE METALLURGY

Extractive metallurgy is the art and science of extracting metals from their ores by chemical methods. It is actually divided into three sectors: hydrometallurgy, pyrometallurgy and electrometallurgy. Hydrometallurgy is the technology of extracting metals from ores by aqueous methods, pyrometallurgy by dry thermal methods, and electrometallurgy by electrolytic methods.

In general, hydrometallurgy involves two distinct steps (Figure 2.1):

- Selective dissolution of the metal values from an ore — a process known as Leaching.
- Selective recovery of the metal values from the solution, an operation that involves a *precipitation* method.

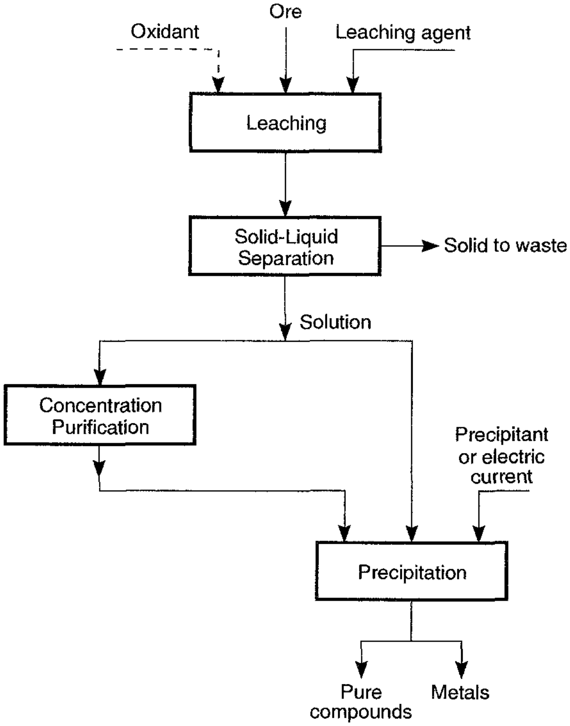

Figure 2.1: General outline of hydrometallurgical processes.

Sometimes a *purification/concentration* operation is conducted prior to precipitation. These processes are aimed at obtaining a pure and a concentrated solution from which the metal values can be precipitated effectively. The methods used are: adsorption on activated charcoal, sorption on ion exchange resins, and extraction by organic solvents. They are common in one respect, namely, the same scheme of loading, washing, and elution is used in all three operations. In the elution step, the material is simultaneously regenerated for another cycle. While the first two materials (activated charcoal and ion exchange resins) are solids, the third material is a liquid phase. That is why it is sometimes referred to as liquid ion exchange.

Hydrometallurgical processing may be used for the following purposes:

- Recovery of salts from their deposits. For example, common salt, sodium carbonate, potash, borax, etc.

- Production of pure solutions from which high purity metals can be produced by electrolysis, e.g., zinc, cadmium, nickel, copper, gold, and silver.
- Production of pure compounds which can be subsequently used for producing the pure metals by other methods. For example, pure compounds of aluminum, magnesium, uranium, and beryllium are produced by hydrometallurgical methods but the metals themselves are produced either by electrometallurgy (aluminum and magnesium), or by pyrometallurgy (uranium and beryllium).
- As a chemical beneficiating method. In this case, the undesirable components of the raw material are leached away and the remaining solids are the valuable product that has to be processed further (Figure 2.2). For example, the treatment of ilmenite to produce synthetic rutile, the desulfurization of coal, the purification of cassiterite concentrates, etc.

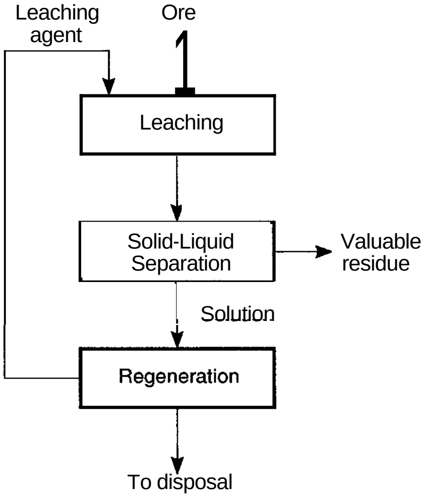

Figure *2.2:* Hydrometallurgy as a chemical beneficiation method.

- Direct production of pure metals suitable for the market after a subsequent minor treatment, e.g., the precipitation of cobalt, nickel, and copper from solution by hydrogen under pressure.

The raw material for leaching is usually crushed and ground and sometimes beneficiated by physical methods before leaching. In some cases the raw or the beneficiated material is treated by thermal methods, e.g., oxidation, reduction, etc., before being leached – the idea is to render the material either more amenable to leaching, or to exclude an undesirable component. Leaching is usually followed by filtration, washing, and solution purification steps. In few cases the ore is crushed but not ground and the leach solution is allowed to percolate through thus combining leaching and filtration in a single step. In special cases the ore is leached in place.

In any hydrometallurgical plant, large amounts of water are needed, and a water balance must be maintained. Surface or subsurface water must be especially treated to remove any suspended matter as well as soluble salts; this topic is discussed in chapter 7.

HYDRO- VERSUS PYROMETALLURGY

In the past fifty years, hydrometallurgy has been vigorously competing with pyrometallurgy. Pyrometallurgy was most successful when high-grade massive sulfide ores were treated in a blast furnace, because such furnace has maximum heat economy being itself a heat exchanger: the cold charge descending from the top is preheated by the hot gases ascending in the furnace. Dust problems were also minimum because the ore was in form of large lumps. With the exhaustion of such raw material, metallurgists turned their attention towards the treatment of low-grade ores. This necessitated extensive grinding and flotation of the sulfides which resulted in a finely divided concentrates as raw material. These, naturally, could not be charged to a blast furnace because if charged, they would block the movement of the ascending gases – hence the birth of the fossil-fired horizontal reverberatory furnace. This was a turning point to the worst with respect to pollution of the environment, high energy consumption, and excessive dust formation.

Probably the first success for hydrometallurgy was at the beginning of this century when the hydrometallurgical process for the production of alumina from bauxite was invented. In this process, bauxite was leached with NaOH at high temperature and pressure to form sodium aluminate, which was then filtered and used for precipitation of pure $Al(OH)_3$. Few years earlier, a pyrometallurgical method was invented in which bauxite was heated with Na_2CO_3 at 1200 °C to form sodium aluminate which is then leached with water, then $Al(OH)_3$ is precipitated by bubbling CO_2 in the solution. In spite of the numerous improvements introduced to this process by later investigators, it was abandoned in favor of the hydrometallurgical process. Another success for hydrometallurgy was the hydrometallurgical route for the production of zinc in favor to pyrometallurgical reduction. It was found more economical to leach ZnO by H_2SO_4 and electrolyze the $ZnSO_4$ solution to get directly high-purity zinc instead of reducing the ZnO by carbon to get raw metallic zinc which has to be refined.

Although extensive research has been conducted to find a hydrometallurgical process for copper, yet it seems that no satisfactory solution has been found. The situation in the copper industry is no doubt more difficult than in the zinc industry because a typical raw material for the copper industry is 30% Cu, 30% Fe, and 30% S while for a zinc industry it is 60% Zn, 30% S; the remaining 10% in both cases is usually silicate gangue minerals. That is, a zinc raw material containing usually twice as much metal value as a copper concentrate.

The advantages and disadvantages of hydrometallurgy can be outlined as follows.

Sulfur dioxide generation

During the pyrometallurgical treatment of sulfide ores, if SO_2 formed is in high enough concentration, it must be used for making acid and nearby market for this acid must be found. If the SO_2 concentration is too low for making acid, disposal methods must be found. These are available but expensive. As a result, in many cases SO_2 is simply emitted to the atmosphere. On the other hand, sulfides can be treated by hydrometallurgical methods without generating SO_2, thus the independence of sulfuric acid manufacture. The sulfide sulfur can be recovered in elemental form which can be easily stockpiled, or transported at low cost.

Material handling

In pyrometallurgical processes, the metallurgist is forced to transfer molten slags and matte from one furnace to the other in large, heavy, refractory-lined ladles. Beside the inconvenience and the cost of handling these materials, there is also the inevitable gas emission from them because they are usually saturated with SO_2 and during transfer they cool down a little resulting in decreased gas solubility hence the inconvenient working conditions. In hydrometallurgical plants, solutions and slurries are transferred by pipelines without any problem.

Energy consumption

Because of the high temperatures involved in pyrometallurgical processes, which is usually around 1200 °C, the reaction rates are high but much fuel will be needed. To make a process economical, heat recovery systems are essential. Heat can be readily recovered from hot gases, but rarely from molten material like slag or metal. Thus, a great deal of energy is lost. Further, the equipment needed for heat economy are bulky and expensive. Further, in a reverberatory furnace heat is mainly transferred from the ceiling of the furnace by radiation and has to penetrate a thick layer of slag which has a low thermal conductivity; that is why it is inefficient. In hydrometallurgical processes, on the other hand, less fuel is needed because of the low temperatures involved (usually below 100 °C). Heat economy is usually no problem, but reaction rates are iisually low.

Dust formation

Combustion of fossil fuels in reverberatory furnaces results in the formation of large volume of gases that carry over large amounts of fine dust. This must be recovered to abate pollution and because the dust itself is also a valuable material. The technology of dust recovery is well established but the equipment are bulky and expensive. In hydrometallurgical processes, this is no problem because wet material is usually handled.

Treatment of complex ores

Treatment of complex ores by pyrometallurgical method is unsuitable because separation is difficult; this is, however suitable by hydrometallurgy.

Treatment of low-grade ores

Treatment of low-grade ores by pyrometallurgy is unsuitable because of the large amount of energy required to melt the gangue minerals. On the other hand it is especially suitable by hydrometallurgy if a selective leaching agent is used.

Waste disposal

Many residues of pyrometallurgical processes are coarse and harmless. For example, slags, which are a silicate phase, can be stored in piles exposed to air and rain without the danger of dissolution and contaminating the streams. They are just unacceptable from the zsthetic point of view. On the other hand most residues of hydrometallurgical processes are finely divided solids. If they are dry, they create dust problems when the wind blows and when wet they will gradually release metal ions in solution which will contaminate the environment. However, disposal of waste solution in hydrometallurgical operations is less troublesome than disposal of gases in pyrometallurgy. Even in a pyrometallurgical process water-scrubbing of a gas before disposal will eventually have a disposal problem with that water.

Economics

The economics of a pyrometallurgical process is usually suitable for large scale operations and this requires a large capital investment. On the other hand, hydrometallurgical processes are suitable for small scale operations and therefore low capital investment. Hydrometallurgy may also fit a special need that cannot otherwise be met.

SOURCES OF INFORMATION

Monographs on general hydrometallurgy as well as on special topics have been published. Numerous symposia and conferences on certain areas of hydrometallurgy were held. Conferences on extractive metallurgy include many papers of interest to hydrometallurgists. Annual reviews on hydrometallurgy now appear regularly in *Journal of Metals* (March issue), *International Metals Reviews,* London (September issue), and other journals. Conferences on solvent extraction, ion exchange, and other separation technologies appear in the series *Recent*

Developments in Separation Science published by CRC Press in Florida. Papers on the treatment of bauxite are published annually in the series *Light Metals* by the American Institute of Mining, Metallurgical, and Petroleum Engineers. Numerous review articles on hydrometallurgy are also available. A periodical entitled *Hydrometallurgy* is being published by Elsevier Publishing House, and another entitled Solvent Extraction and Ion Exchange is published by Marcel Dekker.

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Chapter Three

Solution Chemistry

Structure of Minerals *32*
  Metallic *32*
  Ionic *33*
  Covalent *33*
  Mixed bonds *34*
Water *35*
  Structure *35*
  Ionization *35*
  Dielectric constant *37*
Solubility *38*
  General rules *38*
  Solubility product *41*
  Common ion effect and complex formation *42*
Hydration and Hydrolysis *43*
Acids and Bases *45*
Buffer Solutions *46*
Oxidation and Reduction *47*
  Electrode potential *48*
  Galvanic processes *52*
  Electrolytic processes *54*
Oxyhydrolysis *55*
Free Energy Change *56*
Coordination Compounds *58*
  Complexes *58*
  Chelates *59*
Precipitation *62*

Reacting minerals with aqueous solutions requires a knowledge of the structure of the solid as well as the aqueous phase.

STRUCTURE OF MINERALS

From the structural point of view, minerals may be classified as metallic, ionic, and covalent. While these are idealized cases, in reality, overlapping between these types are common (Figure 3.1). Further, deviations from perfect crystal occur through the presence of dislocations, defects, and impurities. These may influence the electrical properties of the crystal since electrons associated with such regions may be readily removed thus influencing reactivity. Nonstoichiometry, i.e., slight variation of the proportions of the constituent elements of a compound, may also significantly alter the electrical properties of a solid. Many sulfide and oxide minerals are nonstoichiometric compounds, e.g., FeS, ZnS, UO_2, and MnO_2.

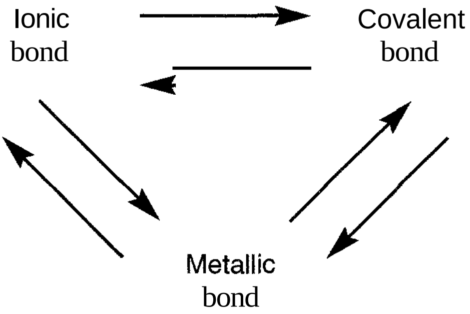


Figure 3.1: Major types of bonds in minerals and their interrelation.

Metallic

In metals, the atoms are as closely packed as possible; this results in the densest possible arrangement. There is overlapping of orbitals between neighboring atoms in the whole crystal. Thus it is possible for an electron to move from an orbital in the valence shell of one atom into a similar orbital of another atom with relative ease, and the valence electrons may be considered to be delocalized, i.e., they no longer belong to individual atoms but to the crystal as a whole. This accounts for the high electrical conductivity of metallic crystals.

Ionic

Minerals of this type contain ions which owe their stability to the tendency of certain atoms to lose electrons and others to gain them. They are held together by electrostatic forces. For example, in the NaCl crystal, every Na+ ion is surrounded by six Cl^- ions, and similarly every Cl^- ion is surrounded by six Na+ ions. Ionic bonding links each ion to all its neighbors throughout the crystal. The entire crystal is one giant ionically bonded unit. As a result, they are relatively hard, rigid, and melt as fairly high temperatures. They are not good conductors of electricity since electrons are strongly held within the ions. When, however, these solids are dissolved in water or melted, the ions become able to move about independently, and the solution or the molten substance is a conductor of electricity. Ionic crystals fracture with some difficulty because of the relatively strong forces of attraction, and when they do, fracture occurs along a plane of ions in the crystal and the same geometrical features are reestablished.

Covalent

Minerals belonging to this group are held together by shared electron bond or covalent bond. They are of two types: minerals formed of discrete units and the network structure.

Discrete units. In this type of minerals, the atoms are arranged in small units; no chemical bonding forces extend beyond these single units. Consequently intermolecular forces in these minerals are weak; they are soft, low-melting and have low heats of vaporization. For example, in solid elemental sulfur, each sulfur atom is bonded to two neighbors to form eight-membered rings: sulfur is fragile and has a low melting point (about 120 °C).

***Network** structure.* In these minerals the bonds extend throughout the whole solid. They are consequently hard, stable, generally insoluble, and cannot easily be broken into smaller units. For example, in silica, SiO_2, the silicon atom occupies the center of a tetrahedron sharing electrons with four oxygen atoms each situated at the apex of this tetrahedron and all four atoms in the tetrahedron are shared with other similar tetrahedra resulting in a three dimensional structure. Any fracture requires that many of these chemical bonds be broken. Feldspars is a group of silicate minerals that result from the substitution of aluminum for some of the silicon.

Mixed bonds

There are many systems which appear to be of types intermediate between true metallic and true covalent bonds and between true metallic and true ionic bonds.

Metallic–ionic. Many of the familiar minerals like galena, sphalerite, and chalcopyrite, exhibit the properties characteristic of metals: lustre, opacity, electrical conductivity. The electrical conductivity, however, is much less than that in metals — that is why it is called semiconductivity. It is the result of a restrictive movement of electrons in the lattice due to structural defect.

Covalent–ionic. An ionic bond may be partially covalent and vice versa a covalent bond may be partially ionic. For example, silver chloride is a predominantly ionic crystal but the electrons of the chloride ions are not all localized about the chlorine nucleus and may spend a small part of the time about the silver nucleus. Since these electrons are shared to some extent between the two ions, the bond between the two ions is partially covalent and as a result it will be stronger than the simple ionic bond as, for example, in sodium chloride. This explains its insolubility in water. There are also minerals which are bond together both ionically and covalently. Thus in carbonates, the bond between carbon and oxygen is covalent while that between carbon and the metal ion is ionic. Enstatite, $Mg_2(Si_2O_6)$, consists of a silicate chain in which the silicon is covalently bonded to oxygen (silicon in the center of a tetrahedron) while magnesium is present in the crystal as ions. Such a crystal is held together simultaneously by the covalent bond within the $(Si_2O_6)^{2-}$ anions and the electrostatic attraction of the negative charge on these anions for the positive charge on the cations.

Metallic–covalent. Pyrite, FeS_2, may be considered to be a metallic–covalent bond mineral. It has a metallic luster, a cubic structure like NaCl with Fe^{2+} ions occupying the positions of Na^+, and with S_2^{2-} groups occupying the position of Cl^-. The disulfide ion is covalent in nature.

WATER

Structure

In the water molecule, the hydrogen nuclei do not lie on a straight line but are at the corners of a triangle (Figure 3.2). Beside the covalent bonds, between the oxygen and hydrogen nuclei, there are two lone pairs of electrons in the outer shell of the oxygen atom. An important consequence of the arrangement of electrons in the water molecule is that the molecule is *polar*, i.e., the center of positive and negative charges do not coincide. One positive charge resides in each hydrogen nucleus, and eight in the oxygen nucleus; the center of positive charge is thus somewhat below the oxygen nucleus. The center of negative charge is higher for two reasons:

- The negative charge carried by the lone pair of electrons is localized largely above the oxygen nucleus.
- There is a displacement of electrons in the bonds towards the more electronegative oxygen atom.

As a result of the high polarity of the water molecules, hydrogen bonding takes place between the dipoles of the water molecules themselves (Figure 3.2). Each water molecule forms four hydrogen bonds with the other surrounding molecules. Hydrogen bonds are weak; on heating, increased molecular vibrations are enough to break them at the boiling point. On cooling, water freezes to form ice crystals which have hexagonal structure.

Ionization

Pure water is a poor conductor of electricity. The feeble conductance is the result of the polarity of water and the association of the H_2O molecules through hydrogen bridges. If a water molecule is split into H^+ and OH–, the H^+ ion is so small, is unprotected by an electron shell, and therefore cannot exist alone; it will be attached to other H_2O molecule at the lone pair of electrons to form H_3O^+ — a hydronium ion:

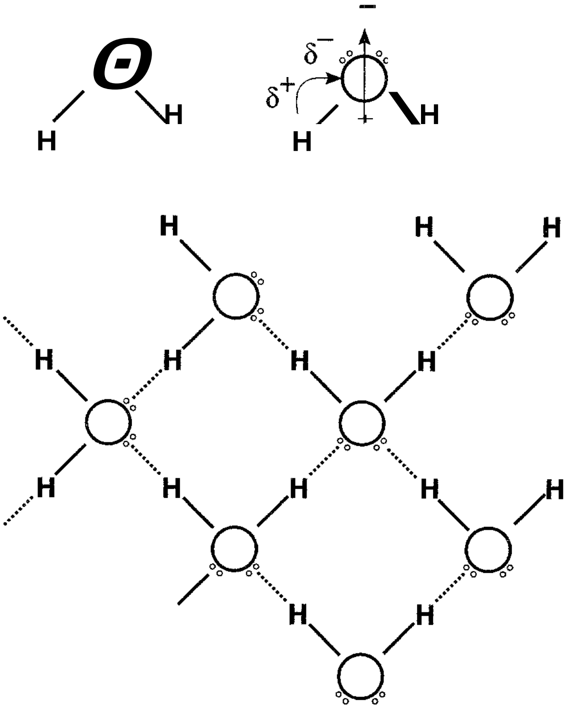
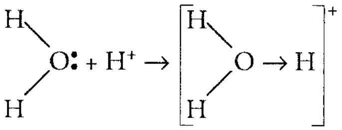


Figure 3.2: The polarity of water and the formation of hydrogen bond.



The bond between O and H represented by an arrow is called a dative or coordinate bond since it is furnished by the lone pair of electrons on the oxygen atom. The number of H^+ and OH– ions are very small and the equilibrium constant for the reaction:

$$H_2O \rightleftharpoons H^+ + OH-$$

at room temperature is given by:

$$K = [H^+][OH^-] = 10^{-14}$$

It increases with increasing temperature as shown in Table 3.1. The reverse reaction is the neutralization of an acid with a base; it is a very fast reaction.

Table 3.1: Ionization constant of water at different temperatures.

Temperature [°C]	$K_w \times 10^{14}$
0	0.1139
10	0.2920
20	0.6809
25	1.008
30	1.469
37	2.57
40	2.919
50	5.474
60	9.614
70	15.1
80	23.4
90	35.5
100	51.3
300	400

Dielectric constant

Water has a high dielectric constant. The dielectric constant of a substance is a measure of the ability of that substance to neutralize an applied electric field. An electric field can be neutralized by orienting the molecules of a substance so that their positively charged ends face the negative pole of the electric field (which means that their negatively charged ends face the positive pole of the field). The degree to which the electric field is neutralized is related directly to the polarity of the substance (Figure 3.3). Polar substances thus have relatively high dielectric constants. The dielectric constant of a vacuum is 1, and the dielectric constant of air is close to 1. The dielectric constant of water has a high value — about 80. The polarity of water and the formation of hydrogen bonds are responsible for this high value. This plays an important role in explaining the solubility of ionic salts in water, the behavior of ion exchange resins, and extraction by organic solvents as explained later.

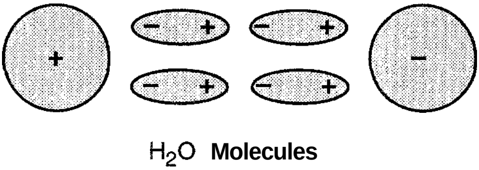


Figure 3.3: Orientation of polar molecules in an electric field.

SOLUBILITY

Solubility of any substance in water is related to the polarity of water and the association of water molecules together by forming hydrogen bonds.

General rules

Aqueous solutions are produced by dispersal of a substance in water to give a homogeneous mixture without chemical reaction, i.e., without breaking of bonds or transfer of electrons. The general rules of solubility are the following:

Gases. Small molecules like oxygen, O_2, or hydrogen, H_2, dissolve in water by fitting into the holes or gaps in the water structure. Solubility of these molecules is small and decreases with increased temperature because of the weak forces holding these molecules.

Polar and nonpolar molecules. Polar molecules like acetone or alcohol, and bases like NH_3 dissolve in water by forming hydrogen bonds as shown in Figure 3.4. Solubility also decreases with increased temperature because of the weakness of such bond with respect to thermal vibrations. Anhydrous acid like HCl, which is also a polar molecule, dissolves in water with interaction forming H_3O^+ and Cl^-. Nonpolar molecules like carbon tetrachloride, CCl_4, or benzene, C_6H_6, are insoluble in water because of the inability of water to form hydrogen bonds with these molecules.

Ionic and non-ionic crystals. Ionic crystals dissolve in water for two reasons (Figure 3.5):

- The weakening of the electrostatic forces of attraction in an ionic crystal (the lattice energy) as a result of the presence of the highly polar water molecules. The high dielectric constant of water means that the attractive forces between the anions and cations in a salt are reduced by a factor of SO when water is the medium between them.

- The tendency of ions in the crystal to hydrate.

On the other hand, non-ionic crystals such as metals (metallic bond) or covalent crystals like quartz, SiO_2, are insoluble because of the inability of water molecules to weaken the strong metallic or covalent bonds holding the atoms together in the crystal.

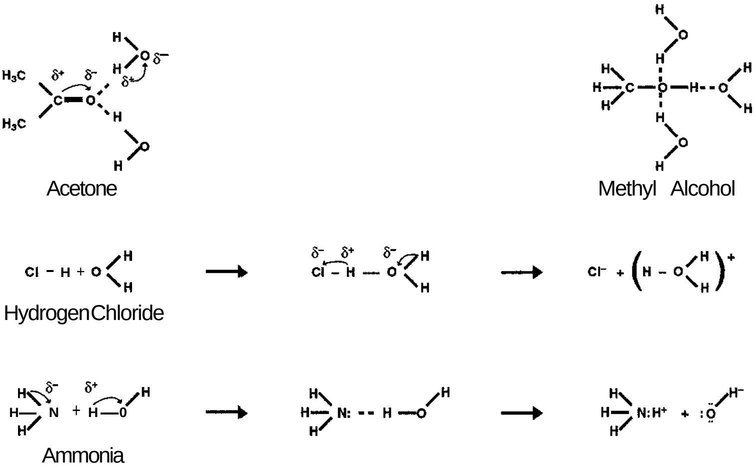


Figure *3.4:* Dissolution of polar molecules in water.

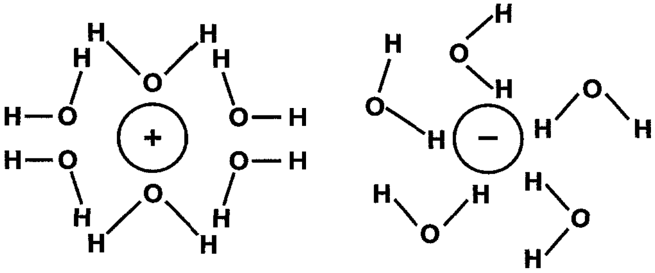


Figure 3.5: Hydration of ions during the dissolution of ionic crystals in water.

Effect of organic solvents. The addition of an organic solvent to an aqueous solution of an electrolyte usually lowers the solubility of the solutes, because the dielectric constant of the medium is decreased and this strengthens the forces between the ions. For example, the addition of acetone (dielectric constant = 20) to ferrous sulfate solution results in the precipitation of $FeSO_4 \cdot nH_2O$ because acetone has a lower dielectric constant than water.

Effect of interionic forces. Slightly soluble electrolytes are more soluble in solutions of foreign salts than in pure water. In dilute solutions the ions are free apart and are not influenced by one another. In concentrated solutions, however:

- Any ion is surrounded more closely by ions of opposite sign.
- The electrostatic interactions are stronger because the ions are close together.

Table 3.2: Solubility data of simple metallic compounds in water.

Compound	Soluble	Slightly soluble	Insoluble
Nitrates	All	—	—
Chlorides	All with few exceptions	$PbCl_2$ (in cold water)	AgCl HgCl CuCl TlCl
Sulfates	All with few exceptions	$CaSO_4$ Hg_2SO_4 Ag_2SO_4 $PbSO_4$	$BaSO_4$ $SrSO_4$ $RaSO_4$
Sulfides	Alkali metals	—	All others, some hydrolyze and precipitate as hydroxides, e.g., Al and Cr sulfides.
Hydroxides	Alkali metals	$Ca(OH)_2$ $Sr(OH)_2$ $Ba(OH)_2$	All others
Carbonates	Alkali metals except Li_2CO_3	Li_2CO_3	All others
Phosphates	Alkali metals, some acid phosphates $Ca(H_2PO_4)_2$	—	All others
Fluorides	Alkali metals except LiF InF, TlF BeF_2, CdF_2, ZnF_2	LiF	All others
Silicates	Alkali metals	—	All others

Table 3.2 gives the general rules for the solubility of solids: nitrates, chlorides, sulfides, hydroxides, etc.

Solubility product

Dissolution processes are heterogeneous and its difference from homogeneous processes may be emphasized from the following example. In the homogeneous process **AB** * **A + B,** the decomposition of ammonia to nitrogen and hydrogen, the rate of the forward reaction V_1 is proportional to the concentration of **AB** while that of the reverse reaction V_2 is proportional ro both **A** and **B.** This can be expressed as:

$$V_1 = k_1[\mathrm{AB}]$$

$$V_2 = k_2[\mathrm{A}][\mathrm{B}]$$

where k_1 and k_2 are the velocity constants of the forward and reverse reactions, respectively. **At** equilibrium, the two rates are equal. Therefore, $V_1 = V_2$, or:

$$\frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{AB}]} = \frac{k_1}{k_2} = K$$

where Kis known as the equilibrium constant.

Consider now the dissolution of a finely divided sparingly soluble salt AB in water which dissociates into ions A^+ and B^-. The rate of dissolution (forward reaction) will depend on the surface area of the salt which is related to its amount. Once the solution becomes saturated, dissolution stops because the rate of recrystallization equals that of dissolution. At equilibrium, one can write:

$$\frac{[\mathrm{A}^+][\mathrm{B}^-]}{[\mathrm{AB}]} = \frac{k_1}{k_2} = K$$

Since the amount of **AB** does not influence the degree of saturation, it can be considered constant. Hence:

$$K_{\mathrm{sp}} = [\mathrm{A}^+][\mathrm{B}^-]$$

where $K_{\mathrm{sp}} = k[\mathrm{AB}]$ = the solubility product. The subscript may be **also** ignored and still signifies the solubility product.

Tables of solubility products of compounds are available and these are determinated from solubility data. For example:

- The solubility of CuCl in water is 0.042 g/L at 20 "C, i.e., the saturated solution contains 0.042/99 g ion/L Cu^+ and an equal amount of Cl^- (atomic weight of CuCl = 99). Hence:

$$K = [Cu^+][Cl^-] = \frac{0.042}{99} \times \frac{0.042}{99} = 1.8 \times 10^{-7}$$

- For $PbCl_2$, the solubility in water is 6.37 g/L at 0 "C, i.e., at equilibrium,

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

the saturated solution contains 6.371278 g ion/L Pb^{2+} and 2 x 6.371 278 g ion/L Cl^-. Hence:

$$K = [Pb^{2+}][Cl^-]^2 = \frac{6.37}{278} \times \left(2 \times \frac{6.37}{278}\right)^2 = 4.8 \times 10^{-5}$$

And vice versa, knowing the solubility product of a substance, its solubility can be determined. For example, the solubility product of $Mg(OH)_2$ in water is given by $K_{sp} = 8.9 \times 10^{-12}$.

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

$$K = [Mg^{2+}][OH^-]^2 = x(2x)^2 = 8.9 \times 10^{-12} \text{ mole3}$$

$$x = 1.3 \times 10^{-4} \text{ mole} = 1.3 \times 10–4 \times 58.3 \text{ g/L}$$

$$= 7.58 \times 10^{-3} \text{ g/L}$$

Common ion effect and complex formation

The solubility changes as a result of the presence of other ions in solution:

- It decreases as a result of the common ion effect.
- It increases as a result of complex formation.

This is illustrated for the case of the solubility of AgCl (Figure 3.6). The slight decrease of solubility at low HCl concentration is due to the presence of Cl^- ion as a common ion:

$$AgCl_{(s)} \rightleftharpoons Al^+ + Cl^- \qquad K = [Ag^+][Cl^-]$$

When $[Cl^-]$ is increased, then $[Ag^+]$ must decrease to keep the value of Kconstant; hence the reaction shifts to the left. The increased solubility at high HCl concentration is due to the formation of a complex ion:

$$Ag^+ + 4Cl^- \rightleftharpoons [AgCl_4]^{3-}$$

In this case, the concentration of the uncomplexed silver ion, $[Ag^+]$, is decreased. To keep the value of Kconstant, the equilibrium shifts to the right favoring more dissolution of AgCl to take place.

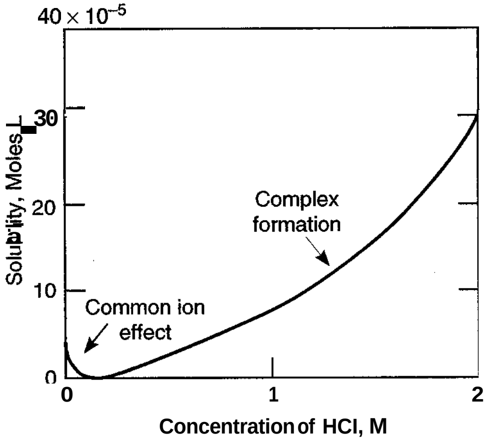


Figure 3.6: Solubility of AgCl in dilute hydrochloric acid.

HYDRATION AND HYDROLYSIS

Ions in aqueous solutions are hydrated, i.e., they are surrounded by water molecules because of the polarity of water. Cations usually are more hydrated than anions because of their small size and hence a more concentrated charge that can attract more H_2O molecules (Table 3.3). Hydration of ions is determined electrolytically by measuring the transference number.

Hydrated ions have the tendency to lose H^+ or OH– ions — a process called *hydrolysis,* which may be represented by the general equation:

$$[M(H_2O)_n]^{a+} \rightleftharpoons [M(H_2O)_{n-1}OH]^{(a-1)+} + H^+$$

Table 3.3: Water of hydration in solution.

Cation	Number of water of hydration	Anion	Number of water of hydration
Rb^+	2		
K^+	2–3		
Ag^+	3–4	ClO_4^-	0
H^+	4	I^-	0–1
Na+	4	Br^-	2
Pb^{2+}	5–7	NO_3^-	2
Li^+	**6**	Cl^-	3
Ba^{2+}	6–8	F^-	5
Ca^{2+}	8–10		
Mg^{2+}	9–13		
Cd^{2+}	10–12		
Zn^{2+}	11–13		
Fe^{2+}	11–13		
Cu^{2+}	11–13		
Al^{3+}	≈ 20		

or simply:

$$M^{a+} + H_2O \rightleftharpoons M(OH)^{(a-1)+} + H^+$$

For example, ferric ion hydrolyses according to:

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$$

Anions also undergo hydrolysis:

$$[X(H_2O)_m] \rightleftharpoons [X(H_2O)_{m-1}(H)]^{(b-1)-} + OH-$$

or simply:

$$X^{b-} + H_2O \rightleftharpoons XH^{(b-1)-} + OH-$$

For example, cyanide ion hydrolyses according to:

$$CN^- + H_2O \rightleftharpoons HCN + OH-$$

For cations having more than three positive charges, oxy- or hydroxy- ions are formed. For example, Ti^{4+}, V^{5+}, and U6+ exist only in aqueous solution as titanyl, vanadyl, and uranyl ions respectively:

$$Ti^{4+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+$$

$$V^{5+} + H_2O \rightleftharpoons VO^{3+} + 2H^+$$

$$U^{6+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+$$

An exception is thorium and uranium(IV) which can exist as Th^{4+} and U^{4+}, respectively. These oxy-ions may react further with water, depending on the pH, to form hydroxy- ions. For example:

$$TiO^{2+} + H_2O \rightleftharpoons TiO(OH)^+ + H^+$$

$$VO^{3+} + H_2O \rightleftharpoons VO(OH)^{2+} + H^+$$

$$UO_2^{2+} + H_2O \rightleftharpoons UO_2(OH)^+ + H^+$$

The tendency for an ion to hydrolyze depends on:

- The ratio of ionic charge to radius, i.e., the charge density. The more dense the charge the more hydrolysis takes place and vice versa. Thus, while the hydrolysis of the alkali and alkaline earth ions is negligible, that of Ti^{4+} and V^{5+} is appreciable.
- The electronic structure. Ions with inert gas structure have a minimum tendency to hydrolyze. Thus Ag^+ and Pb^{2+} hydrolyze easier than Ba^{2+} and Sr^{2+}; and Fe^{3+}, Co^{3+}, and Cr^{3+} much easier than Al^{3+}.

ACIDS AND BASES

Acids and bases are common reagents in hydrometallurgy. An acid is a substance that dissociates in water to produce hydrogen ions. A base is a substance that dissociates in aqueous solution to form the hydroxyl ion. In more general terms an acid is a substance that can give up a proton, and base is a proton acceptor. The acidity or basicity of a solution is defined by the pH scale which is a highly convenient scale:

$$pH = -\log[H^+]$$

A pH 7 means that the hydrogen ion concentration in the solution = 10^{-7} gram ion/liter. The pH of 0.1 M HCl *(3.75* g/L or *0.44%)* equals 1 and that of 0.1 M NaOH *(4* g/L or *0.48%)* equals 13 (Table *3.4).*

An amphoteric substance is a substance that dissolves in both acid and base. For example, aluminum hydroxide:

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$$

Table 3.4: pH values of hydrochloric acid and sodium hydroxide solutions.

pH	% HCl	pH	% NaOH
0.00	4.3	8.00	4.0×10^{-6}
0.10	3.6	9.00	4.0×10^{-5}
0.36	1.8	10.00	4.0×10^{-4}
1.00	0.44	11.00	4.0×10^{-3}
2.00	0.036	12.00	0.040
3.00	3.6×10^{-3}	13.00	0.48
4.00	3.6×10^{-4}	13.60	2.0
5.00	3.6×10^{-5}	13.90	3.8
6.00	3.6×10^{-6}	14.00	4.6
7.00	pure water		

BUFFER SOLUTIONS

In many hydrometallurgical processes it is important that the pH not deviate very much from a certain value. This is normally achieved by adding a buffer solution to the system so that when an acid or a base is added, the pH does not change considerably. The buffer solution is a mixture of a weak acid and any of its salts, e.g., acetic acid and sodium acetate. The reason for this is the following. The ionization of acetic acid is given by:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[H^+] = K\frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$pH = -\log K - \log\frac{[CH_3COOH]}{[CH_3COO^-]}$$

When the ratio $[CH_3COOH]/[CH_3COO^-] = 1$, then:

$$pH = -\log K = -\log(1.8 \times 10^{-3}) = 4.74$$

If a small amount of a strong acid is added to such a solution, some of the acetate ion is converted to acetic acid; if a base is added, some of the acetic acid is converted to acetate ion. In either case, the ratio $[CH_3COOH]/[CH_3COO^-]$ changes slightly from unity and the pH changes even less. For example, let us calculate the pH of a solution made by adding 0.001 mole of NaOH to 100 ml of 0.5 M CH_3COOH and 0.5 M CH_3COONa.

100 ml of the solution contains 0.05 mole CH_3COOH and 0.05 mole CH_3COONa. When 0.001 mole of NaOH is added to this solution, it will convert an equivalent amount of acetic acid into sodium acetate. This gives 0.049 mole of acid and 0.051 mole of acetate ion in the final solution. The respective concentrations will be 0.49 M and 0.51 M, and the pH is:

$$pH = -\log(1.8 \times 10^{-3}) - \log\frac{0.49}{0.51} = 4.74 + 0.017 = 4.76$$

Thus, the pH changed from 4.74 to 4.76. In contrast, when 0.001 mole of NaOH is added to 100 ml of water, the pH becomes 10.

OXIDATION AND REDUCTION

Oxygen is a readily available gas that is responsible for many reactions in everyday life. The addition of oxygen to an atom, ion, or molecule is known as oxidation reaction, and reduction as the reverse reaction, i.e., the removal of oxygen from a system. For example, a metal heated in air is oxidized. When the oxide is heated with carbon, it is reduced because the oxygen is removed from the oxide. In more general terms, oxidation is the removal of electrons from an atom or group of atoms, and reduction is the addition of electrons to an atom or group of atoms. Typical oxidation reactions in aqueous systems are:

$$S^{2-} + 20, \rightarrow \text{sei-}$$

$$Fe + Fe^{2+} + 2e^-$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

Typical reduction reactions are:

$$2H^+ + 2e^- \rightarrow H_2$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

The reduction of oxygen in solution is of particular importance in hydrometallurgy since it plays a dominant role in many reactions. In alkaline medium, the following reaction takes place:

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

and in acid medium:

$${}^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Hydrogen at high temperature and pressure is a powerful reducing agent and is used to precipitate metals from aqueous solutions, e.g., nickel:

$$Ni^{2+} + H_2 \rightarrow Ni + 2H^+$$

Oxidation and reduction reactions take place simultaneously. Thus in the dissolution of iron in acid, iron is oxidized and the hydrogen ions are reduced:

$$Fe \rightarrow Fe^{2+} + 2e-$$

$$2H^+ + 2e- \rightarrow H_2$$

Electrode potential

The tendency of a substance to be oxidized or reduced, i.e., to lose or gain electrons, is measured in volts and is known as *potentid.* For example, when a strip of zinc is immersed in a 1 M $ZnSO_4$ solution and a strip of copper in a 1 M $CuSO_4$ solution and the *two* strips are connected by a wire and the solutions by a salt bridge to avoid mixing as shown in Figure 3.7, it will be seen that the voltmeter will indicate 0.78 volt. Zinc will dissolve in the zinc sulfate compartment and copper will deposit in the copper sulfate compartment. Electrons liberated from the zinc electrode are transferred through the wire to the copper electrode, and sulfate ions diffuse slowly from the $CuSO_4$ to the $ZnSO_4$ solution through the salt bridge to complete the electric circuit.

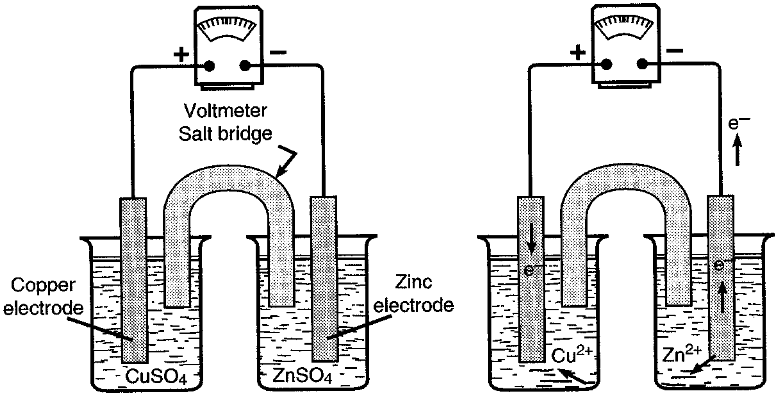


Figure 3.7: Flow of electrons between two different metals immersed in an electrolyte and connected by a wire.

By convention, the standard electrode potential for the reaction of hydrogen ion is taken as zero, i.e., the tendency of H^+ ion to gain an electron at ambient conditions for a normal solution is taken as a basis of reference for other reactions. Any reaction involving transfer of electrons can be conducted in an electrochemical cell and its potential measured.

Effect of concentration. The electrode potential varies with concentrations. The standard state is taken at one-molar solutions at ambient conditions and in this case, the potential measured is known as the *standard electrode potential* and is denoted by E^0. The potential, E, measured at any other concentration, is related to the standard potential by Nernst's equation:

$$E = E^0 - \frac{RT}{n\mathcal{F}} \ln[M^{n+}]$$

where R is the gas constant = 8.31441 joule/kelvin·mole, T in degrees Kelvin, and $\mathcal{F}$ is the faraday constant (1 faraday = 96 500 ampere-second ot 96 500 coulombs). For a hydrogen electrode at room temperature:

$$E = -\frac{RT}{n\mathcal{F}} \ln[H+] = \frac{8.314 \times 298 \times 2.303}{1 \times 96\,500} \ln[H^+]$$

$$= 0.0592\ \mathrm{pH}$$

since $pH = -\log[H^+]$.

Effect of pH. For reactions involving hydrogen ions, the electrode potential will be dependent on the pH. This can be illustrated by the Pourbaix Diagrams (after their inventor). Figure 3.8 shows, for example, the stability of iron in different environment. In acid medium and in a reducing atmosphere, ferrous ion is formed. At high oxidizing atmosphere, Fe^{3+} ion is formed. In basic medium and in a reducing atmosphere, $Fe(OH)_2$ is formed. Ferric hydroxide forms in highly oxidizing conditions even at a pH as low as 1.8. Similar diagrams are available for a variety of metals and compounds.

Electrode potential and free energy. For reactions involving a loss or gain of electrons, the electrode potential represents the maximum work done by an electrochemical cell. The quantity of electricity supplied per equivalent of substance reacting is one faraday and for n equivalents reacting, the quantity of electricity is $n\mathcal{F}$.

$$\text{Work}_{,,} = -AF = -n\mathcal{F}E$$

where AF is the free energy charge. At the standard states:

$$\Delta F^0 = -n\mathcal{F}E^0$$

Since the standard free energy change is related to the equilibrium constant K, by the relation:

$$\Delta F^0 = -RT\ln K$$

it follows that:

$$RT\ln K = n\mathcal{F}E^0$$

$$\log K = \frac{n\mathcal{F}E^0}{2.303RT}$$

The gas constant $R = 1.987$ calorie/degree.

The electrochemical series. It is found further that if a piece of one metal is put into a solution containing ions of another metal, the first metal may dissolve, i.e., oxidize, and the second metal deposits, i.e., reduced. For example, a strip of iron placed in a solution of $CuSO_4$ causes metallic copper to deposit as the iron goes into solution:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

The overall reaction:

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$

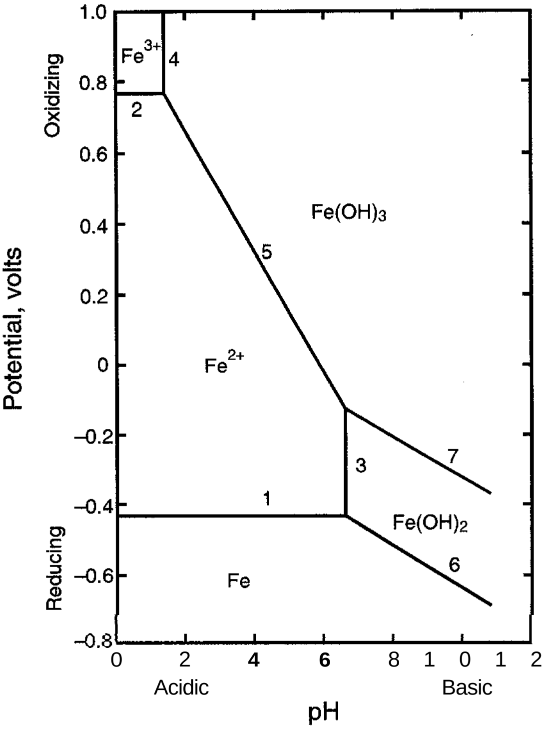


Figure 3.8: The solubility of iron as a function of pH and the potential.

Data for Figure *3.8:*

1. $Fe^{2+} + 2e^- \rightleftharpoons Fe$, $E^0 = -0.44$ V (independent of pH)
2. $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$, $E^0 = 0.77$ V (independent of pH)
3. $Fe(OH)_2 \rightleftharpoons Fe^{2+} + 2OH^-$, $\log K = -14.8$; at $[Fe^{2+}] = 1$, pOH = *7.4;* pH = *6.6* (independent of E)
4. $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$; $\log K = -37.4$, at $[Fe^{3+}] = 1$, pOH = 12.5, pH = *1.5* (independent of E)
5. $Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O$, at $[Fe^{2+}] = 1$, from $1.5 < pH < 6.6$, $E = 0.77 - 3 \times 0.0591(pH - 1.5)$
6. $Fe(OH)_2 + 2H^+ + 2e- \rightleftharpoons Fe + 2H_2O$; at $pH > 6.6$, $E = -0.44 - 0.0591(pH - 6.6)$
7. $Fe(OH)_3 + H^+ + e^- \rightleftharpoons Fe(OH)_2 + H_2O$; at $pH > 6.6$, $E = -0.0134 - 0.0591(pH - 6.6)$

On the other hand, a strip of metallic copper in a ferrous sulfate solution will not precipitate iron but in a $AgNO_3$ solution it will precipitate silver:

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$$

Metals can therefore be arranged according to their ability to reduce ions of other metals (Table 3.5). The metal with the greatest reducing power is at the top of the list; it is able to reduce the ions of all the other metals below. The standard reference point in this table is the reduction of hydrogen ions taken as zero.

Galvanic processes

The electric potential that develops between two different metals and results in one metal being dissolved and the other being precipitated as mentioned above is called a galvanic process after Luigi Galvani, the Italian scientist who discovered electric current. A similar situation will exist when two pieces of the same metal are immersed in a solution of its ions — an electric current will flow under the following conditions:

- When each solution has a different ionic concentration. For example, when a piece of iron immersed in a solution of $FeSO_4$ of low concentration is connected to a similar piece immersed in a solution of $FeSO_4$ of high concentration, it will be observed that iron in the first solution will dissolve while Fe^{2+} ion in the second solution will precipitate (Figure 3.9). Iron in the first solution acted as an anode while that in the second solution acted as a cathode:

  Anode: $Fe \rightarrow Fe^{2+} + 2e-$

  Cathode: $Fe^{2+} + 2e^- \rightarrow Fe$

The process will continue until the two solutions become of equal concentration. The reason is that the electrode potential in each compartment is different (Nernst's equation), hence an electric current will flow.

Table 3.5: Electrochemical series of metals.

Group	Metals	E^0 [volts]
Reactive metals	Lithium	+3.045
	Potassium	+2.925
	Calcium	+2.870
	Sodium	+2.715
	Lanthanum	+2.52
	Cerium	+2.48
	Magnesium	+2.37
	Yttrium	+2.37
	Scandium	+2.08
	Thorium	+1.90
	Beryllium	+1.85
	Uranium	+1.80
	Hafnium	+1.70
	Aluminum	+1.66
	Titanium	+1.63
	Zirconium	+1.53
	Manganese	+1.19
	Vanadium	+1.18
	Chromium	+0.86
Less reactive metals	Zinc	+0.763
	Gallium	+0.53
	Iron	+0.440
	Cadmium	+0.403
	Indium	+0.335
	Thallium	+0.335
	Cobalt	+0.277
	Nickel	+0.250
	Tin	+0.140
	Lead	+0.126
	Hydrogen	0.00
Least reactive metals (noble)	Copper	−0.337
	Mercury	−0.789
	Silver	−0.799
	Platinum-group metals	−0.8 to −1.2
	Gold	−1.50

- When each solution has the same ionic concentration but different oxygen concentration. A galvanic current will also flow between the two pieces of iron if they are immersed in solutions of $FeSO_4$ of the same concentration but in one nitrogen gas was bubbled through while in the other, oxygen was bubbled. The oxygen concentration in each solution is different, hence the following reactions will take place: At low O_2 concentration, iron will function as an anode:

$$Fe \rightarrow Fe^{2+} + 2e-$$

while at high O_2 concentration, iron will function as a cathode on which oxygen will be reduced:

$$^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

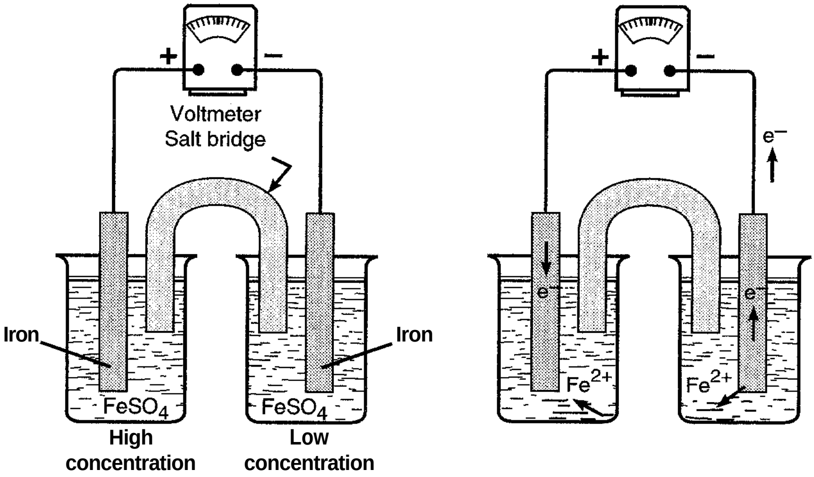


Figure 3.9: Flow of electrons between two strips of the same metal due to different concentration of electrolytes.

Electrolytic processes

Oxidation and reduction may be conducted by imposing an EMF from a direct current source. For example, a metal can be oxidized when made anode in a circuit:

$$M \rightarrow M^{n+} + ne-$$

and the reverse takes place, i.e., a metal ion in solution can be reduced at an inert cathode. In both cases Faraday's laws apply, i.e., the quantity of electricity theoretically required to oxidize 6.02×10^{23} monovalent atoms or reduce the same number of monovalent ions is equal to one faraday which represents the flow of 6.02×10^{23} electrons. For higher valency atoms or ions a corresponding multiple of faradays will be required. One faraday equals 96 500 coulombs, or 96 500 ampere second[1].

Example: To calculate the weight of nickel deposited from a $NiCl_2$ solution when a current of *0.4* ampere flows for 2.5 hours:

$$\begin{array}{ccccc} Ni^{2+} & + & 2e^- & \rightarrow & Ni \\ & & 2 \times 6.02 \times 10^{23} \text{ electrons} & & 6.02 \times 10^{23} \text{ atoms} \\ & & 2\mathcal{F} & & 58.7\,g \\ & & 2 \times 96\,500 \text{ coulombs} & & 58.7\,g \\ & & 0.4 \times 2.5 \times 60 \times 60 \text{ coulombs} & & x \end{array}$$

$$x = \frac{58.8 \times 0.4 \times 2.5 \times 60 \times 60}{2 \times 96\,500} = 1.094\,g$$

OXYHYDROLYSIS

Oxidation of a divalent metal ion in solution requires acid:

$$M^{2+} \rightarrow M^{3+} + e^-$$

$$^1/_2O_2 + 2H^+ + 2e^- + H_2O$$

Overall reaction:

$$2M^{2+} + 2H^+ + {}^1/_2O_2 \rightarrow 2M^{3+} + H_2O$$

On the other hand, hydrolysis of a trivalent metal ion in solution regenerates acid:

$$M^{3+} + H_2O \rightarrow M(OH)^{2+} + H^+$$

$$M(OH)^{2+} + H_2O \rightarrow M(OH)_2^+ + H^+$$

$$M(OH)_2^+ + H_2O \rightarrow M(OH)_3 + H^+$$

Overall reaction:

$$M^{3+} + 3H_2O \rightarrow M(OH)_3 + 3H^+$$

---

[1] Quantity of electrons = Rate of flow × Time
1 coulomb = 1 ampere x 1 second
$6.02 \times 10^{23}/96\,500$ electrons = 6.23×10^{18} electrons/second ¥ 1 second

Oxyhydrolysis is oxidation accompanied by hydrolysis. By combining the above two overall reactions:

$$2M^{2+} + {}^{1}/_{2}O_2 + 5H_2O \rightarrow 2M(OH)_3 + 4H^+$$

it can be seen that the process generates acid. For volatile acids like HCl, the process can be made to go to completion by distilling off the acid, thus shifting equilibrium to the right. This is the basis of recovering HCl from $FeCl_2$ solutions:

$$2FeCl_2 + {}^{1}/_{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 4HCl$$

In the case of nonvolatile acids like H_2SO_4 this is only possible at high temperature which renders the process uneconomical.

FREE ENERGY CHANGE

Free energy data and standard electrode potentials are available in Tables from which it is possible to calculate the free energy change and hence the equilibrium constant for reactions. Free energy of the elements at their standard states is taken as zero by convention, and similarly that for H^+ ions. Examples of calculations:

- The equilibrium constant for the reaction:

$$Cu^{2+} + Fe \rightleftharpoons Cu + Fe^{2+}$$

can be calculated in two ways:

1. *Standard free energy change data:*

$$\Delta F^0_{\text{reaction}} = \Delta F^0_{\text{products}} - \Delta F^0_{\text{reactants}}$$
$$= (0 - 20.3) - (15.5 + 0) = -35.8 \text{ kcal}$$

$$\log K = -\frac{\Delta F^0}{2.303RT} = \frac{35\,800}{2.303 \times 1.987 \times 298} = 26.25$$

$$K = 1.78 \times 10^{26}$$

2. *Standard electrodepotential data:*

Oxidation: $Fe \rightarrow Fe^{2+} + 2e-$ $E^0 = 0.44$ V

Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = 0.34$ V

$$E^0_{\text{reaction}} = E^0_{\text{oxidation}} + E^0_{\text{reduction}}$$
$$= 0.44 + 0.34 = 0.78 \text{ V}$$

$$\log K = \frac{n\mathcal{F}E^0}{2.303RT} = \frac{2 \times 96\,500 \times 0.78}{2.303 \times 8.314 \times 298} = 26.38$$

$$K = 2.4 \times 10^{26}$$

- The equilibrium for the reaction:

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S$$

can be similarly calculated in two ways.

1. *Standard free energy change data:*

$$\Delta F^0_{\text{reaction}} = \Delta F^0_{\text{products}} - \Delta F^0_{\text{reactants}}$$
$$= [15.5 + (2 \times -20.3) + 0] - [-11.7 + (2 \times 2.52)]$$
$$= -8.4 \text{ kcal}$$

$$\log K = \frac{\Delta F^\circ}{2.303RT} = \frac{8400}{2.303 \times 1.987 \times 298} = 6.176$$

$$K = 1.5 \times 10^6$$

2. *Standard electrodepotential data*:

The above reaction can be divided into the following steps:

$$CuS_{(s)} \rightleftharpoons Cu^{2+} + S^{2-} \qquad K_1 = [Cu^{2+}][S^{2-}] = 8 \times 10^{-36}$$

$$S^{2-} \rightarrow S + 2e^- \qquad E^0 = 0.48 \text{ V}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^0 = 0.77 \text{ V}$$

$$2Fe^{3+} + S^{2-} \rightleftharpoons 2Fe^{2+} + S \qquad E^0 = 0.48 + 0.77 = 1.25 \text{ V}$$

$$\log K_2 = \frac{n\mathcal{F}E^0}{2.303RT} = \frac{2 \times 96\,500 \times 1.25}{2.303 \times 8.314 \times 298} = 41.6$$

$$K_2 = 1.3 \times 10^{41} = \frac{[Fe^{2+}]^2}{[Fe^{3+}]^2[S^{2-}]}$$

For the reaction:

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S$$

$$K = \frac{[\mathrm{Cu}^{2+}][\mathrm{Fe}^{2+}]^2}{[\mathrm{Fe}^{3+}]^2} = K_1K_2$$

$$= 8 \times 10^{-36} \times 1.3 \times 10^{41} = 1.4 \times 10^{6}$$

COORDINATION COMPOUNDS

Coordination compounds result from a donor–acceptor mechanism. A donor is any nonmetallic atom or ion, whether free or contained in a neutral molecule or in an ionic compound which can donate an electron pair. The acceptor is frequently a metallic ion which accepts a share in the pair of electrons. The difference between a coordinate bond and a covalent bond is that in the first case the shared electron pair is provided by one atom, while in the second case each atom contributes one electron. Coordination compounds of interest in hydrometallurgy are two types: Complexes and chelates.

Complexes

Complexes are water-soluble compounds or ions having distinct chemical properties when compared to the uncomplexed ion. For example, when ammonia is added to copper sulfate solution which is light blue, it turns dark blue due to the formation of copper ammine complex:

$$\mathrm{Cu}^{2+} + n\mathrm{NH}_3 \rightarrow [\mathrm{Cu(NH}_3)_n]^{2+}$$

instead of forming an insoluble copper hydroxide. Thus, the copper ion shares the electron pair of the nitrogen atom in ammonia. Ammonia is the donor and Cu^{2+} is the acceptor. In this case the donor is an uncharged species. Figure 3.10 shows the concentration of the species formed as a function of NH_3 concentration.

Donor species carrying negative charge, i.e., anions, are common. These include CN^-, F^-, Cl^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, OH–, PO_4^{3-}, and S^{2-} (Table 3.6). Complex ions can be identified by many physical and physicochemical methods including color change, infrared and ultraviolet measurements, conductivity, ion exchange, solvent extraction, and many others.

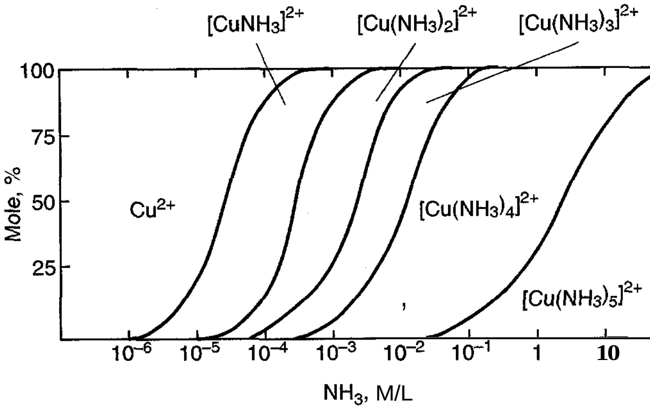


Figure 3.10: Copper ammine complexes as a function of ammonia concentration (Bjerrum, 1941).

A complexed ion behaves differently from an uncomplexed ion. For example, AgCl precipitates when Cl^- ion is added to a solution of $AgNO_3$ but not from a solution containing $[Ag(CN)_2]^-$ because the silver in the second case is complexed and not free to react with Cl^- ion. Also, AgCl precipitates when Ag^+ ion is added to NaCl solution but not from a solution containing $[PtCl_6]^{2-}$ ion because the chlorine in this case is complexed and not free to react with Ag+ion.

Chelates

Chelates[1] are complexes with ring structure, usually 5 or 6 membered which may be soluble or insoluble in water. For example:

- Ethylenediamine tetraacetic acid (EDTA) reacts with Be^{2+} ion to form the five-membered water-soluble chelate:

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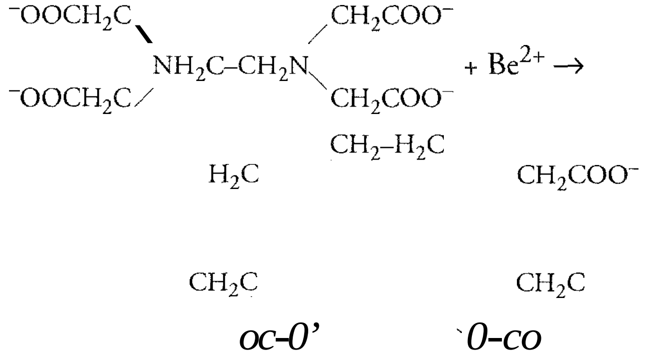
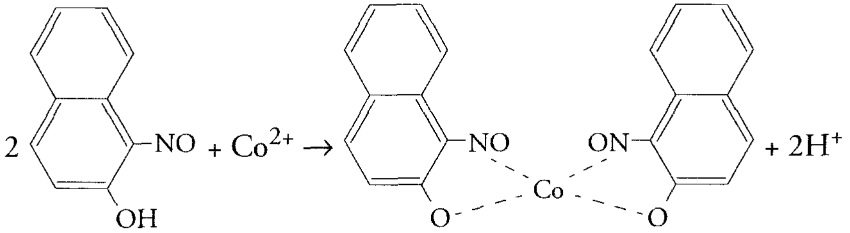
[1] From Greek meaning claw because of the way the metal is held in the complex. Also known as "inner complexes" because the metal is entrapped inside the organic structure.



- α-Nitroso-β-naphthol reacts with Co^{2+} ion to form an insoluble chelate:



The solubility of chelates in water depends on:

- The size of the hydrocarbon grouping. The greater the size of the hydrocarbon groupings the lower will be the solubility in water and the higher the solubility in less polar solvents.
- The presence of highly hydrated groups such as sulfonic, carboxylic, amino, and phenolic groups in the organic residue. The presence of these groups renders the chelate soluble in water and insoluble in polar solvents.

Chelates play an important role in many life processes, e.g., hemoglobin, chlorophyll, and vitamin B_{12}. These are chelates containing iron, magnesium, and cobalt, respectively. In chelates electron donor is usually nitrogen, oxygen, or sulfur atom. When the metal is directly bonded to carbon, the product is known as organometallic compounds and these have completely different properties from coordination compounds.

Table **3.6:** Soluble complexes of importance in hydrometallurgy.

	NH_3	CN^-	Cl^-	F^-	OH^-	S^{2-}	SO_4^{2-}	CO_3^{2-}
Ag^+	$Ag(NH_3)_2^+$	$Ag(CN)_2^-$	$AgCl_2^-$					
Al^{3+}				AlF_6^{3-}	$Al(OH)_4^-$			
As^{3+}						AsS_3^{3-}		
As^{5+}						AsS_4^{3-}		
Au^+	$Au(NH_3)_2^+$	$Au(CN)_2^-$						
Au^{3+}			$AuCl_4^-$					
Be^{2+}				BeF_3^-	$Be(OH)_3^-$			
Co^{2+}	$Co(NH_3)_6^{2+}$	$Co(CN)_6^{4-}$						
Co^{3+}	$Co(NH_3)_6^{3+}$	$Co(CN)_6^{3-}$						
Cu^+	$Cu(NH_3)_2^+$	$Cu(CN)_2^-$	$CuCl_2^-$					
Cu^{2+}	$Cu(NH_3)_4^{2+}$		$CuCl_3^-$					
Fe^{2+}		$Fe(CN)_6^{4-}$						
Fe^{3+}		$Fe(CN)_6^{3-}$					$Fe(SO_4)_2^-$	
Hg^{2+}	$Hg(NH_3)_2^{2+}$	$Hg(CN)_4^{2-}$	$HgCl_4^{2-}$			HgS_2^{2-}		
Mn^{2+}		$Mn(CN)_6^{4-}$						
Nb^{5+}				NbF_7^{2-}				
Ni^{2+}	$Ni(NH_3)_6^{2+}$	$Ni(CN)_4^{2-}$						
Pb^{2+}			$PbCl_4^{2-}$		$Pb(OH)_3^-$			
Pt^{4+}			$PtCl_6^{2-}$					
Sb^{3+}					$Sb(OH)_4^-$	SbS_3^{3-}		
Sb^{5+}					$Sb(OH)_6^-$	SbS_4^{3-}		
Si^{4+}				SiF_6^{2-}				
Sn^{4+}			$SnCl_6^{2-}$		$Sn(OH)_6^{2-}$	SnS_3^{2-}		
Ta^{5+}				TaF_7^{2-}				
UO_2^{2+}							$UO_2(SO_4)_3^{4-}$	$UO_2(CO_3)_3^{4-}$
Zn^{2+}	$Zn(NH_3)_4^{2+}$	$Zn(CN)_4^{2-}$			$Zn(OH)_3^-$			

PRECIPITATION

Precipitation is an important step in hydrometallurgy. It is essential to remember some facts about soluble and insoluble compounds in different media since this facilitates process design. The scheme of qualitative analysis devised by Carl Remigius Fresenius (1818–1897) in 1841 not only helps to identify the metal ions in solution but also to remember solubility data that are important in hydrometallurgy. It is based mainly on the solubility data of chlorides, sulfides, hydroxides and carbonates and makes use of certain differences in solubility when dilute HCl is added followed by H_2S, then after expelling excess H_2S from solution by boiling, excess NH_4OH is added at a later stage. The scheme is outlined in Figure 3.1 1 and Table 3.7.

Group I includes metal chlorides insoluble in dilute HCI. *Group* 2 includes metal sulfides insoluble in dilute HCl and is characteristic by a variety of colors. After separating the sulfides of *Group* 2 and neutralizing the filtrate with NH_4OH, only few metal hydroxides precipitate *(Group3)*.The reason is that the hydroxides of cobalt, nickel, and manganese are soluble in ammonia, and a great part of metal ions that form insoluble hydroxides have been precipitated in the previous groups. After filtering the hydroxides, H_2S is passed again in the filtrate to precipitate *Group 4* metal sulfides. These are distinguished from *Group* 2 sulfides by the fact that they are soluble in dilute HCl. When these sulfides are filtered off, and the solution boiled to expel excess H_2S, then cooled and saturated with ammonium carbonate $(NH_4)_2CO_3$, *Group 5* metal ions precipitate as carbonates. What remains in solution will be alkali metal ions.

The scheme of qualitative analysis involves also the separation of the individual metals in each group for identification purposes. For example, the sulfides of arsenic, antimony, tin, and mercury are separated from the other sulfides of *Group* 2 by boiling with ammonium sulfide, a fact that is also made use of occasionally in hydrometallurgy. These sulfides are soluble due to the formation of thiosalts, while the remaining sulfides are not. The reader is referred to textbooks on Qualitative Chemical Analysis for further details.

It is significant to observe that metals of *Groups* 2 and *4* which are precipitated as sulfides in the scheme of analysis occur in nature mainly as sulfides with the exception of manganese which occurs as MnO_2. Metals of *Group 3* which are precipitated as hydroxides occur in nature mainly as oxides and hydroxides, while metals of *Group 5* which are precipitated as carbonates occur in nature also as carbonates.

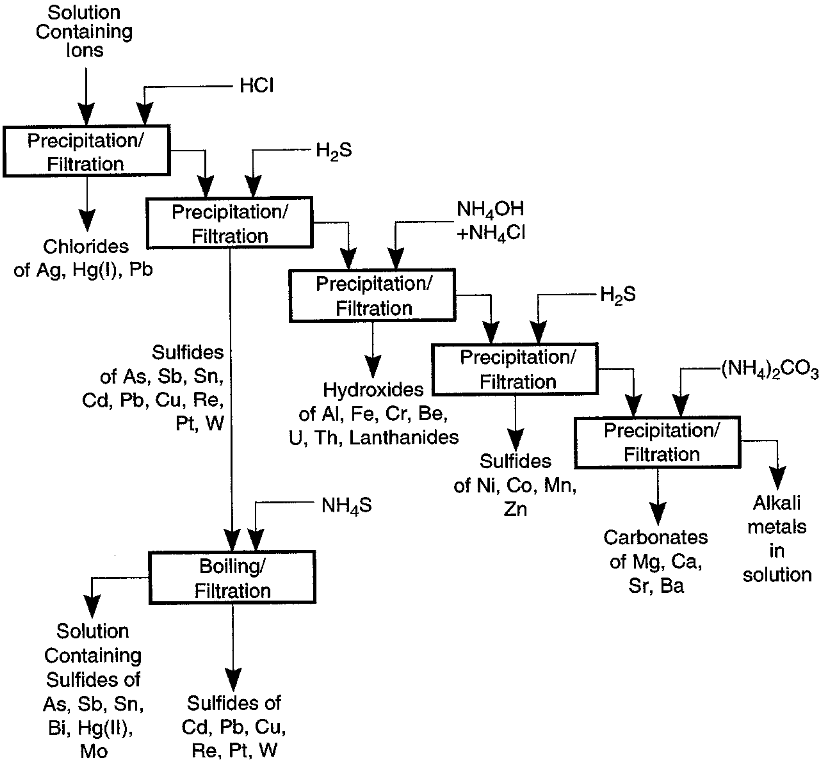


Figure 3.11: Scheme for separating metal ions in solution.

Table 3.7: Scheme of identification of metal ions in solution.

Group	Metal ion precipitated as:	Reagent	Precipitates	Color
1	Chloride	0.5M HCl	AgCl	white
			$PbCl_2$ (slightly soluble)	white
			Hg_2Cl_2 (mercurous)	white
2[a]	Sulfide	H_2S:A)	As_2S_3	yellow
			Sb_2S_3	orange
			SnS	brown
			SnS_2	yellow
			Bi_2S_3	dark brown
			HgS (mercuric)	black
			MoS_3	black
			GeS_2	
		B)	CdS	yellow
			PbS	black
			CuS	dark brown
			Re_2S_7	black
			PtS_2	black
			WS_3	black
3[b]	Hydroxide	NH_4OH + NH_4Cl	$Al(OH)_3$	white
			$Fe(OH)_2$	green
			$Fe(OH)_3$	red-brown
			$Cr(OH)_3$	green
			$Be(OH)_2$	white
			$UO_2(OH)_2$	white
			$Th(OH)_4$	white
			$Ln(OH)_3$[c]	white
4	Sulfide	H_2S	NiS	black
			CoS	black
			MnS	pink
			ZnS	white
5	Carbonate	$(NH_4)_2CO_3$	$MgCO_3$	white
			$CaCO_3$	white
			$SrCO_3$	white
			$BaCO_3$	white

a. Group 2A sulfides soluble in ammoniacal, $(NH_4)_2S$, while 2B are insoluble. MoS_3 is precipitated but not MoS_2 which occurs in nature. Separation of Re from Mn by precipitation as sulfide is of historical interest; this method was used for the first time to isolate rhenium.

b. NH_4Cl is added to prevent the precipitation of $Mn(OH)_2$ and $Mg(OH)_2$. $Fe(OH)_2$ is partially precipitated under these conditions. For effective precipitation, the original solution should be oxidized before adding NH_4OH to convert Fe^{2+} to Fe^{3+}.

c. Ln = Lanthanides.

Part Two

Leaching — General

Chapter Four

Leaching Agents

Introduction 67
Water 69
Acids 71
  Sulfuric 72
  Hydrochloric 75
  Nitric 78
  Hydrofluoric 82
  Fluorosilicic 82
  Sulfurous 83
  Aqua regia 85
Bases 86
  Sodium hydroxide 86
  Ammonium hydroxide 88
Aqueous Salt Solutions 91
  Alkali carbonates 91
  Cyanides 92
  Sodium sulfide 93
  Sodium chloride 93
  Others 94
Chlorine Water and Hypochlorite 94
Oxidizing and Reducing Agents 97
  Oxygen 97
  Ozone 97
  Hydrogen peroxide 98
  Ferric ion 98
  Solid oxidants 99
Summary 100

INTRODUCTION

Leaching is the process of extracting a soluble constituent from a solid by means of a solvent. In this respect. either one of two purposes can be achieved:

- Opening of ores, concentrates, or metallurgical products to solubilize the metal values.
- Leaching easily soluble constituents (usually gangue minerals) of an ore or a concentrate to have it in a more concentrated pure form, i.e., a chemical beneficiation method.

The choice of a leaching agent depends on the following factors:

- *Solubility.* Large and rapid solubility of the material to be leached in the leaching agent.
- *Cost.* An expensive reagent is undesirable because any traces lost during handling will represent a large economic loss.
- *Materials of construction.* If the leaching agent is corrosive and has to be handled in tanks made of stainless steel, titanium, or Hastalloy, the capital cost will be high, and therefore its use will be less desirable.
- *Selectivity.* An ideal reagent will extract only the desired component.
- *Regeneration.* Ability of regenerating the reagent for recycle is also an important criteria.

Water is an ideal leaching agent because it is cheap and noncorrosive, but its action is only limited to few minerals. Leaching agents commonly used other than water fall into the following categories: Acids, bases, and aqueous salt solutions; chlorine water is used to a minor extent (Table 4.1). Leaching agents may be used either alone or in combination with oxidizing agents. In few cases they are used in combination with reducing agents. Bases such as NaOH or NH_4OH are more expensive than H_2SO_4 but they are used because of the following advantages:

1. Negligible corrosion problems.
2. More selective, i.e., suitable for ores containing much gangue which reacts with acids but not with the bases. Examples of such gangue minerals are limestone, dolomite, iron oxide, iron carbonate, etc. The reaction of H_2SO_4 with limestone leads to the formation of insoluble $CaSO_4$ as well as foaming due to the evolution of CO_2:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

Table 4.1: Common leaching agents.

Category	Reagent
Water	H_2O
Acids	H_2SO_4, HCI, HNO_3, HF, H_2SO_3, aqua regia, H_2SiF_6
Bases	NaOH, NH_4OH
Aqueous salt solutions	Na_2CO_3, NaCN, Na_2S, NaCI, $(NH_4)_2SO_3$, $Na_2S_2O_3$
Aqueous chlorine and hypochlorite	$Cl_{2(aq)}$, HCIO, NaClO

On the other hand the reaction with iron oxide leads to the formation of soluble iron sulfate:

$$Fe_2O_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$$

Thus, not only the acid is consumed but the leach solution will be contaminated with Fe^{3+} iron whose separation will be necessary.

WATER

Water is an ideal solvent since it is the cheapest and noncorrosive reagent, but it is effective only on few minerals, flue dusts, and calcines. It is used in treating the following raw materials.

- *Naturally occurring salts.* Naturally occurring sodium and potassium salts such as borates, carbonates, chlorides, nitrates, and sulfates are readily soluble in water (Table 4.2). They are leached, filtered to separate clays, the solutions concentrated by evaporation, and the pure salts recovered by crystallization (**see** chapter 23).

- *Flue dusts.* Some flue dusts contain water-soluble components, e.g., those produced during the oxidation of molybdene, MoS_2, are enriched in rhenium oxide. This is soluble in water to form perrhenic acid:

$$Re_2O_7 + H_2O \rightarrow 2HReO_4$$

- *Calcines.* Calcines produced by sulfating or chloridizing roasting usually contain water-soluble ingredients that can be extracted with water. For example, recovery of cobalt sulfate and other nonferrous metals from pyrite cinder (see chapter 17).

- *Sulfide concentrates.* Water in the presence of air or oxygen under pressure and at about 200 °C dissolves sulfides, converting them to sulfates (see chapter 12). For example:

$$NiS_{(s)} + 2O_{2(aq)} \rightarrow NiSO_{4(aq)}$$

Table *4.2:* Principal water-soluble minerals.

Group	Mineral	Formula
Chlorides	Halite	$NaCl$
	Sylvite	KCI
	Sylvinite	$KCI + NaCl$
	Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
Sulfates	Langbeinite	$K_2SO_4 \cdot 2MgSO_4$
	Schonite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
	Polyhalite	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$
	Thenardite	Na_2SO_4
	Glauberite	$Na_2SO_4 \cdot CaSO_4$
	Aphthitalite	$(Na, K)_2SO_4$
	Mirabilire	$Na_2SO_4 \cdot 10H_2O$
	Bloedite	$Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
	Loeweite	$2Na_2SO_4 \cdot 2MgSO_4 \cdot 5H_2O$
Carbonates	Natron	$Na_2CO_3 \cdot 10H_2O$
	Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
	Thermonatrite	$Na_2CO_3 \cdot H_2O$
	Nahcolite	$NaHCO_3$
	Pirssonite	$Na_2CO_3 \cdot CaCO_3 . 2H_2O$
Borates	Tincal	$Na_2B_4O_7 \cdot 10H_2O$
	Tincalconite	$Na_2B_4O_7 \cdot 5H_2O$
	Kernite	$Na_2B_4O_7 \cdot 4H_2O$
	Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$
	Ulexite	$(Na, Ca)B_5O_9 \cdot 5H_2O$
	Boracite	$Mg_3B_7O_{13} \cdot Cl$
Nitrates	Soda niter	$NaNO_3$
	Niter	KNO_3
Mixed chlorides–sulfates	Kainite	$KCl \cdot MgSO_4 \cdot 3H_2O$
	Sulfohalite	$Na_2SO_4 \cdot NaCl$

Notes:

1. Borates containing calcium are insoluble in water; they are usually leached with Na_2CO_3 solution.
2. All potassium salts are known by the collective term potash.

ACIDS

Acids are the most commonly used leaching agents, they may be non-oxidizing, oxidizing, or reducing. An acid may react in more than one way depending on the conditions.

Non-oxidizing acids. An acid is considered a non-oxidizing acid when its reactions involve only its hydrogen ion. For example, $Fe(OH)_3$ dissolves in any acid forming ferric ion:

$$Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O$$

Or metallic iron dissolves in any dilute acid with liberation of hydrogen (an oxidation–reduction process):

$$Fe \rightarrow Fe^{2+} + 2e-$$

$$2H^+ + 2e- \rightarrow H_2$$

Overall reaction:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

Oxidizing acids. An acid is considered oxidizing when both the hydrogen ion and the anion participate in the reaction. For example, nitric acid is an oxidizing acid when both the H^+ and NO, ions participate in the reaction:

$$4H^+ + NO_3^- + 3e^- \rightarrow NO + 2H_2O$$

$$2H^+ + NO, + e^- \rightarrow NO, + H_2O$$

Concentrated sulfuric acid, contrary to the dilute acid, is an oxidizing acid because when it reacts both the H^+ ion and the SO_4^{2-} ion participate in the reaction:

$$4H^+ + SO_4^{2-} + 2e- \rightarrow SO, + 2H_2O$$

Gases evolved during these reactions have to be collected and used to regenerate the respective acid for recycle.

Reducing acids. An acid is a reducing acid when itself undergoes oxidation during reaction. For example, sulfurous acid in many reactions is oxidized to sulfuric acid:

$$H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e-$$

Sulfuric

Sulfuric acid is the most common leaching agent. It is manufactured by the oxidation of SO_2 to SO, on V_2O_5 catalyst at *400* °C then absorbing SO, in 96% H_2SO_4 to increase its concentration to 98% (Figure 4.1). Water cannot be used because the reaction is highly exothermic and the water would evaporate. Sulfur dioxide is obtained either by the oxidation of brimstone (sulfur), pyrite, or as a by-product of the oxidation of nonferrous metal sulfides. Sulfur dioxide and air must be cleaned from dust, dried, and preheated before entering the catalyst chamber. The reaction is highly exothermic and therefore the gases leaving the catalyst are used to preheat the SO_2–air mixture. Figure *4.2* shows a typical view of a sulfuric acid plant while Figure *4.3* gives the boiling points of H_2SO_4 at different concentrations and Table *4.3* shows density data.

Sulfuric acid may also be produced by the aqueous oxidation of sulfur dioxide:

$$SO_2 + {}^1/_2O_2 + H_2O \rightarrow H_2SO_4$$

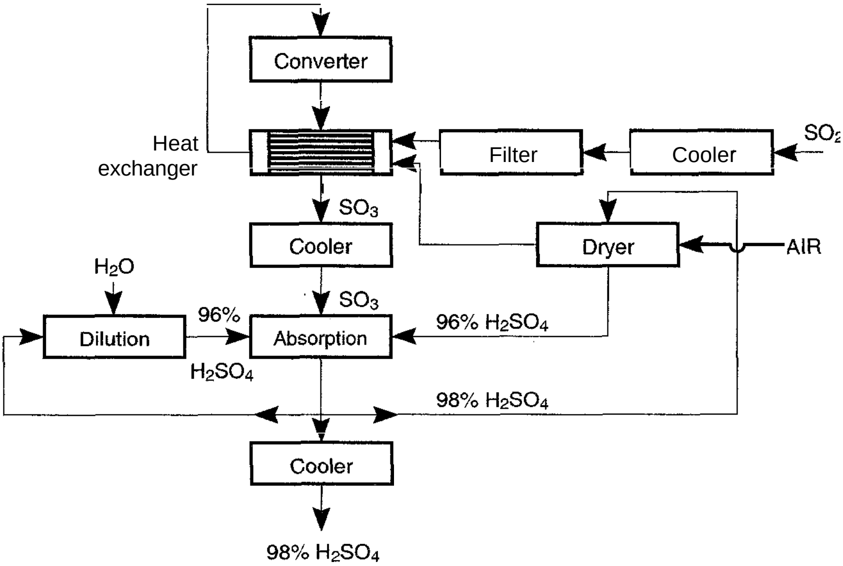


Figure 4.1 : Sulfuric acid manufacture.

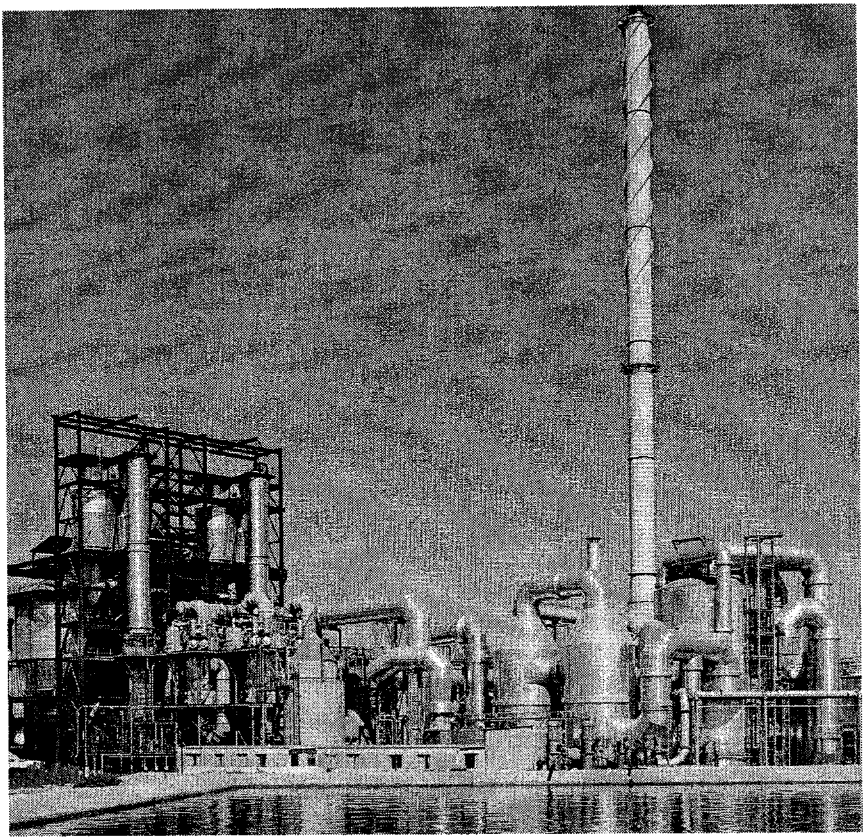


Figure 4.2: A view of a sulfuric acid plant (Lurgi).

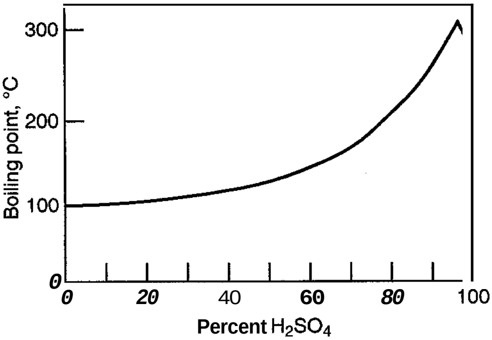


Figure 4.3: Boiling points of sulfuric acid solutions.

Table 4.3: Data on sulfuric acid.

H_2SO_4 %	Density	Concentration g/L	Concentration *M*
0	1.0000	0	.000
1	1.0068	10.1	.102
2	1.0135	20.2	.206
3	1.0202	30.6	.311
4	1.0269	41.0	.418
5	1.0336	51.6	.526
6	1.0404	62.3	.635
7	1.0472	73.2	.746
8	1.0540	84.2	.858
9	1.0609	95.3	.972
10	1.0679	106.6	1.087
11	1.0750	118.0	1.204
12	1.0821	129.6	1.322
13	1.0893	141.4	1.441
14	1.0966	153.3	1.563
15	1.1039	165.3	1.685
16	1.1113	177.5	1.810
17	1.1188	189.9	1.936
18	1.1263	202.4	2.063
19	1.1339	215.1	2.193
20	1.1416	227.9	2.324
22	1.1570	254.1	2.591
24	1.1725	280.9	2.864
26	1.1883	308.4	3.145
28	1.2043	336.6	3.432
30	1.2205	365.5	3.727
32	1.2370	395.1	4.029
34	1.2536	425.5	4.338
36	1.2705	456.6	4.655
38	1.2877	488.5	4.980
40	1.3052	521.2	5.314
42	1.3230	554.7	5.655
44	1.3411	589.0	6.006
46	1.3595	624.3	6.365
48	1.3783	660.4	6.733
50	1.3975	697.5	7.112
52	1.4172	735.6	7.500
54	1.4373	774.8	7.900
56	1.4580	815.1	8.310
58	1.4793	856.5	8.733
60	1.5013	899.2	9.168

The reaction is slow although catalyzed by Fe^{2+} and Mn^{2+} ions, and the acid produced cannot exceed 40%; to produce a stronger acid, concentration by evaporation would be necessary, which is usually not economical.

Sulfuric acid is usually handled in lead-lined equipment; the lead lining forms a protective layer of lead sulfate. Dilute sulfuric acid is widely used for leaching copper oxide ores, zinc oxide, phosphate rock, and a variety of other ores. In combination with an oxidizing agent it is used for leaching uranium ores and sulfides. Concentrated H_2SO_4 is used for treating more resistant minerals such as sulfide concentrates, laterites, monazite, and titanium slag. Although sulfuric acid is the cheapest acid, yet it is facing competition with hydrochloric and nitric acids because of two problems:

- When the raw material contains appreciable amounts of iron, the formation of ferrous sulfate creates a disposal problem because it cannot be discharged in streams and therefore must be either precipitated or crystallized and decomposed; both are costly operations. Decomposition of ferrous sulfate is expensive because a high temperature is needed, and the gases have to be transformed back to H_2SO_4 for recycle with is an added cost.
- When the raw material contains radium, e.g., in the leaching of uranium ores, the residue represents a radioactive health hazard because of its radium sulfate content, which disintegrates to radioactive radon gas.

Hydrochloric

Hydrogen chloride is formed by the reaction of chlorine with hydrogen, then absorbing the gas in water. It is also produced as waste product during the manufacture of polyvinyl chloride and other organic intermediates, for example, during the chlorination of ethylene:

$$H_2C{=}CH_2 + Cl_2 \xrightarrow{300\,^\circ C} H_2C{=}CHCl + HCl$$

which is a step in the production of polyvinyl chloride. **As** a result, hydrochloric acid sometimes finds metallurgical application within polyvinyl chloride plants.

Figure 4.4 shows the boiling points of aqueous solutions of HCl. If a solution of HCl containing more than 20.2% HCl is heated, HCl with little water is given off; the solution becomes less concentrated. This continues until the solution contains nearly 20.2% HCl, when its boiling point attains the maximum 110 °C; any further boiling does not affect the concentration of the aqueous phase because dilute acid containing 20.2% HCl distils unchanged. Again, if an acid containing less than 20.2% HCl is boiled, water accompanied by a little HCl passes off; the boiling point of the solution gradually rises; and the solution at the same time becomes more concentrated until it contains 20.2% HCl, when the acid distils over unchanged at 110 °C. Hence 110 °C is the maximum boiling point of hydrochloric acid at atmospheric pressure, and an acid boiling at this temperature is called an *azeotropic*[1] mixture. This is the acid concentration commonly used in practice. Figure 4.5 shows vapor pressure data of HCl solutions at different temeratures, and Table 4.4 gives density data.

Hydrochloric acid has replaced sulfuric acid in many reactions involving iron oxide, e.g., pickling of steel and leaching of ilmenite. This is because ferrous chloride produced in these reactions can be decomposed to ferric oxide and HCl according to:

$$2FeCl_2 + 2H_2O + {}^1/_2O_2 \rightarrow Fe_2O_3 + 4HCl$$

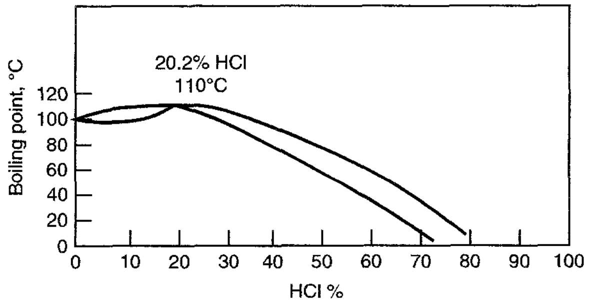


Figure 4.4: Boiling points of hydrochloric acid. Maximum boiling point 110°C at 20.2% HCl (≈ 6 N).

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[1] From Greek words meaning to boil without change.

Table 4.4: Data on hydrochloric acid.

HCl %	Density	Concentration	
		g/L	*M*
.00	1.0000	0	.000
.50	1.0025	5.0	.137
1.00	1.0050	10.0	.275
1.50	1.0075	15.1	.414
2.00	1.0099	20.2	.553
2.50	1.0124	25.3	.693
3.00	1.0148	30.4	.833
3.50	1.0173	35.5	.975
4.00	1.0198	40.7	1.116
4.50	1.0222	45.9	1.259
5.00	1.0247	51.1	1.401
5.50	1.0272	56.4	1.546
6.00	1.0296	61.7	1.691
6.50	1.0321	67.0	1.836
7.00	1.0346	72.3	1.982
7.50	1.0370	77.6	2.129
8.00	1.0395	83.0	2.276
8.50	1.0420	88.4	2.424
9.00	1.0445	93.8	2.573
9.50	1.0469	99.3	2.722
10.00	1.0488	104.7	2.871
11.00	1.0540	115.7	3.173
12.00	1.0592	126.9	3.479
13.00	1.0643	138.1	3.787
14.00	1.0695	149.5	4.098
15.00	1.0746	160.9	4.412
16.00	1.0798	172.5	4.729
17.00	1.0849	184.1	5.048
18.00	1.0901	195.9	5.371
19.00	1.0952	207.7	5.696
20.00	1.1003	219.7	6.023
22.00	1.1105	243.9	6.687
24.00	1.1207	268.5	7.362
26.00	1.1308	293.5	8.048
28.00	1.1409	318.9	8.744
30.00	1.1510	344.7	9.451
32.00	1.1610	370.9	10.169
34.00	1.1710	397.4	10.898
36.00	1.1809	424.4	11.636
38.00	1.1908	451.7	12.385
40.00	1.2006	479.4	13.145

which also shows that the acid can be regenerated. The process is known as *oxyhydrolysis*. Hydrochloric acid is a corrosive acid and is usually handled in rubber-lined equipment.

Nitric

Nitric acid is prepared industrially by the oxidation of NH_3 by air over platinum catalyst at 900 °C (Figure 4.6). The nitric oxide formed is oxidized further to NO_2 which is then absorbed in water to give nitric acid:

$$2NH_3 + {}^5/_2O_2 \rightarrow 2NO + 3H_2O$$

$$NO + {}^1/_2O_2 \rightarrow NO_2$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

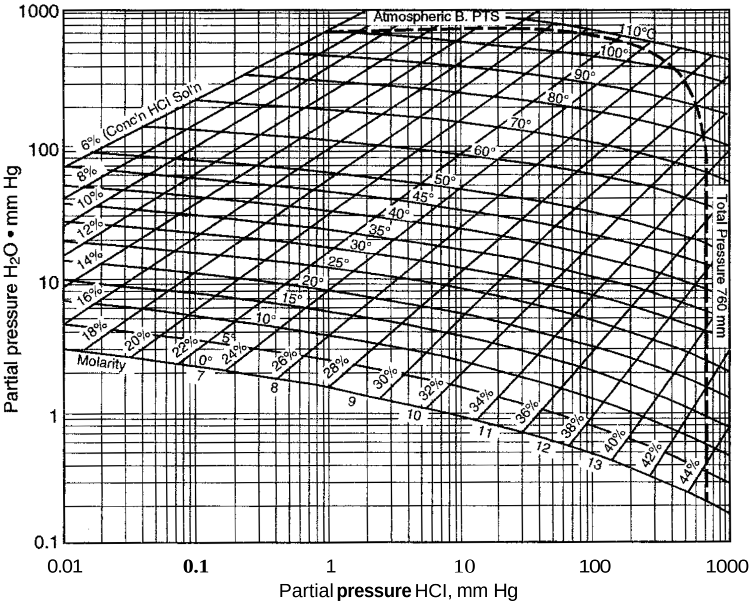

Figure 4.5: Vapor pressure of aqueous solutions of hydrochloric acid.

Figure 4.7 gives the boiling point curve of HNO_3 from which it can be seen that the maximum boiling point is 122 °C at 68%. Table 4.5 shows density data. Nitric acid is an expensive acid and any small loss will influence the economics of the process. It can be readily handled in stainless steel equipment — but these are also expensive. It has the advantage, however, that its salts decompose readily at low temperature to give nitric oxides which can be absorbed in water to yield HNO_3. Thus, it is possible to recover the acid waste solutions.

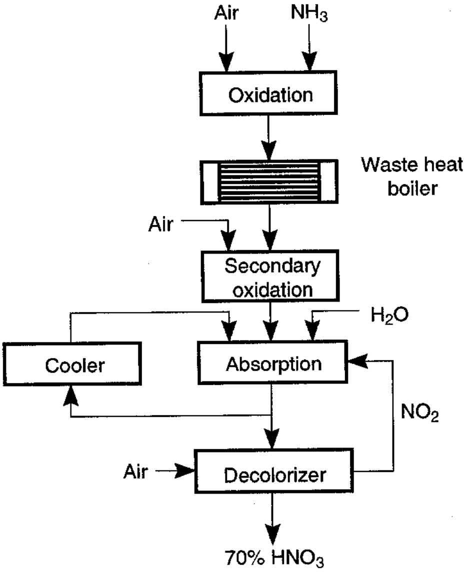

Figure 4.6: Nitric acid manufacture.

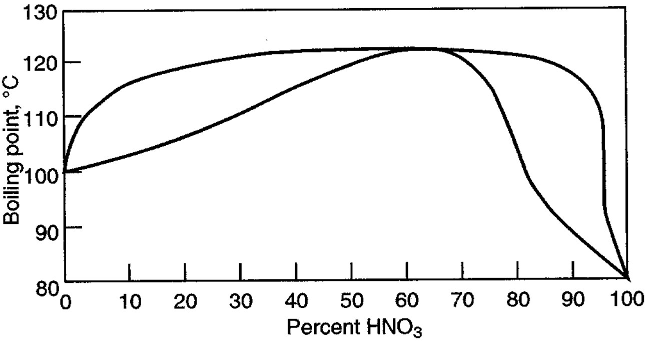

Figure 4.7: Boiling points of aqueous solutions of nitric acid. Maximum boiling point 122 °C at 68% HNO_3.

Table 4.5: Data on nitric acid.

HNO_3	Density	Concentration	
%		g/L	*M*
.00	1.0000	0	000
.50	1.0027	5.0	.079
1.00	1.0054	10.0	.159
1.50	1.0081	15.1	.240
2.00	1.0109	20.2	.320
2.50	1.0136	25.3	.401
3.00	1.0164	30.4	.483
3.50	1.0191	35.6	.565
4.00	1.0219	40.8	.647
4.50	1.0247	46.0	.730
5.00	1.0274	51.3	.814
5.50	1.0302	56.6	.898
6.00	1.0329	61.9	.982
6.50	1.0358	67.2	1.066
7.00	1.0387	72.6	1.152
7.50	1.0416	78.0	1.237
8.00	1.0446	83.4	1.324
8.50	1.0475	88.9	1.410
9.00	1.0504	94.4	1.497
9.50	1.0533	99.9	1.585
10.00	1.0563	105.4	1.673
11.00	1.0622	116.6	1.851
12.00	1.0681	127.9	2.030
13.00	1.0740	139.4	2.212
14.00	1.0800	150.9	2.395
15.00	1.0861	162.6	2.580
16.00	1.0921	174.4	2.768
17.00	1.0983	186.4	2.957
18.00	1.1044	198.4	3.149
19.00	1.1106	210.6	3.343
20.00	1.1169	223.0	3.538
22.00	1.1296	248.1	3.936
24.00	1.1425	273.7	4.343
26.00	1.1555	299.9	4.759
28.00	1.1688	326.7	5.184
30.00	1.1822	354.0	5.618
32.00	1.1956	381.9	6.060
34.00	1.2091	410.4	6.512
36.00	1.2225	439.3	6.971
38.00	1.2357	468.7	7.438
40.00	1.2486	498.6	7.911

The use of nitric acid in hydrometallurgy is limited, but it has a potential in displacing H_2SO_4 in some uranium extraction operations because when used radium gases go into solution together with uranium and can be disposed of in a controlled way. Thus the residues from leach operation do not represent a health hazard. Nitric acid is an oxidizing acid and therefore can be used to solubilize sulfide minerals by an oxidation–reduction process:

$$MS \rightarrow M^{2+} + S + 2e^-$$

$$4H^+ + NO_3^- + 3e^- \rightarrow NO + 2H_2O$$

$$2H^+ + NO_3^- + e^- \rightarrow NO_2 + H_2O$$

Nitrogen oxide gases formed during leaching are collected and used for making HNO_3 for recycle:

$$2NO + {}^{3}/_{2}O_2 + H_2O \rightarrow 2HNO_3$$

$$2NO_2 + {}^{1}/_{2}O_2 + H_2O \rightarrow 2HNO_3$$

It is also possible to leach and regenerate the acid in the same vessel by injecting oxygen. In this way the acid consumption would be decreased. It is preferable, however, to conduct the leaching such that NO is produced and not NO_2 because the consumption of HNO_3 in the first case is much less than in the second case as shown by the above equations. The HNO_3 concentration is another factor in determinating whether NO or NO_2 is evolved. Below about *20%* HNO_3 nearly pure NO is produced, at *40%* HNO_3 about *50%* NO and *50%* NO_2, while at 70% HNO_3 the gases analyze *90%* NO_2 (Figure *4.8)*. When concentrated acid is used, there is excessive decomposition as follows:

$$2HNO_3 \rightarrow 2NO_2 + {}^{1}/_{2}O_2 + H_2O$$

When used as oxidizing acid, e.g., during leaching of sulfides, it was also found that about *0.5%* N_2O is always produced. This represents a loss in the regeneration system because it cannot be converted to HNO_3, and a pollution hazard because it cannot be emitted in the atmosphere.

The consumption of HNO_3 can be decreased when concentrated H_2SO_4 is added during leaching to convert the nitrates into sulfates:

$$M(NO_3)_2 + H_2SO_4 \rightarrow 2HNO_3 + MSO_4$$

Beside the economy in acid, the recovery of metal values will be facilitated since standard methods will be used, i.e., recovery from sulfate medium.

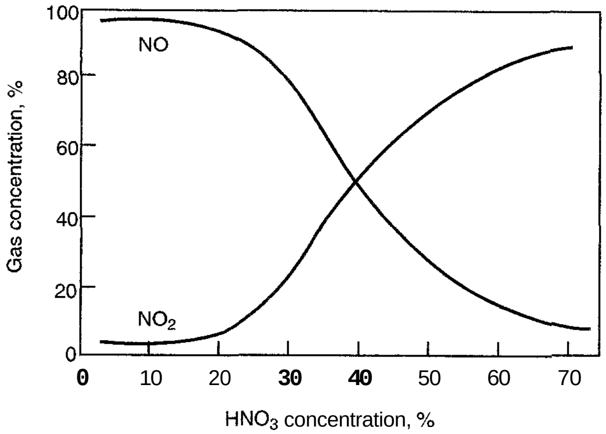

Figure *4.8:* Composition of gases formed during leaching chalcopyrite with HNO_3 at 95 °C (Prater et al., 1973).

Hydrofluoric

Hydrofluoric acid is prepared by the action of concentrated H_2SO_4 on the mineral fluorspar:

$$H_2SO_4 + CaF_2 \rightarrow CaSO_4 + 2HF$$

This acid is used in special cases when the ore is insoluble in all the previous acids, e.g., for the treatment of niobium and tantalum ores. Figure 4.9 shows the boiling point curve of hydrofluoric acid; the azeotropic mixture is at 38.26% HF and the constant boiling point is 112 °C. Hydrofluoric acid is handled in mild steel containers.

Fluorosilicic

Also known as hexafluorosilicic acid and hydrofluosilicic acid, H_2SiF_6 is obtained as a waste product of the phosphatic fertilizer industry (see chapter 15). In treating phosphate rock with H_2SO_4, silica present in the rock is partially volatilized as SiF_4 which is scrubbed with water to form the acid:

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

The other part remains in the phosphoric acid product and can be precipitated by adding a sodium salt:

$$2Na^+ \text{ t } SiF_6^{2-} \rightarrow Na_2SiF_6$$

This salt is also a source of the acid. Fluorosilicic acid is used to prepare AlF_3 from clays and other sources.

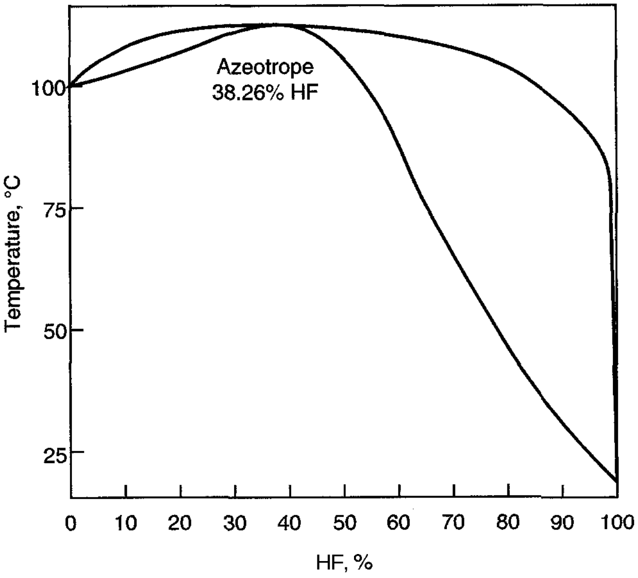

Figure *4.9:* Boiling points of hydrochloric acid solutions. Azeotropic mixture boils at 112 °C.

Sulfurous

Sulfurous acid has a limited use in hydrometallurgy. It is prepared by dissolving sulfur dioxide in water:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-}$$

The solubility of SO_2 in water at 0 °C is 228 g/L and at 25 °C it is about 90 g/L (Figure 4.10). Figure 4.11 gives the species present in solution as a function of pH. Sulfurous acid reacts as a non-oxidizing acid, e.g., dissolution of CuO:

$$CuO + 2H^+ \rightarrow Cu^{2+} + H_2O$$

or as a reducing acid, e.g., dissolution of MnO_2:

$$H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

With acid-soluble sulfides it reacts at 120–150 °C forming elemental sulfur because of the formation of H_2S:

$$MS + 2H^+ \rightarrow M^{2+} + H_2S$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

Overall reaction:

$$2MS + 4H^+ + SO_2 \rightarrow 2M^{2+} + 3S + 2H_2O$$

This reaction may be accompanied by disproportionation of sulfite ion to sulfate ion and elemental sulfur:

$$3SO_3^{2-} + 2H^+ \rightarrow 2SO_4^{2-} + S + H_2O$$

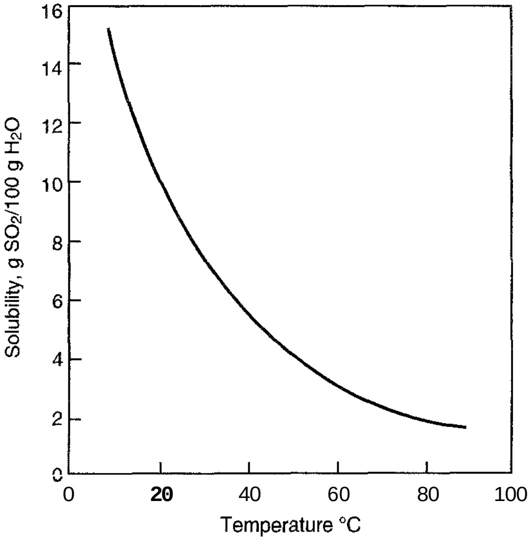

Figure *4.10:* Solubility of SO_2 in water.

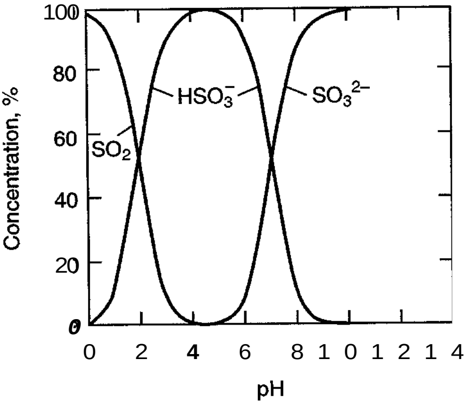

Figure 4.11: Species present in solution as a function of pH when SO_2 is dissolved in water.

As a result, on adding these last two reactions, and taking into consideration the ionization equilibrium of SO_2 in water the following reaction is obtained:

$$MS + 2SO_2 \rightarrow MSO_4 + 2S$$

Aqua regia

Aqua regia, also known as *royal water* or *eau régale* because it can solubilize gold the most noble metal, is a mixture of one part concentrated nitric acid and three parts concentrated hydrochloric acid. It is used mainly to dissolve gold alloys for refining. The dissolving action is due to the formation of chlorine and nitrosyl chloride[1]:

$$HNO_3 + 3HCl \rightarrow Cl_2 + NOCl + 2H_2O$$

At 109 °C, a mixture of HNO_3 and HCl distills over unchanged. Aqua regia is handled in glass or fused silica containers.

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[1] The reaction is oxidation–reduction:
$2Cl^- \rightarrow Cl + 2e^-$
$4H^+ + NO_3^- + 3e^- \rightarrow NO + 2H_2O$
followed by formation of nitrosyl chloride:
$2NO + Cl_2 \rightarrow 2NOCl$

BASES

Sodium hydroxide

Sodium hydroxide is used chiefly for dissolving aluminum from bauxite, for decomposing monazite sand, and for leaching wolframite and scheelite ores. It is manufactured by the following methods:

- Electrolysis of NaCl solutions using a mercury cathode:

$$Na^+ + e^- + xHg \rightarrow NaHg_x$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

By decomposing the amalgam with water, NaOH and hydrogen are formed:

$$NaHg_x + H_2O \rightarrow NaOH + {}^1/_2H_2 + xHg$$

This process produces a pure and concentrated product but suffers from pollution problems due to mercury.

- Electrolysis of NaCl solutions in a diaphragm cell: NaOH forms at the cathode and chlorine at the anode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

The product is less pure because of contamination with NaCl and less concentrated. Therefore evaporation is necessary to concentrate the solution and remove NaCl which crystallizes out during heating.

- From Na_2CO_3 by reaction with $Ca(OH)_2$:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow NaOH + CaCO_3$$

Calcium carbonate is filtered off and the solution is concentrated by evaporation. This process is less used because of low purity and low concentration. However this reaction is sometimes made use of in some leaching processes where NaOH is generated in situ. Figure 4.12 shows the boiling point diagram of NaOH and Table 4.6 shows the density data.

Table 4.6: Data on sodium hydroxide.

NaOH %	Density	Concentration	
		g/L	*M*
.00	1.0000	0	.000
.50	1.0056	5.0	.125
1.00	1.0112	10.1	.252
1.50	1.0167	15.2	.381
2.00	1.0223	20.4	.510
2.50	1.0279	25.7	.641
3.00	1.0334	30.9	.773
3.50	1.0390	36.3	.907
4.00	1.0445	41.7	1.042
4.50	1.0501	47.2	1.179
5.00	1.0556	52.7	1.317
5.50	1.0612	58.3	1.456
6.00	1.0667	63.9	1.597
6.50	1.0722	69.6	1.739
7.00	1.0778	75.3	1.882
7.50	1.0833	81.1	2.027
8.00	1.0888	87.0	2.173
8.50	1.0944	92.9	2.321
9.00	1.0999	98.8	2.470
9.50	1.1054	104.8	2.620
10.00	1.1110	110.9	2.772
11.00	1.1220	123.2	3.079
12.00	1.1331	135.7	3.392
13.00	1.1441	148.5	3.711
14.00	1.1551	161.4	4.035
15.00	1.1662	174.6	4.364
16.00	1.1772	188.0	4.699
17.00	1.1882	201.6	5.040
18.00	1.1993	215.5	5.386
19.00	1.2103	229.5	5.737
20.00	1.2213	243.8	6.094
22.00	1.2432	273.0	6.824
24.00	1.2651	303.1	7.576
26.00	1.2869	334.0	8.348
28.00	1.3086	365.8	9.142
30.00	1.3301	398.3	9.956
32.00	1.3513	431.7	10.789
34.00	1.3722	465.7	11.641
36.00	1.3928	500.5	12.510
38.00	1.4128	535.9	13.394
40.00	1.4322	571.9	14.293

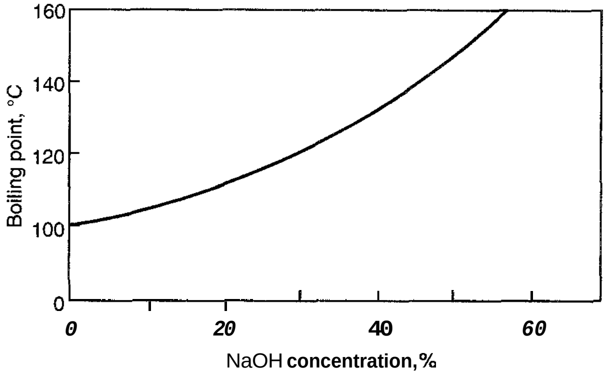

Figure 4.12: Boiling point diagram of sodium hydroxide solutions.

Ammonium hydroxide

Ammonium hydroxide is used for extracting metals such as copper, cobalt, and nickel from their ores by forming soluble ammine complexes, $[M(NH_3)_n]^{2+}$. Ammonium hydroxide is prepared by dissolving gaseous ammonia in water:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The solubility of NH_3 in water is shown in Figure 4.13. To minimize the ionization of the hydroxide a mixture of ammonium hydroxide and ammonium carbonate is usually used; the ammonium salt is added to shift the above equilibrium to the left, thus favoring the formation of NH_3 the active complex species. Figure 4.14 shows the concentration of NH_4^+ and NH_3 as a function of pH, Figure 4.15 shows the vapor pressure of aqueous ammonia solutions as a function of temperature, and Table 4.7 gives density data.

Ammonia is prepared industrially by the reaction of hydrogen and nitrogen at about 500 °C and under pressure of 50 000 kPa in presence of iron as a catalyst:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

It is transported as a liquid in specially designed ships for overseas, or in specially refrigerated trucks or in pipelines over long distances on land.

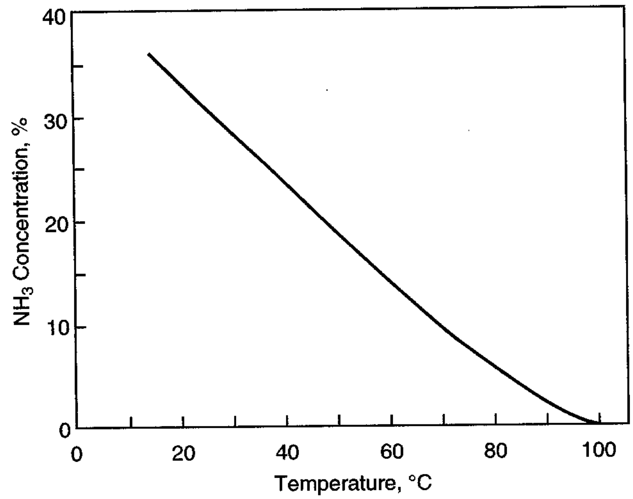

Figure 4.13: Solubility diagram of ammonia in water.

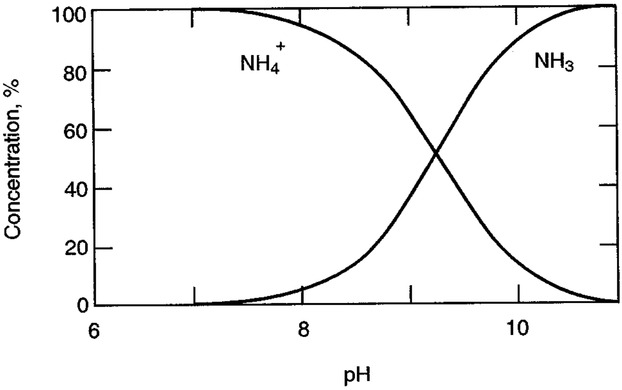

Figure 4.14: Concentration of ammonium ion (NH_4^+) and molecular ammonia (NH_3) in aqueous solution.

Table 4.7: Data on ammonium hydroxide.

NH_4OH	NH_3	Density	Concentration	
%	%		g/L	*M*
0	.00	1.0000	0	.000
1	.49	.9979	10.0	.284
2	.97	.9957	19.9	.567
3	1.46	.9936	29.8	.849
4	1.94	.9915	39.6	1.130
5	2.43	.9894	49.4	1.409
6	2.92	.9874	59.1	1.687
7	3.40	.9853	68.9	1.964
8	3.89	.9833	78.5	2.240
9	4.37	.9813	88.2	2.515
10	4.86	.9793	97.8	2.789
11	5.34	.9773	107.3	3.062
12	5.83	.9754	116.8	3.333
13	6.32	.9734	126.3	3.604
14	6.80	.9715	135.8	3.874
15	7.29	.9696	145.2	4.142
16	7.77	.9677	154.6	4.410
17	8.26	.9658	163.9	4.676
18	8.75	.9639	173.2	4.942
19	9.23	.9621	182.5	5.206
20	9.72	.9603	191.7	5.470
22	10.69	.9567	210.1	5.994
24	11.66	.9531	228.3	6.515
26	12.63	.9496	246.5	7.031
28	13.60	.9461	264.4	7.545
30	14.58	.9427	282.3	8.055
32	15.55	.9393	300.1	8.561
34	16.52	.9360	317.7	9.064
36	17.49	.9328	335.2	9.563
38	18.46	.9295	352.6	10.060
40	19.44	.9263	369.9	10.553
42	20.41	.9232	387.0	11.043
44	21.38	.9200	404.1	11.529
46	22.35	.9170	421.1	12.013
48	23.32	.9139	437.9	12.493
50	24.29	.9109	454.6	12.971
52	25.27	.9079	471.3	13.445
54	26.24	.9049	487.8	13.917
56	27.21	.9019	504.2	14.385
58	28.18	.8990	520.5	14.850
60	29.15	.8961	536.7	15.313

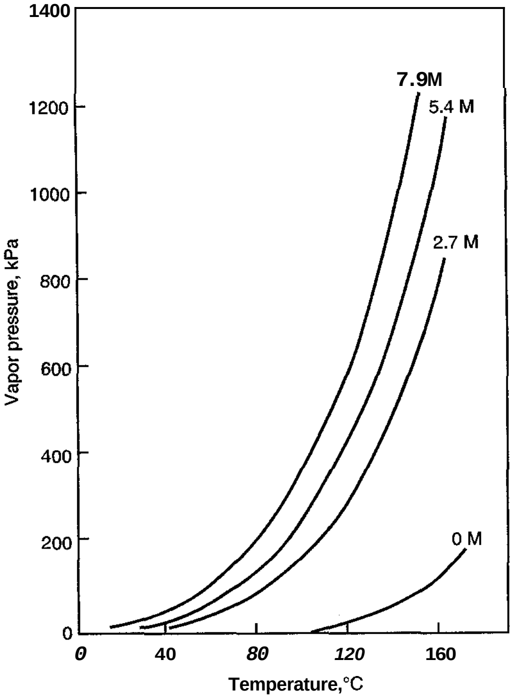

Figure 4.15: Vapor pressure of aqueous ammonia solutions.

AQUEOUS SALT SOLUTIONS

Alkali carbonates

Sodium carbonate occurs in nature as the mineral trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ can be prepared industrially from sodium chloride and limestone by the Solvay Process using ammonia as an intermediate (Figure 4.16):

$$NH_3 \text{ t } CO_2 \text{ t } H_2O \rightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium bicarbonate is crystallized and decomposed by heating to sodium carbonate:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O \text{ t } CO_2$$

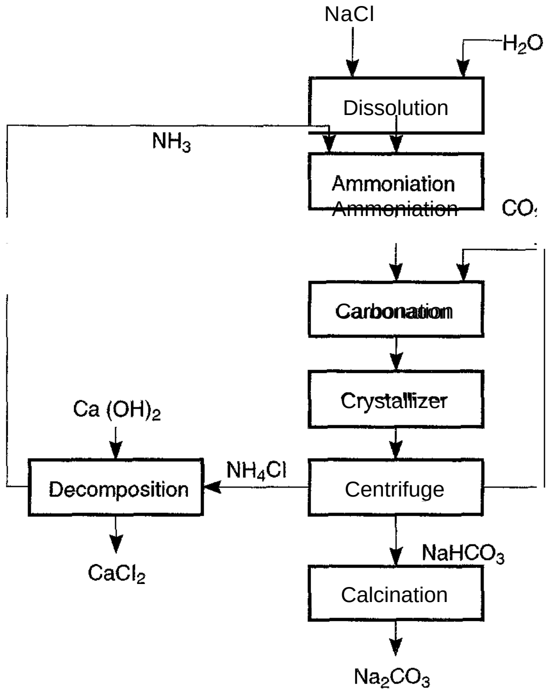

Figure 4.16: Flowsheet for the production of sodium carbonate by the Solvay Process.

Ammonia is recovered from NH_4Cl by heating with CaO:

$$CaO + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + H_2O$$

Solutions of sodium carbonate are basic and therefore they are suitable for treating ores containing acid-consuming gangue. It is mainly used for leaching uranium and some tungsten ores. Ammonium carbonate is sometimes used instead of sodium carbonate because it is less reactive towards silicate gangue minerals.

Cyanides

Κυανος is a Greek word meaning blue, and at one time hydrocyanic acid was known as the blue acid because it was first obtained by decomposing Prussian Blue — a blue pigment. Alkali cyanides are used mainly for leaching gold and silver from their ores; the process is called *yunidation process.* They are prepared industrially by absorbing HCN in alkali hydroxide, e.g.,:

$$HCN + NaOH \rightarrow NaCN + H_2O$$

Hydrogen cyanide itself is prepared from NH_3 by the following reactions:

$$CO + NH_3 \xrightarrow{MgO} HCN + H_2O$$

$$NH_3 + CH4 + {}^1/_2O_2 \xrightarrow{Pt} HCN + 3H_2O$$

Alkali cyanides and hydrogen cyanide are highly poisonous and must be oxidized to the harmless cyanate or nitrogen and CO_2 before disposal, e.g., by chlorine:

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^-$$

$$2CNO^- + 4OH^- \rightarrow 2CO_2 \; t \; N_2 \; t \; 2H_2O \; t \; 6e^-$$

Sodium sulfide

Sodium sulfide is produced by reducing the naturally occurring sodium sulfate with carbon at high temperature. It is used for leaching sulfide minerals that form soluble sulfide complexes such as those of arsenic, antimony, tin, and mercury, e.g.,:

$$Sb_2S_3 + 3S^{2-} \rightarrow 2[SbS_3]^{3-}$$

Sodium chloride

Saturated solutions of sodium chloride are mainly used for dissolving lead sulfate and lead chloride:

$$PbSO_4 + 4Cl^- \rightarrow [PbCl_4]^{2-} + SO_4^{2-}$$

$$PbCl_2 + 2Cl^- \rightarrow [PbCl_4]^{2-}$$

Solubility data for $PbSO_4$ in NaCl solutions is given in Table *4.8.*

Table *4.8:* Solubility of $PbSO_4$ in NaCl solution **at** 18°C.

NaCl [molarity]	Solubility g/L
0.0	0.04
0.1	0.17
0.2	0.27
0.3	0.38
0.4	0.50

Others

Ammonium sulfite is prepared by absorbing SO_2 in ammonium hydroxide:

$$SO_2 + 2NH_4OH \rightarrow (NH_4)_2SO_3 + H_2O$$

It has nearly a neutral pH and has been suggested for leaching copper oxide minerals, e.g.,:

$$CuO + (NH_4)_2SO_3 + H_2O \rightarrow CuSO_3 + 2NH_4OH$$

Sodium thiosulfate was used for leaching silver chloride produced by salt roasting of silver ores:

$$2AgCl + 3S_2O_3^{2-} \rightarrow [Ag_2(S_2O_3)_3]^{4-} + 2Cl^-$$

The process is now obsolete.

In the southern provinces of China, there are many large deposits of rare-earth-containing clays from which the metals are recovered by leaching with a sodium chloride solution. The leaching process is an ion exchange system in which Na^+ ions displace the rare earth ions.

CHLORINE WATER AND HYPOCHLORITE

Chlorine is produced as a co-product during the electrolytic production of NaOH (p. 86). It dissolves in water at 0 °C to the extent of *14.6* g/L and at 25 °C to the extent of 9.1 g/L (Figure 4.17). The solubility decreases in presence of electrolytes in solution but increases in presence of HCl (Figure 4.18). Aqueous chlorine solutions are known as chlorine water and can be used in acidic or basic media (Figure 4.19). Below pH 2 chlorine is present predominantly in the elemental form, between pH 2 and 3 there is a mixture of Cl_2, HClO, and HCl, while in the pH range 4–6 only HClO and HCl due to the hydrolytic reaction:

$$Cl_2 + H_2O \rightarrow HClO + HCl$$

In basic medium the hypochlorite and chloride ions are formed:

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$$

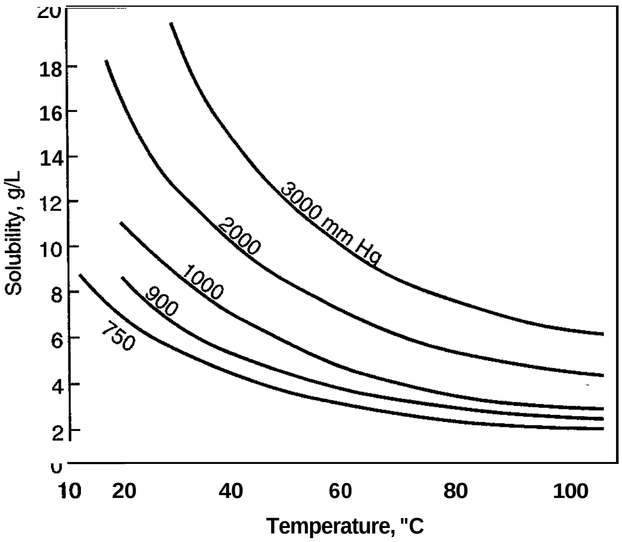

Figure 4.17: Solubility of chlorine in water.

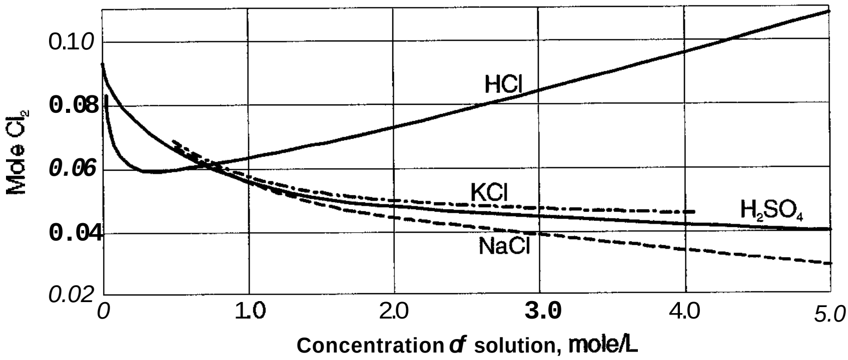

Figure *4.18:* Solubility of chlorine in solutions containing HCl, NaCl, KCl, and H_2SO_4.

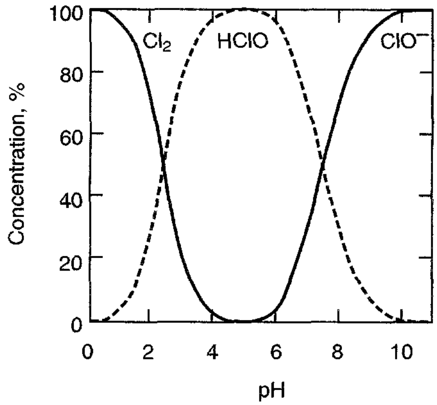

Figure *4.19:* Species present in solution when chlorine is dissolved in water.

That is why when electrolysis of NaCl is carried out in the absence of a diaphragm, a solution of sodium hypochlorite, NaClO, is obtained as a result of the dissolution of chlorine in NaOH. The solution is known as *eau de Javel* and is used as an oxidizing agent. Hypochlorite may be formed in situ during leaching by a method known as "electro-oxidation process". Chlorine can be absorbed by calcium hydroxide to form chloride of lime, Ca(Cl)ClO, known as bleaching powder. this is a mean for transporting chlorine in form of a solid; it dissolves in water forming chloride and hypochlorite ions.

The oxidizing action of chlorine and hypochlorite can be represented by the reactions:

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

$$ClO^- + H_2O \text{ t } 2e- \rightarrow 2OH^- \text{ t } Cl^-$$

Aqueous chlorine solutions were once used for leaching gold from its ores before the discovery of the cyanidation process:

$$Au \rightarrow Au^{3+} + 3e-$$

$$Au^{3+} + 4Cl^- \rightarrow [AuCl_4]^-$$

The process, however, was abandoned because chlorine was incapable of solubilizing silver commonly present in gold ores.

Sodium hypochlorite finds application in the oxidation of organic matter present in some gold ores, which should be removed prior to cyanidation.

OXIDIZING AND REDUCING AGENTS[1]

An oxidizing or a reducing agent is sometimes needed during leaching to solubilize certain minerals which do not dissolve otherwise. For example, during leaching of gold, sulfide minerals, uranium ores, etc. Commonly used oxidizing agents are: oxygen (or air), ozone, hydrogen peroxide, ferric ion, manganese dioxide, sodium nitrate, and sodium chlorate, while commonly used reducing agents are ferrous ion, and sulfur dioxide.

Oxygen

Oxygen (or air) is an ideal oxidant since it does not need regeneration. It is used in acidic or alkaline medium:

$$^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

$$^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

Oxygen is prepared on large scale by liquefaction of air and its subsequent fractional distillation. Nitrogen boils at a lower temperature and hence tends to leave the oxygen behind when the mixture is warmed. After separation, the latter is vaporized and compressed into steel cylinders for distribution, or holding tanks for storage. Some industrial oxygen is also obtained by electrolysis of water when electric energy is available at low cost.

Ozone

Ozone, O_3, is a gas with a sharp odor and its name is derived from the Greek verb to smell. It is much more soluble in water than oxygen, and decomposes readily to form oxygen. It is prepared on industrial

---

[1] Reducing agents used in the treatment of leach solutions are discussed in chapter 25.

scale by passing a low-temperature electrical discharge through air or oxygen. The silent electrical discharge obtained by connecting two metallic plates through an induction coil with a source of current is suited for this purpose. Ozone has been proposed for destroying cyanide ion before disposal.

Hydrogen peroxide

Hydrogen peroxide is prepared commercially by the electrolysis of a cold concentrated solution of sulfuric acid:

$$2HSO_4^- \rightarrow S_2O_8^{2-} + 2H^+ + 2e^-$$

$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^- + H_2O_2$$

The commercial product is obtained by distillation and contains about 30% H_2O_2 in the aqueous solution. Hydrogen peroxide decomposes readily to liberate oxygen:

$$H_2O_2 \rightarrow H_2O + {}^1/_2O_2$$

Ferric ion

Ferric sulfate or ferric chloride are prepared by dissolving Fe_2O_3 in the corresponding acid and are mainly used as an oxidant in leaching sulfide minerals:

$$MS \rightarrow M^{2+} + S + 2e^-$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

Overall reaction:

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S$$

The disadvantage of this oxidant as compared to oxygen (or air) is the necessacity of its regeneration.

Ferric ion undergoes hydrolysis at ambient conditions to form less effective leaching species:

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+$$

$$FeOH^{2+} + H_2O \rightarrow Fe(OH)_2^+ + H^+$$

Further hydrolysis leads to precipitation:

$$Fe(OH)_2^+ + H_2O \rightarrow Fe(OH)_3 + H^+$$

Therefore the pH of the solution must be below 3 to prevent the precipitation of hydroxy ferric salts if leaching is conducted at ambient temperature, and below 1.5 if leaching is conducted at higher temperature because of the accelerated hydrolysis of ferric ion with increased temperature. The ferrous ion formed during leaching can be regenerated by oxidation with air (or oxygen) or chlorine:

$$2Fe^{2+} + 2H^+ + {}^1/{}_2O_2 \rightarrow 2Fe^{3+} + H_2O$$

$$FeCl_2 + {}^1/{}_2Cl_2 \rightarrow FeCl_3$$

Ferric sulfate is also prepared industrially by the aqueous oxidation of pyrite:

$$2FeS_2 + {}^{15}/{}_2O_2 + H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4$$

Solid oxidants

The action of a solid oxidant during leaching may be due to:

- *Decomposition and liberation of oxygen.* For example, sodium nitrate and sodium chlorate are water soluble and decompose on heating as follows:

$$NaNO_3 \rightarrow NaNO_2 + {}^1/{}_2O_2$$

$$NaClO_3 \rightarrow NaCl + {}^3/{}_2O_2$$

- Generation of an oxidizing species in solution. For example, MnO_2 is insoluble in dilute acid but in the presence of a reducing species such as ferrous ion an oxidation-reduction couple immediately sets in:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

$$Fe^{2+} \rightarrow Fe^{3+} \text{ t } e^-$$

Overall reaction:

$$MnO_2 + 4H^+ + 2Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+} + 2H_2O$$

The ferric ion then acts further as an oxidizing agent.

SUMMARY

Table 4.9 gives a summary of commonly used leaching agents and their applications.

Table *4.9:* Summary of commonly used or potential leaching agents and their applications.

Group	Reagent	Examples
Water		Sulfates, chlorides, borates
Acids	H_2SO_4 (dil.)	Copper oxide ores, zinc oxide, phosphate rock
	H_2SO_4 (dil.) + oxidant	Uranium ores, sulfides
	H_2SO_4 (conc.)	Sulfide concentrates, laterites, monazite, titanium slag
	HCl	Chemical beneficiation of ilmenite
	HNO_3	Uranium concentrates
	HF	Niobium and tantalum ores
	Aqua regia	Refining of gold bullion and platinum metals
	H_2SO_3	Manganese ores
	H_2SiF_6	Clay (for alumina recovery)
Bases	$NaOH$	Bauxite
	NH_4OH + air	Laterites after reduction, nickel sulfide concentrates
Aqueous salt solutions	Na_2CO_3	Tungsten ores (scheelite)
	Na_2CO_3 + oxidant	Uranium ores
	$NaCN$ + air	Gold and silver ores
Chlorine	Cl_2 (aqueous)	Gold ores

Chapter Five

Theory

Physical Processes. 101
Chemical Processes 102
  Ionic-covalent solids 102
  Covalent solids. 107
Electrochemical Processes 108
  Metals in oxygenated water 110
  Metals in dilute acid 111
  Metals by displacement. 111
  Metal with complex formation. 111
  Oxides 113
  Sulfides 114
Electrolytic Processes. 116
The Boundary Layer. 117
Summary 120

The leaching of a solid in an aqueous phase depends primarily on the nature of the solid whether it is ionic, covalent, or metallic. Since bonding in solids is intermediate between these three extreme cases as shown earlier, a variety of leaching processes may be identified. These may be physical, chemical, electrochemical, reduction, or electrolytic.

PHYSICAL PROCESSES

In this case the aqueous phase is water and there is no chemical transformation. This is the simplest case and applies mainly for ionic solids for example, sodium chloride. The dissolution of NaCl in water can be represented by the equation:

$$Na^+Cl^-_{(s)} + (n+m)H_2O \rightarrow Na(H_2O)^+_{n(aq)} + Cl(H_2O)^-_{m(aq)}$$

Being highly polar, the water molecules when approach the surface of the crystal exert a force on the ions in the crystal lattice: the negative side of the dipole attracts the positive ion and the positive side of the dipole attracts the negative ion to form hydrates. If the force of hydrating the positive and the negative ions exceeds the force holding the two ions together in the crystal, then the solid will go into solution. While sodium chloride and calcium chloride are soluble in water, silver chloride and calcium fluoride are insoluble. The reason is in the case of AgCl the bond between the silver ion and the chloride ion is partially ionic and partially covalent. Thus, the force of attraction between Ag^+ and Cl^- is stronger than the force of hydration. Similarly, the case with CaF_2.

The variation in solubilities between the different ionic crystals is a function of the size of the ions composing the crystal since this factor governs the force of attraction in the solid. If there is a great disparity in the size of the ions, the stability of the crystal decreases because the small-sized ions are not big enough to keep the large ions separated. As the large ions approach one another more and more closely, mutual repulsion increases and the crystal becomes more unstable and consequently more soluble. Also cations that are small and highly charged exert the strongest attraction on water molecules.

Physical processes are strongly influenced by the speed of agitation: the higher the speed the faster is the rate, but less influenced by temperature.

CHEMICAL PROCESSES

In these cases the crystalline solid may be partly ionic and partly covalent or mainly covalent. The first type of solids covers a variety of compounds: oxides, hydroxides, sulfides, sulfates, some halides and carbonates while the second type covers mainly silica and the silicates. These are insoluble in water but may be solubilized in the presence of a certain reagent in solution.

Ionic–covalent solids

Because of their slightly ionic character these solids form minor amounts of ions when they are added to water. Thus, when a crystalline solid MX, where M is a divalent metal, is in contact with water the following equilibrium will be set up:

$$MX_{(s)} \rightleftharpoons M^{2+}_{(aq)} + X^{2-}_{(aq)} \qquad K = [M^{2+}][X^{2-}]$$

The value of the equilibrium constant is so small. Equilibrium is disrupted when the concentration of any of the ions M^{2+} or X^{2-} is decreased, thus more solid will go into solution to keep the value of K constant. Decreasing any of these ions may be the result of a neutralization reaction, complex formation, displacement, oxidation, or protonation. The rate of dissolution increases with increased concentration of the reagent and with increased temperature.

1. *Neutralization.* Oxides and hydroxides are insoluble in water but soluble in acids. For example, aluminum hydroxide has a low solubility in water:

$$Al(OH)_{3(s)} \rightarrow Al^{3+}_{(aq)} + 3OH^{-}_{(aq)}$$

$$K_1 = [Al^{3+}][OH^{-}]^3 = 1.9 \times 10^{-33}$$

In presence of an acid, the OH– ions are neutralized:

$$H^+ + OH^- \rightleftharpoons H_2O \qquad K_2 = \frac{1}{[H^+][OH^-]} = 1.0 \times 10^{14}$$

This shifts the equilibrium to the right and more hydroxide goes into solution:

$$Al(OH)_3 \mathrm{\ t\ } 3H^+ \rightarrow Al^{3+} \mathrm{\ t\ } 3H_2O$$

$$K = \frac{[Al^{3+}]}{[H^+]^3} = K_1K_2^3 = 1.9 \times 10^9$$

Most hydroxides are soluble in acids because the ionic product of water when raised to the proper power (depending on the hydroxide) is smaller than the solubility product of the hydroxide.

Aluminum hydroxide is an amphoteric hydroxide, i.e., it may behave as an acid:

$$Al(OH)_{3(s)} \rightarrow AlO(OH)^{-}_{2(aq)} + H^+$$

$$K_1 = [AlO(OH)_2^-][H^+] = 4 \times 10^{-13}$$

In presence of an alkali, the H^+ ions are neutralized:

$$H^+ + OH^- \rightarrow H_2O \qquad K_2 = \frac{1}{[H^+][OH^-]} = 1 \times 10^{14}$$

The equilibrium is shifted to the right and more hydroxide dissolves:

$$Al(OH)_{3(s)} + OH^- \rightarrow AlO(OH)^-_{2(aq)} + H20$$

$$K = \frac{[AlO(OH)_2^-]}{[OH^-]} = K_1K_2 = 40$$

Thus, aluminum hydroxide is soluble in both an acid and an alkali. Not all hydroxides, however, are soluble in alkalies. Most oxides behave similar to hydroxides; in water they form a hydroxide surface.

2. *Complex formation.* The dissolution of lead sulfate in sodium chloride solution is an exemple of complex formation. Lead sulfate has a low solubility in water:

$$PbSO_{4(s)} \rightarrow Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

In presence of chloride ions, the chloroplumbate ion is formed:

$$Pb^{2+} + 4Cl^- \rightarrow [PbCl_4]^{2-}$$

thus decreasing considerably the concentration of Pb^{2+} ion. This disrupts the equilibrium of Pb^{2+} in contact with the solid phase, $PbSO_4$, thus more solid goes into solution. The overall reaction can be represented by the equation:

$$PbSO_4 + 4Cl^- \rightarrow [PbCl_4]^{2-} + SO_4^{2-}$$

The dissolution of HgS in a solution of sodium sulfide can be represented similarly:

$$HgS_{(s)} \rightarrow Hg^{2+} + S^{2-}_{(aq)}$$

$$Hg^{2+} + 2S^{2-} \rightarrow [HgS_2]^{2-}$$

3. *Displacement.* The dissolution of a sulfide in a solution containing a metal ion that forms a less soluble sulfide is a displacement reaction. For example, the dissolution of ZnS in $CuSO_4$ solution:

$$ZnS + Cu^{2+} \rightarrow Zn^{2+} + CuS \qquad K = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

This reaction can be considered to take place in the following steps:

$$ZnS_{(s)} \rightarrow Zn^{2+} + S^{2-}_{(aq)} \qquad K_1 = [Zn^{2+}][S^{2-}]$$

$$S^{2-}_{(aq)} + Cu^{2+}_{(aq)} \rightarrow CuS_{(s)} \qquad K_2 = \frac{1}{[Cu^{2+}][S^{2-}]}$$

where K_1 is the solubility product of ZnS and K_2 is the inverse of the solubility product of CuS. It is obvious that $K = K_1K_2$. Since $K_1 = 1 \times 10^{-20}$ and $K_2 = 0.125 \times 10^{45}$, therefore, the value of K will be a large number and the reaction will proceed.

4. *Oxidation.* The dissolution of sulfides in oxygenated water is a typical example. Ferrous sulfide dissolves as a result of the oxidation of sulfide ion to sulfate:

$$FeS_{(s)} \rightarrow Fe^{2+}_{(aq)} + S^{2-}_{(aq)}$$

$$S^{2-} \text{ t } 20, \rightarrow SO_4^{2-}$$

The overall reaction:

$$FeS_{(s)} \text{ t } 2O_{2(aq)} \rightarrow Fe^{2+} + SO_4^{2-}$$

In this reaction, oxygen shares electrons with sulfide ion which is different from oxidation–reduction processes where transfer of electrons takes place (page 47).

5. *Protonation.* Protonation reactions involve the dissolution of compounds of weak acids in strong acids, or formation of volatile acids. For example:

- The dissolution of $CaCO_3$ in acids:

$$CaCO_{3(s)} \rightarrow Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

$$CO_3^{2-} \text{ t } H^+ \rightarrow HCO_3^-$$

$$HCO_3^- \text{ t } H^+ \rightarrow H_2CO_3$$

$$H_2CO_3 \rightarrow H_2O + CO_2$$

The overall reaction:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

If H_2SO_4 is used then $CaSO_4$ forms as a precipitate.

- The decomposition of CaF_2 by concentrated H_2SO_4:

$$CaF_{2(s)} \rightarrow Ca^{2+} + 2F^-$$

$$F^- + H^+ \rightarrow HF$$

- The dissolution of ferrous sulfide in hydrochloric acid:

$$FeS_{(s)} \rightarrow Fe^{2+}_{(aq)} + S^{2-}_{(aq)}$$

$$S^{2-} + H^+ \rightarrow HS^-$$

$$HS^- + H^+ \rightarrow H_2S$$

The overall reaction:

$$FeS + 2H^+ \rightarrow Fe^{2+} + H_2S$$

Not all sulfides, however, are soluble in dilute acid; this can be determined from solubility product of the sulfide (Table 5.1). For example, to calculate the amount of FeS that can be solubilized in 1 liter of 1 M HCl:

$$FeS \rightarrow Fe^{2+} + S^{2-} \qquad K_1 = [Fe^{2+}][S^{2-}] = 5 \times 10^{-18}$$

$$S^{2-} + 2H^+ \rightarrow H_2S \qquad K_2 = \frac{[H_2S]}{[S^{2-}][H^+]^2} = 0.91 \times 10^{22}$$

If X is the molar concentration of FeS that dissolves, then $X = [Fe^{2+}] = [H_2S]$:

Table 5.1: Solubility product K of sulfides: $MS \rightleftharpoons M^{2+} + S^{2-}$, $K = [M^{2+}][S^{2-}]$.

Acid-insoluble sulfides	K	Acid-soluble sulfides	K
HgS	1.6×10^{-52}	ZnS	7.0×10^{-26}
CuS	8.0×10^{-36}	CoS	5.0×10^{-22}
CdS	5.0×10^{-28}	NiS	1.0×10^{-22}
PbS	1.3×10^{-28}	FeS	5.0×10^{-18}
SnS	1.3×10^{-27}	MnS	2.5×10^{-13}

$$\begin{array}{cccc} FeS + 2H^+ \rightleftharpoons Fe^{2+} + H_2S \\ X \quad 2X \quad X \quad X \end{array} \qquad K = \frac{[Fe^{2+}][H_2S]}{[H^+]^2} = K_1K_2$$

$$\frac{X^2}{(1-2X)^2} = 5 \times 10^{-18} \times 0.91 \times 10^{22}$$

Therefore $X = 0.5$ molar or $0.5 \times 88 = 44$ g/L. If the same procedure is conducted for CuS ($K = 10^{-36}$), it will be found that $X = 9.5 \times 10^{-7}$ g/L, hence CuS in insoluble. If, however, the reaction were conducted in an open vessel to permit the removal of H_2S as soon as it is formed then the equilibrium would be shifted continuously to the right. The amount of FeS that can be dissolved approaches the stoichiometric amount according to the overall equation, i.e., 88 g.

Covalent solids

Covalent bond, e.g., that between silicon and oxygen in silica and the silicates, is a strong bond that cannot be broken easily by aqueous solutions: An understanding of the structure of these solids is essential for understanding their dissolution behavior. The basic building block of the silicates is the SiO_4^{4-} tetrahedron, i.e., a silicon atom in the center of the tetrahedron sharing electrons with four oxygen atoms each situated in the apex of the tetrahedron. In silica, all four oxygen atoms in the tetrahedron are shared with other tetrahedra in a three-dimensional network. This results in a very stable and hard structure. In silicates, the SiO_4^{4-} tetrahedra may be sharing corners to form rings, chains, sheets, or a framework structure similar to silica as shown in Figure 5.1. In the framework silicates some of the Si^{4+} ions are substituted by Al^{3+} ions. To compensate for the charge deficit that arises, alkali or alkaline earth ions are incorporated in the holes between the tetrahedra. These ions are labile, i.e., they are easily removed from the solid by exchange with other ions in solution, by acids, or even by water, but the silicate network is not.

As a result of the strong Si–0 bond silica is not solubilized by boiling with concentrated acids except hydrofluoric acid because of the formation of SiF_4 which is a gas that may volatilize or react with water to form fluorosilicic acid, H_2SiF_6. Alumino silicates are attacked slowly by boiling with concentrated acids because the H^+ ions can attack the Al–O bond thus replacing Al^{3+} by H^+ which will become attached to the oxygen and form $Si(OH)_4$ groups which are free to move. However, they are not stable in the hot acid solutions and they will polymerize and precipitate as silica gel. Sometimes the action of the acid stops because the Al–O bonds are deeply buried in the structure and are shielded by the Si–0 groups that the H^+ ions cannot reach. Silicates in form of rings, chains, and sheets are easier to attack because the metal ion, e.g., lithium in spodumene, beryllium in beryl, copper in chrysocolla, magnesium in serpentine, etc., are not incorporated in the SiO_4^{4-} tetrahedra. They can be solubilized leaving behind a silica network. In many cases, however, a preliminary thermal treatment is necessary before leaching to breakdown the silicate network (see chapter 16).

ELECTROCHEMICAL PROCESSES

These processes differ from the previous ones in the following aspects:

- The solid is a conductor, e.g., a metal, or a solid with partially ionic and partially covalent bonds that possesses semiconducting properties, e.g., UO_2, ZnS, and $CuFeS_2$.
- There is a transfer of electrons from the solid phase or from solution to the reacting species, i.e., the process involves an oxidation–reduction couple. The ions or molecules in solution simply diffuse through the boundary layer to meet the solid surface to pick up or give away electrons.
- The solid dissolves at certain localized points while the electron transfer takes place at other points usually much further.
- The oxidation and the reduction reactions proceed simultaneously.
- The kinetics of these reactions are influenced by the presence of lattice defects in the solid and/or the presence of trace impurity which may increase or decrease the electrical conductivity of the solid, and hence the availability of the electrons.
- The rate of dissolution increases with increased reagent concentration and with increased temperature. When two reagents are present, the rate depends only on one at a time.

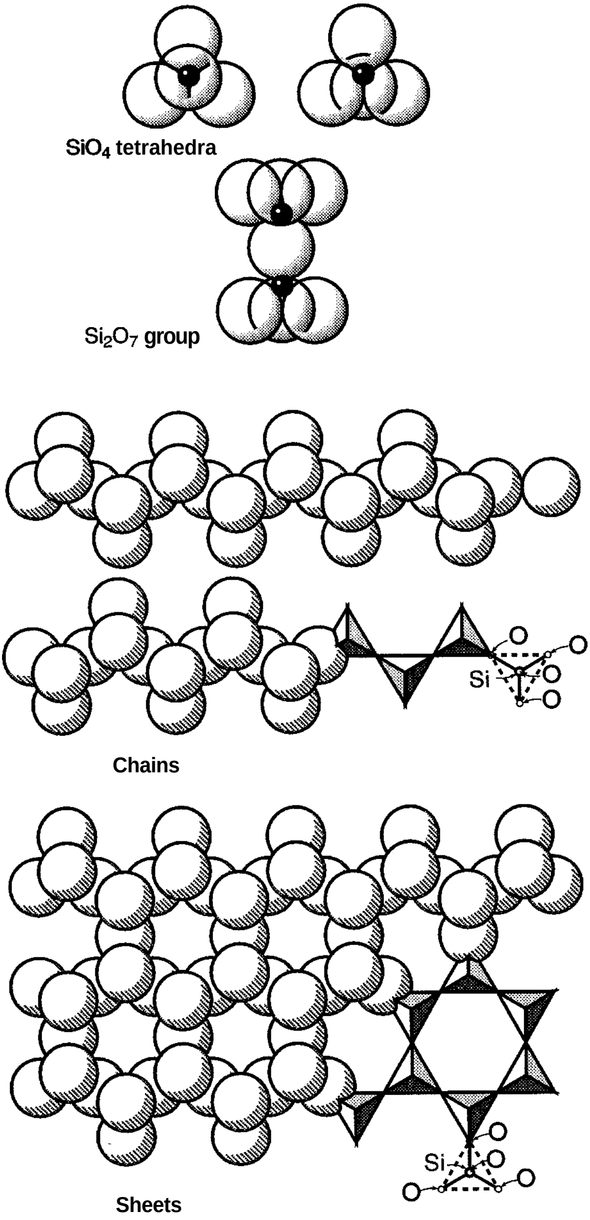

Figure 5.1: Covalent bond in **silicates.**

Metals in oxygenated water

When oxygen is bubbled in water containing a piece of metal, it will be observed that oxygen will be reduced on certain localized regions of the metal (the cathodic zone):

$$^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

while the metal passes into solution at another region (the anodic zone):

$$M \rightarrow M^{n+} + ne-$$

This reaction was demonstrated in a number of ways. For example, when an iron nail was immersed in a salt gel containing few drops of phenolphthalein and potassium ferrocyanide, it was found that after some time, the region surrounding the head of the nail became blue because the Fe^{2+} ions liberated at the anodic region reacted with ferrocyanide ion to form Prussian blue, while the region surrounding the tip of the nail became red because of the $OH-$ liberated at the cathodic region reacted with the phenolphthalein to form the red color. If the iron is freely suspended in the oxygenated water then ferrous ion liberated will react with $OH-$ ions forming $Fe(OH)_2$ which oxidizes further forming $Fe(OH)_3$, the red brown precipitate known as rust. Other metals behave similarly, e.g., when zinc is suspended in water and oxygen is bubbled through the slurry it will be observed that after some time a white precipitate of $Zn(OH)_2$ forms.

When two pieces of iron are immersed in a sodium chloride solution and are separated by a porous diaphragm but connected together with a wire, and nitrogen is bubbled in one compartment and oxygen in the other, it will be observed that the piece in the oxygen-deficient compartment dissolves and precipitate forms due to the hydrolysis of ferrous ion liberated while in the other compartment (oxygen-saturated), the solution remains clear because no dissolution takes place. In this case one piece acted as anode (oxygen-deficient compartment) while the other (oxygen-saturated compartment) acted as cathode. This electrochemical nature of dissolution can be confirmed by inserting a voltmeter in the connecting wire and observing the potential difference generated. Also, a similar potential difference can be observed when one piece of iron is immersed in a dilute $FeSO_4$ solution while the other immersed in a concentrated $FeSO_4$ solution. Here again one piece acts as anode (low-ion concentration compartment) while the other acts as a cathode. Such cells are called concentration cells.

Metals in dilute acid

In this case, when oxygen is absent but an acid is added, the H^+ ions pick up electrons at certain regions of the metal and the metal goes into solution:

$$2H^+ + 2e^- \rightarrow H_2$$

$$M \rightarrow M^{n+} + ne-$$

Usually, in reactions of this type, the hydrogen evolved can be seen taking place on localized spots, and the metal also dissolves at localized spots forming pits. Due to the acid medium, M^{2+} ion remains in solution, i.e., no precipitation takes place, and the rate will be proportional to the acid concentration.

Metals by displacement

Another type of these oxidation–reduction processes is the dissolution of a metal in the aqueous solution of a salt of another more noble metal, e.g., iron in copper sulfate solution:

$$Fe + CuSO_4 \rightarrow Cu + FeSO_4$$

This reaction takes place according to:

Cathodic reaction: $Cu^{2+} + 2e^- \rightarrow Cu$

Anodic reaction: $Fe \rightarrow Fe^{2+} + 2e-$

While iron can displace copper from solution, copper can displace silver. In the first case copper is a noble metal as compared to iron, in the second case it is a base metal as compared to silver. Hydrogen can displace copper but at a high temperature and pressure.

Metal with complex formation

In this case the cation liberated from the solid phase is kept into solution by a complexing agent. The dissolution of gold in cyanide solution may be cited as an example. Here oxygen is adsorbed at the surface of the metal picking up electrons as in the previous case with the difference that the reduction proceeds to H_2O_2 stage (which was confirmed experimentally):

$$O_2 \text{ t } 2H_2O + 2e- \rightarrow 2OH^- + H_2O_2$$

The oxidation of the metal leads to Au^+ ion which is then complexed by the cyanide ion:

$$Au \rightarrow Au^+ \text{ t } e-$$

$$Au^+ + 2CN^- + [Au(CN)_2]^-$$

The overall reaction:

$$2Au + 4CN^- + O_2 \text{ t } 2H_2O \rightarrow 2[Au(CN)_2]^- \text{ t } 2OH^- + H_2O_2$$

The electrochemical nature of this process has been demonstrated by embedding a small gold sphere in a KCN gel to which air was introduced from one direction. It was found that the gold corroded at the surface far away from the air flow, i.e., an oxygen concentration cell was formed around the sphere (Figure 5.2): the surface less exposed to oxygen acted as anode while the surface in direct contact with oxygen acted as cathode.

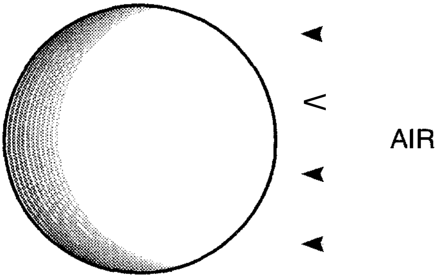

Figure 5.2: A gold bead embedded in potassium cyanide gel corroded at the surface less exposed to the air: an illustration of the electrochemical phenomenon during the dissolution of metals (after Thompson, 1947).

Oxides

Most oxides dissolve in acids or bases by a chemical process as described earlier. However, there are few that are insoluble and require either an oxidizing or a reducing agent for their dissolution. Such processes follow an electrochemical mechanism.

- Uranium dioxide is a semiconductor that is insoluble in dilute sulfuric acid but dissolves in presence of oxygen in the following way:

  Anodic reaction: $UO_2 \rightarrow UO_2^{2+} + 2e^-$

  Cathodic reaction: $^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

  Overall reaction: $UO_2 + {}^1/_2O_2 + 2H^+ \rightarrow UO_2^{2+} + H_2O$

  The function of the acid is to neutralize the OH^- ions liberated thus preventing the precipitation of uranyl hydroxide. In a similar way, the dissolution of uranium dioxide in sodium carbonate solution takes place through the steps:

  Anodic reaction: $UO_2 \rightarrow UO_2^{2+} + 2e^-$

  $$UO_2^{2+} + 3CO_3^{2-} \rightarrow [UO_2(CO_3)_3]^{4-}$$

  Cathodic reaction: $^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

  Overall reaction:

  $$UO_2 + 3CO_3^{2-} + {}^1/_2O_2 + H_2O \rightarrow [UO_2(CO_3)_3]^{4-} + 2OH^-$$

- Manganese dioxide is insoluble in dilute H_2SO_4 and insoluble in a solution of $FeSO_4$ but is soluble in a mixture of the two according to:

  $$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$$

  This is an oxidation–reduction process that takes place as follows:

  Oxidation: $Fe^{2+} \rightarrow Fe^{3+} + \mathbf{e-}$

  Reduction: $MnO_2 + 4H^+ + 2e^- + Mn^{2+} + 2H_2O$

  Oxalate ion or sulfurous acid can also be used as reducing agents:

  $$[C_2O_4]^{2-} \rightarrow 2CO_2 + 2e^-$$

  $$SO_2 + 2H_2O \rightarrow H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

In the reduction step it is observed that tetravalent manganese ion in MnO_2 is reduced to a divalent ion:

$$Mn^{4+} + 2e^- \rightarrow Mn^{2+}$$

Once this takes place, the electrostatic forces of attraction in the crystalline solid becomes weak and H^+ ions in solution can remove the oxide ions from the solid phase as H_2O. This oxidation–reduction process is different from other electrochemical processes in two respects:

- Electrons are furnished to the solid in the reduction process while they are given away by the solid in other electrochemical processes.
- Both oxidation and reduction processes occur at the same spot in the reduction process and not at two different locations as in other electrochemical processes, i.e., there are no anodic and cathodic zones.

Sulfides

Most sulfides are insoluble in water but it has been shown that they can be solubilized by a chemical mechanism when oxygen is present, e.g.:

$$FeS_{(s)} \rightarrow Fe^{2+} + S^{2-}$$

$$S^{2-} \text{ t } 20, \rightarrow SO_4^{2-}$$

It was also shown that sulfides can be acid-soluble or acid-insoluble. Those soluble follow a chemical mechanism, e.g.:

$$FeS_{(s)} \rightarrow Fe^{2+} \text{ t } S^{2-}$$

$$S^{2-} + 2H^+ \rightarrow H_2S$$

Acid-insoluble sulfides, however, can be solubilized by an electrochemical mechanism when an oxidizing agent is present. For example, copper sulfide, which is acid-insoluble, can be solubilized in a dilute acid in presence of oxygen. Oxygen is adsorbed on the surface of the solid whereby electron transfer takes place.

$$^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

At the same time, the solid gives electrons as follows:

$$CuS_{(s)} \rightarrow Cu^{2+}_{(aq)} + S_{(s)} + 2e_{-}$$

The electrochemical nature of these types of reactions has been demonstrated by embedding a piece of massive sulfide, e.g., pyrite in a salt gel containing few drops of phenolphthalein. After few days a red color formed at the sulfide–air interface thus indicating the liberation of OH– ions where oxygen is reduced cathodically on the surface (Figure 5.3). To accelerate such process, OH– ions formed at the cathodic region must be neutralized as soon as formed so that more oxygen can be reduced and more Cu^{2+} ions go into solution.

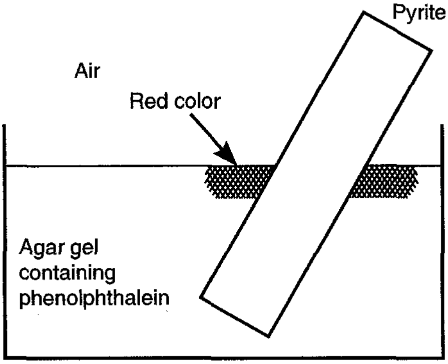

Figure **5.3**: **A** piece of pyrite embedded in a gel containing phenolphthalein showed red color at the sulfide–air interface; an illustration of the formation of cathodic zone during leaching of sulfides (after Thornber, 1975).

A metal in contact with a sulfide mineral may promote the formation of a galvanic cell. Thus, chalcopyrite is quite stable in dilute acid at room temperature, but when a small amount of iron powder is added to it, an immediate generation of H_2S takes place (Figure 5.4). The chalcopyrite is attacked leaving behind a phase rich in copper sulfide, and the iron goes into solution according to the scheme:

Anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^{-}$

Cathodic reaction: $2CuFeS_2 + 2e- \rightarrow Cu_2S + 2Fe^{2+} + 3S^{2-}$

The sulfide ion liberated forms H_2S with the H^+ ions in solution:

$$S^{2-} + 2H^+ \rightarrow H_2S$$

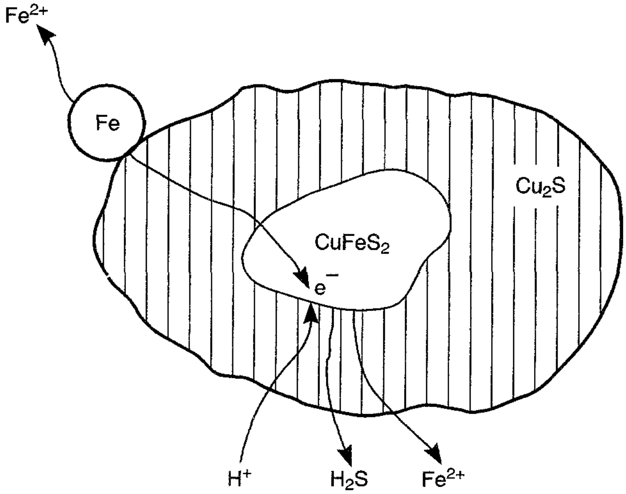

Figure 5.4: Formation of a galvanic cell when chalcopyrite is in contact with metallic iron; Fe accelerates the decomposition of chalcopyrite to Cu_2S (Baur et al., 1974).

The overall reaction:

$$2CuFeS_2 + Fe + 6H^+ \rightarrow Cu_2S + 3Fe^{2+} + 3H_2S$$

A similar reaction takes place if copper powder was used instead of iron powder. It has been shown further that when two sulfide minerals are in contact, the one having higher electrode potential will act as a cathode while the other will act as the anode. Thus, zinc sulfide when in contact with copper sulfide will dissolve more rapidly than when copper sulfide is absent. Similarly pyrite was found to enhance the aqueous oxidation of PbS, ZnS, and CuS minerals as shown in Figure 5.5, while the same minerals retard the dissolution of pyrite. This explains in part why ores from different localities may behave differently on leaching because of their different mineralogical composition.

ELECTROLYTIC PROCESSES

In electrolytic processes, an outside potential (EMF) is imposed on the solid which is made as anode in an electrolytic cell to cause its dissolution. For a metal, the reaction would be:

$$M \rightarrow M^{n+} + ne^-$$

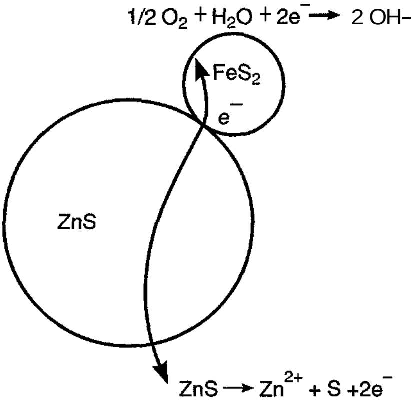

Figure **5.5:** Formation of galvanic cells when two sulfides are in contact; FeS_2 accelerates the dissolution of ZnS in acid medium (Mizoguchi and Habashi, 1983).

For a semiconducting divalent sulfide:

$$MS \rightarrow M^{2+} + S + 2e^-$$

Both processes are used industrially; in the first case as a metal refining process, in the second as a metal and elemental sulfur recovery. The rate of dissolution increases with increased current density.

THE BOUNDARY LAYER

A solid in contact with a liquid is covered by a stagnant film of liquid about 0.03 mm in thickness called the Nernst boundary layer after its discoverer Walther Nernst. Its existence is manifested in a stream line flow where the velocity of a liquid in a pipe is maximum at the center and gradually decreases to zero at the inside walls. This concept was applied to explain the dissolution of a solid in water. When a solid was agitated in water and the solution analyzed at intervals, it was found that the rate of increase of the solute concentration followed by the equation:

$$\frac{dC}{dt} = k(C_s - C)$$

where C is the concentration of the solute at time t, C_s is the solubility of the compound in water at the experimental temperature, and k is the velocity constant.

It was suggested that a saturated layer is rapidly formed at the interface and that the observed velocity is the rate at which the solvated molecules diffuse from this layer into the bulk of the solution. On applying Fick's law of diffusion to this process, then at a constant volume:

$$\frac{dn}{dt} = \frac{\mathcal{D}A}{\delta}(C_s - C)$$

where n is the number of species diffusing in unit time, $\mathcal{D}$ is the diffusion coefficient, A is the surface area of the solid, and δ is the thickness of the saturated layer adhering to the surface of the solid, i.e., the boundary layer. Since:

$$C = \frac{n}{V}$$

where V is the volume of solution, the above equation becomes:

$$\frac{dC}{dt} = \frac{\mathcal{D}A}{\delta V}(C_s - C) = k(C_s - C)$$

Thus, the rate constant k was identified by $\mathcal{D}A/\delta V$. This explained why the rate of dissolution increased with increased agitation because under these conditions, the thickness of the boundary layer decreases hence the increased rate of dissolution.

The rate equation for physical processes was later extended to chemical processes. It has been supposed that the reacting species must diffuse through the boundary layer before reacting. The rate equation would then be:

$$-\frac{dC}{dt} = k(C - C_i)$$

where k is the rate constant, C is the concentration in the bulk of the solution, and C_i is the concentration of the reactant at the interface; the negative sign indicates a decrease in concentration. The interaction between a solid and a leaching agent therefore takes place through the following steps:

1. Diffusion of reacting species to the interface
2. Adsorption at the interface
3. Reaction at the interface
4. Desorption of the products
5. Diffusion of the products from the interface

Any of these may be rate-controlling depending on its relative speed with respect to the others.

Diffusion-controlled processes. This is the case when the rate of chemical reaction at the interface is much faster than the rate of diffusion of reactants to the interface, resulting in $C_i = 0$:

$$\text{Rate} = \frac{\mathcal{D}}{\delta} A(C - C_i) = k_1 AC$$

These processes are characterized by:

- A strong dependence on the speed of agitation since agitation decreases the thickness of the boundary layer.
- Slight dependence on temperature since the rate of diffusion is only slightly influenced by temperature.

Chemically controlled processes. This is the case when the rate of chemical reaction is much slower than the rate of diffusion hence it determines the observed rate:

$$\text{Rate} = k_2 AC_i$$

These processes are characterized by independence on the speed of agitation because diffusion does not play an important role, and strongly dependent on temperature since the rate of chemical reaction increases exponentially with temperature.

Intermediate-controlprocesses. This is the case when both rates are of the same magnitude, i.e., when a concentration gradient is formed across the boundary layer, but $C_i \neq 0$:

$$\text{Rate} = k_1 A(C - C_i) = k_2 AC_i$$

Therefore,

$$C_i = \frac{k_1}{k_1 + k_2} C$$

$$\text{Rate} = \frac{k_1 k_2}{k_1 + k_2} AC = kAC$$

where $k = k_1 k_2/(k_1 + k_2)$.

This represents the general case of leaching processes. If $k_1 \ll k_2$, then $k = k_1 = \mathcal{D}/d$, i.e., the process is diffusion-controlled. If $k_2 \ll k_1$, then $k = k_2$, i.e., the process is chemically-controlled.

SUMMARY

Table 5.2 gives a summary of the different leaching processes.

Table 5.2: Summary of dissolution reactions in aqueous solutions.

Type	Characteristic	Examples
Physical	Ionic solids, dissolution is based on hydration.	$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$
Chemical	*a)* Partially ionic and covalent bond solids, based on neutralization, complex formation, oxidation, or protonation.	• Neutralization $Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$ $Al(OH)_{3(s)} + OH^- \rightarrow [AlO(OH)_2]^-_{(aq)} + H_2O$ • Complex formation $PbSO_{4(s)} + 4NaCl_{(aq)} \rightarrow Na_2[PbCl_4]_{(aq)} + Na_2SO_{4(aq)}$ • Oxidation $ZnS_{(s)} + 2O_{2(aq)} \rightarrow ZnSO_{4(aq)}$ • Protonation $FeS + 2H^+ \rightarrow Fe^{2+} + H_2S$ $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$
	6) Mainly covalent solids, like silica and silicates.	Insoluble
Electrochemical	Conducting or semiconducting solids, based on electron transfer from solid to liquid, i.e., oxidation–reduction process.	$ZnS + 2H^+ + {}^1/_2O_2 \rightarrow Zn^{2+} + S + H_2O$ $2Au + 4CN^- + O_2 + 2H_2O \rightarrow 2[Au(CN)_2]^- + 2OH^- + H_2O_2$ $UO_2 + 3CO_3^{2-} + {}^1/_2O_2 + H_2O \rightarrow [UO_2(CO_3)_3]^{4-} + 2OH^-$
	High-valency oxides, based on electron transfer from liquid **to** solid.	$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$
Electrolytic	Imposed EMF, conducting or semiconducting solids.	Metals $Ni \rightarrow Ni^{2+} + 2e^-$ Sulfides $Ni_3S_2 \rightarrow 3Ni^{2+} + 2S + 6e^-$

Chapter Six

Methods and Equipment

Leaching in Place 123
    Spraying technique 125
    Injection technique 127
Heap or Dump Leaching 128
    Pyrite 135
    Copperores 137
    Uranium ores 137
    Gold ores 137
Percolation or Vat Leaching 138
    Thin layer leaching 139
Agitation or Pulp Leaching 140
    Methods of agitation 140
    Ambient pressure 140
    High pressure 144
    Autoclaves 146
Baking Process 157
    Digesters 157
    Rotary kilns 158
    Pugmills 158
Summary 158

The method used for leaching an ore depends on the grade of the ore and the ease with which the mineral values are dissolved in a particular reagent. The most common methods of leaching are the following.

LEACHING IN PLACE

This method is also known as leaching *in situ* or *solution mining*. The ore is simply shattered and leached in place over long periods of time because it is usually too low in grade to justify mining and transportation expenses. Recently. however. because of its success. the method has been used for high-grade ores as well. It is applied for extracting soluble salt deposits from the underground, for example, potash, sodium chloride, sodium sulfate, and sodium carbonate (trona) as well as for leaching of uranium and copper ores (Table 6.1). The following solvents are generally used:

- Water for leaching potash and trona and other water-soluble salts.
- Dilute sulfuric acid for leaching copper ores. When copper sulfide minerals are also present, these are solubilized by the combined action of air and water. The presence of pyrite enhances the leaching because of its oxidation and the formation of sulfuric acid and ferric sulfate. The oxidation reactions are exothermic and the heat generated facilitates continued oxidation.
- Dilute sulfuric acid and sodium chlorate, or ammoniacal ammonium carbonate and hydrogen peroxide are used for leaching uranium deposits.

Table **6.1:** Leaching in place.

Deposit	Grade	Leaching agent	Plant location, examples
Copper	low	H_2SO_4	Arizona
	high	H_2SO_4	Nevada
Uranium	low	$H_2SO_4 + NaClO_3$	Wyoming
	low	$(NH_4)_2CO_3 + H_2O_2$	Texas
Potash	high	water	Saskatchewan
Sodium sulfate	high	water	Alberta
Trona (sodium carbonate)	high	water	Wyoming

The use of nuclear explosives as a cheap mean for fracturing the rocks has been suggested to be used in conjunction with this method of leaching. Leaching in place involves dissolving selectively the mineral values by spraying or injecting the leaching agent in the deposit, then collecting the pregnant solution. The basic criteria required for an underground deposit to be considered suitable for leaching in place are:

- The ore body must be enclosed between impermeable strata that will prevent the loss of solution.
- It must be permeable to the leaching solution.

Two techniques are used: spraying when the ore body is exposed, and injection when it is buried (Figure 6.1).

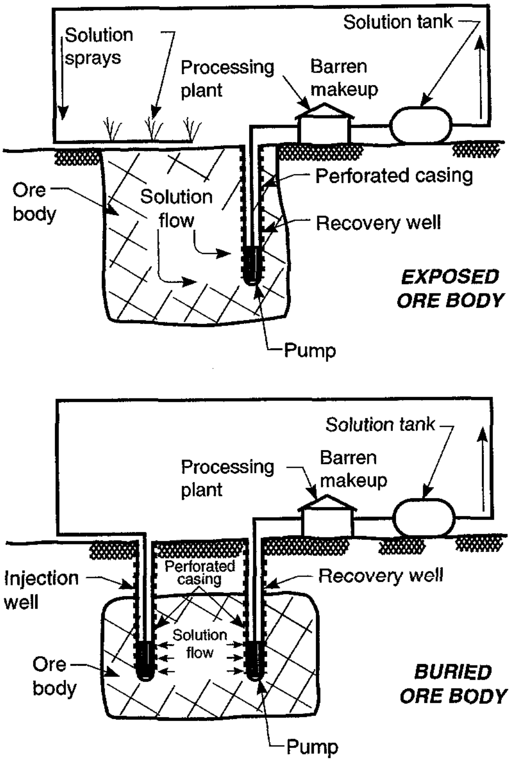

Figure 6.1: Methods of in-situ leaching. *Top*: Spraying technique when the ore body is exposed. *Bottom*: Injection technique when the ore body is buried.

Spraying technique

Figure 6.2 shows a general scheme of such technique as applied for the leaching of an exhausted copper mine in Arizona, U.S.A. In this case, the mine was exploited for many years by conventional methods until the grade of the ore became too low to justify mining. The mine was then reopened when the leaching in place method was proposed. Dilute sulfuric acid is sprayed at the top and allowed to penetrate through the whole mine to dissolve the copper minerals. The pregnant solution is then collected in an underground reservoir then pumped to the surface for copper recovery and recycling the acid.

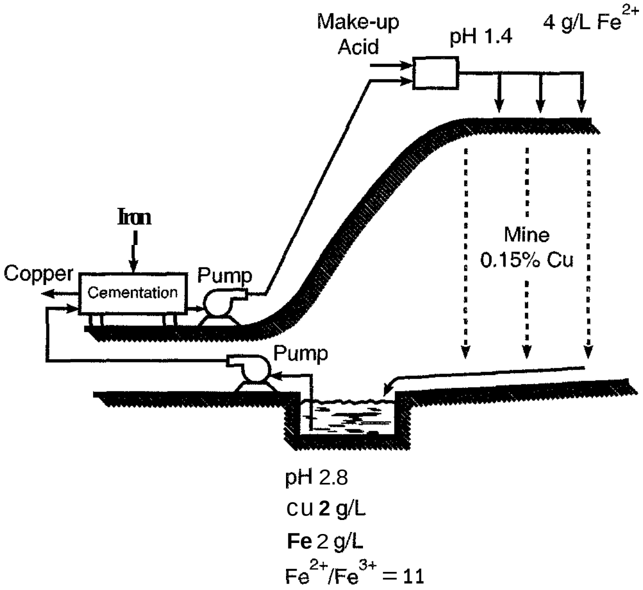

Figure 6.2: Leaching in-situ at Miami Mine, Arizona (25 t/d cement copper).

A slightly modified technique has also been applied in leaching a relatively high-grade copper oxide ore containing about 2% Cu. This takes place, for example, at the Big Mike Mine in Nevada (Figure 6.3). The walls of the open pit and a part of the bottom of the pit as blasted and the shattered ore and rock are leveled and leached by sprinkling 1% H_2SO_4. The solution percolates through the crushed ore leaching out the copper. The copper-bearing solution is then drawn from the bottom of the pit by a pump in a pipe-encased hole sunk at the bottom. The leach solution drains in the hole through a perforated casing and is pumped to the ground level. Another operation is the in-situ leaching of copper from Old Reliable Mine in Mammoth, Arizona (Figure 6.4). In this case the leaching agent is pumped to the top of the deposit and the pregnant solution recovered at the bottom.

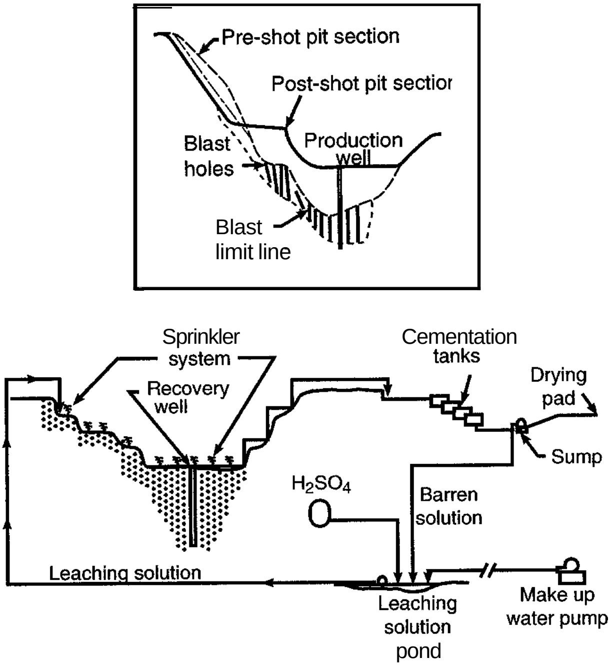

Figure *6.3:* In-situ leaching operation at Big Mike Copper Mine, Nevada.

Injection technique

In this method the leaching agent is injected in the ore deposit by means of vertical perforated pipes arranged in a regular pattern (Figure 6.5). For a group of injection pipes there is a recovery well with an underground pump to collect and pump the pregnant solution to the surface. In mining water-soluble salts from underground (Figure 6.6), the temperature in the mine may be above 50 °C; the dissolution process is, however, endothermic and as a result the brine brought to surface may be at a temperature between that of the injected water and that of the mine.

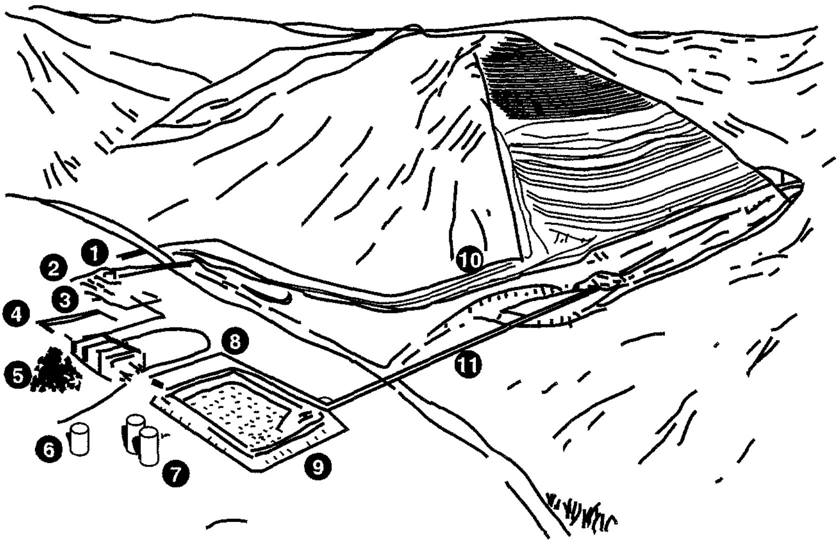

Figure *6.4:* A typical in-situ leaching of copper ore (Old Reliable Mine, Mammoth, Arizona). (1) Pumps; (2) Barren solution pond; *(3)* Make-up water; *(4)* Precipitation tanks; *(5)* Shredded and de-tinned cans; (6) Fresh water; (7) Acid tanks; (8) By-pass; (9) Pregnant solution pond; (10) Acid pipeline; (11) Pregnant solution.

HEAP OR DUMP LEACHING

In this method an area is first cleared from all vegetation then leveled at a slight inclination, compacted, and covered with an asphalt layer or a flexible plastic sheet (Figure 6.7). The crushed ore is then transported from the mine to the prepared site by dump trucks to a level of 10–15 m high (Figure 6.8). The leaching agent is then sprayed at the top of the dump (Figures 6.9 and 6.10) through which it percolates and the leach solution is collected in streams at the bottom. When the material is fully leached, the dump is either abandoned or loaded on trucks for disposal and the site re-used for leaching another batch.

Main problems in operating a heap are the plugging with fine clays, ferric hydroxide or basic sulfate, evaporation losses, leakage of solution at the bottom of the heap, and channelling. The behavior of leach solution in the heap can be studied using a neutron source and a detector. Fast neutrons undergo elastic collisions with most atoms except hydrogen atoms since these have a mass essentially the same as a neutron, and as a result the neutrons lose much of their energy during collision. Therefore, neutron flux variation at the detector can be attributed to variations in the water content of the material surrounding the drill hole. Studies based on tritiated water, HTO (tritium is a beta emitter having half-life of 12.26 years) injected into the leach solution gave also valuable information. Typical examples of heap or dump leaching are the following (Table 6.2).

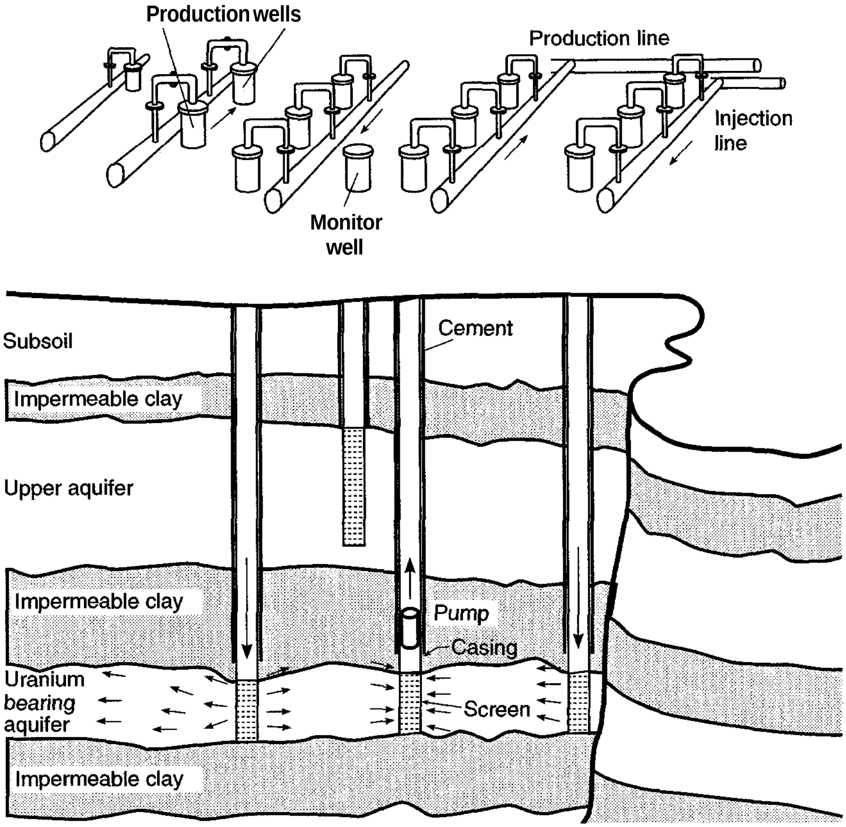

Figure 6.5: In-situ leaching by injection.

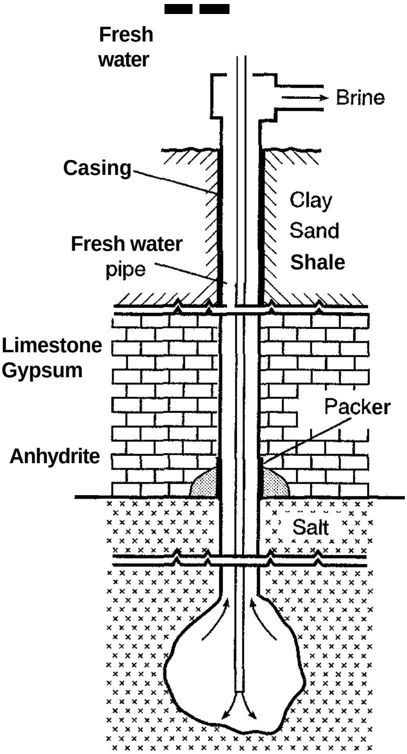

Figure 6.6: Mining of water-soluble salts from underground.

Table *6.2:* Summary of heap leaching processes.

Deposit	Grade	Leaching agent	Plant location, examples
Pyrite containing Cu, Zn, and Pb	high	water + air	Rio Tinto, Spain
Copper oxide	low high	dilute H_2SO_4 dilute H_2SO_4	Utah, Montana
Uranium	low	dilute H_2SO_4 + air	Arizona
Gold	low	NaCN + air	Nevada

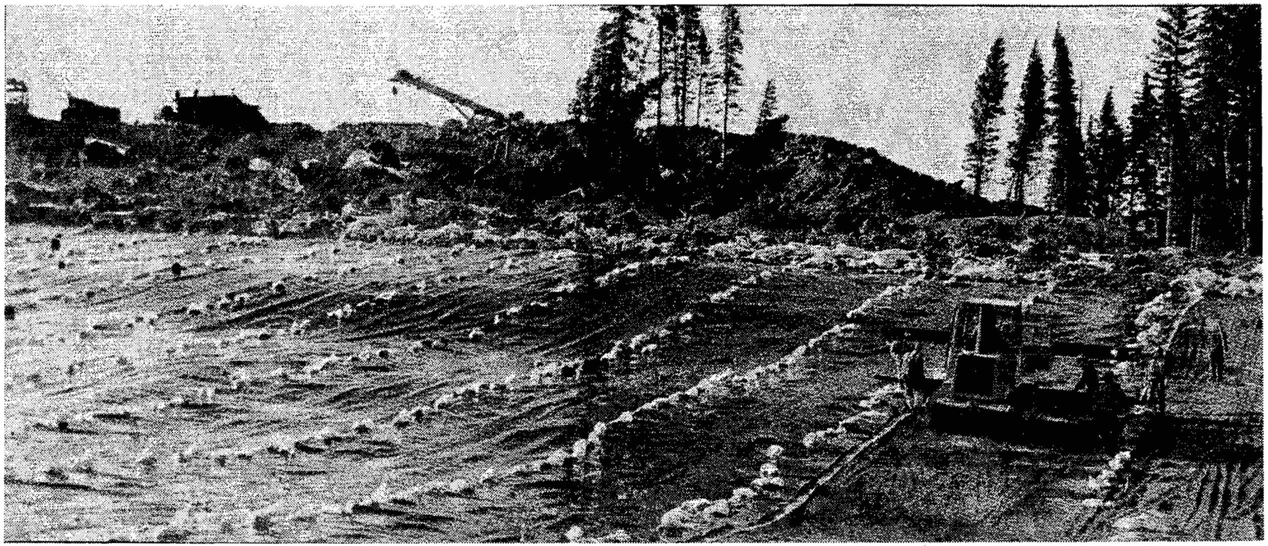

Figure 6.7: Preparation of **site** for dump **leaching.**

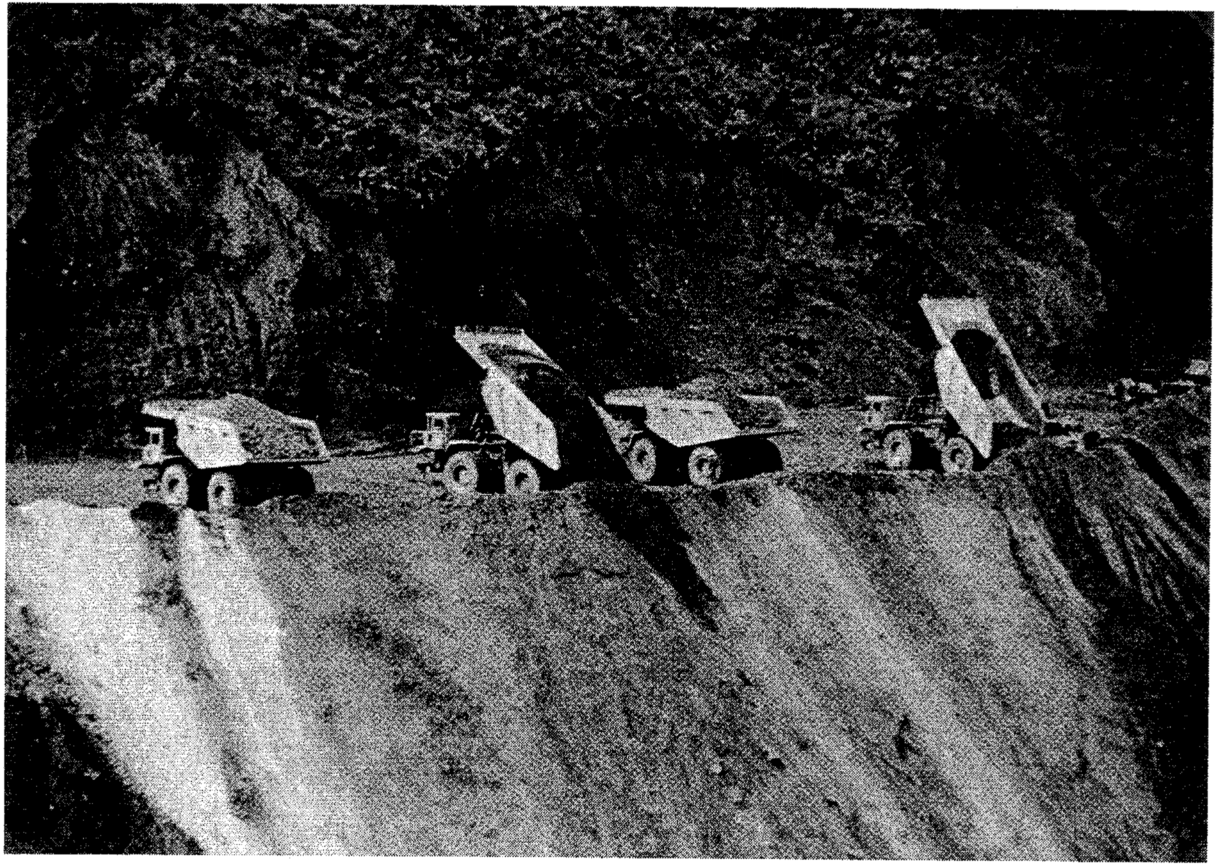

Figure 6.8: Transportation of ore for dump leaching.

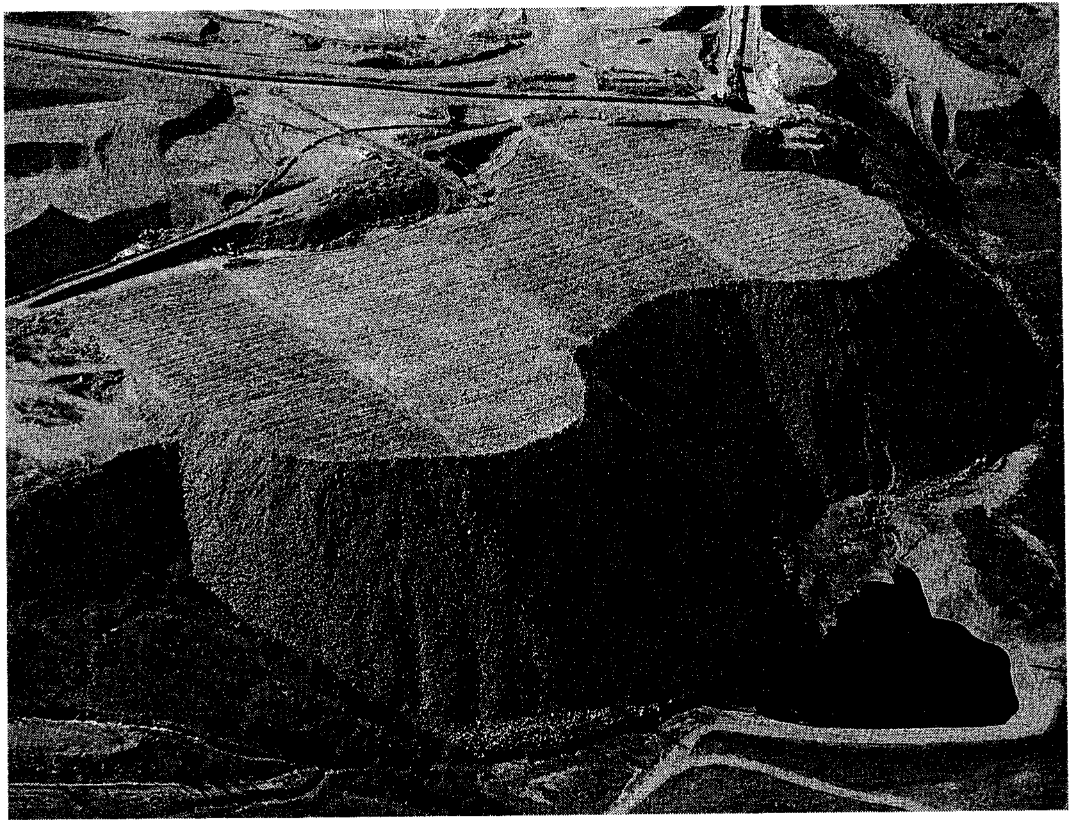

Figure 6.9: A dump leaching operation.

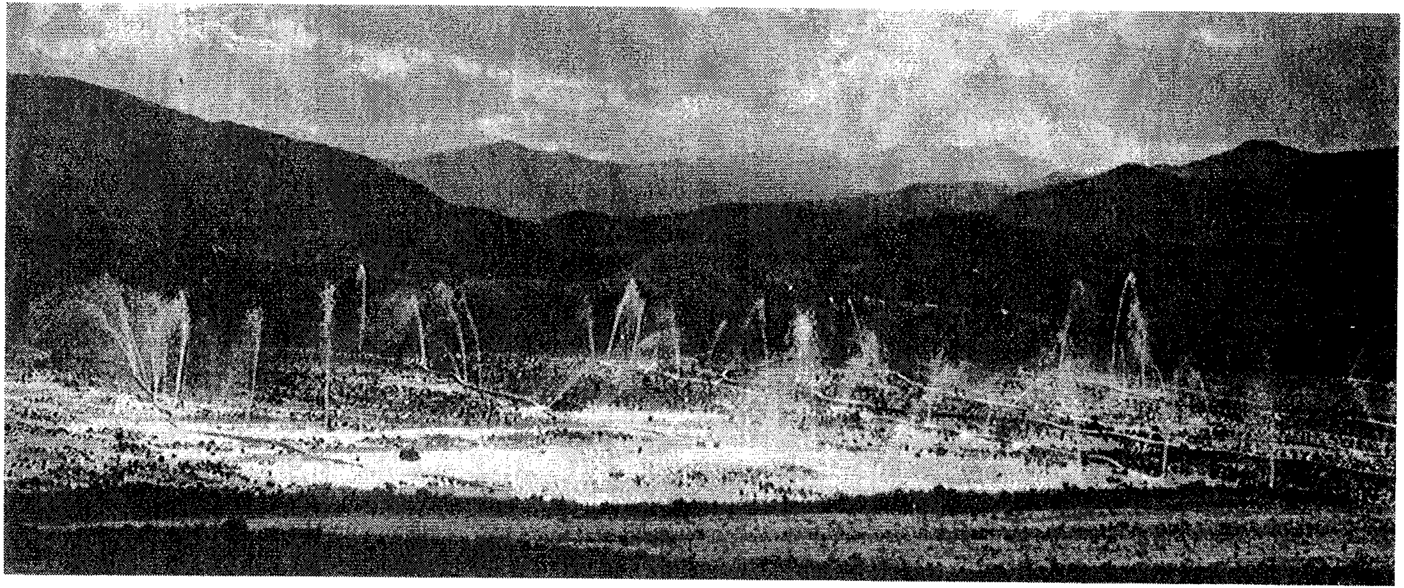

Figure 6.10: Spraying of leaching agent on the top of the dump.

Heap leaching was first limited to warm climates. Recently, it was adapted to cold regions by heating the leach solutions and insulating the piping system. Material handling and ore stock-piling became an enormous engineering operation as shown in Figures 6.11 and 6.12.

Pyrite

Heap leaching is used on a large scale for leaching copper and zinc from pyrite ores. The heap is sprayed with water and left for long periods of time to undergo action by air, water, and ferric salts, till most of the copper is converted to copper sulfate. Table 6.3 gives some data for the process. When the pyrite is fully leached, it is loaded on trucks and shipped to sulfuric acid manufacturers.

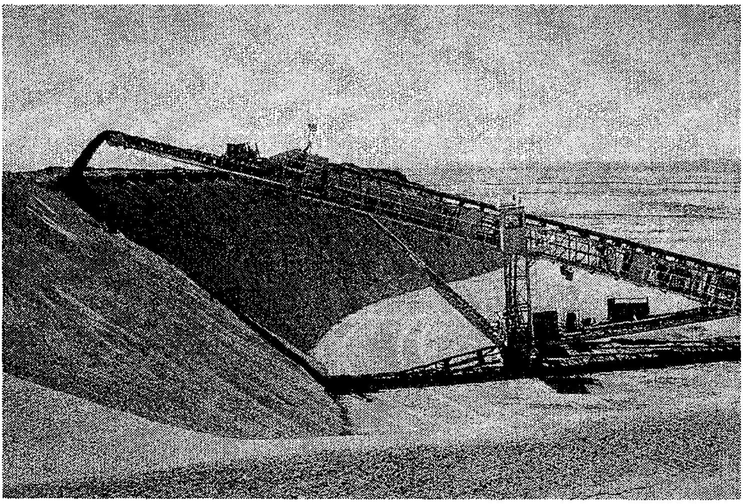

Figure **6.11**: Stockpiling crushed ore on the leach pad at Newmont's Zaragshan operation in Uzbekistan.

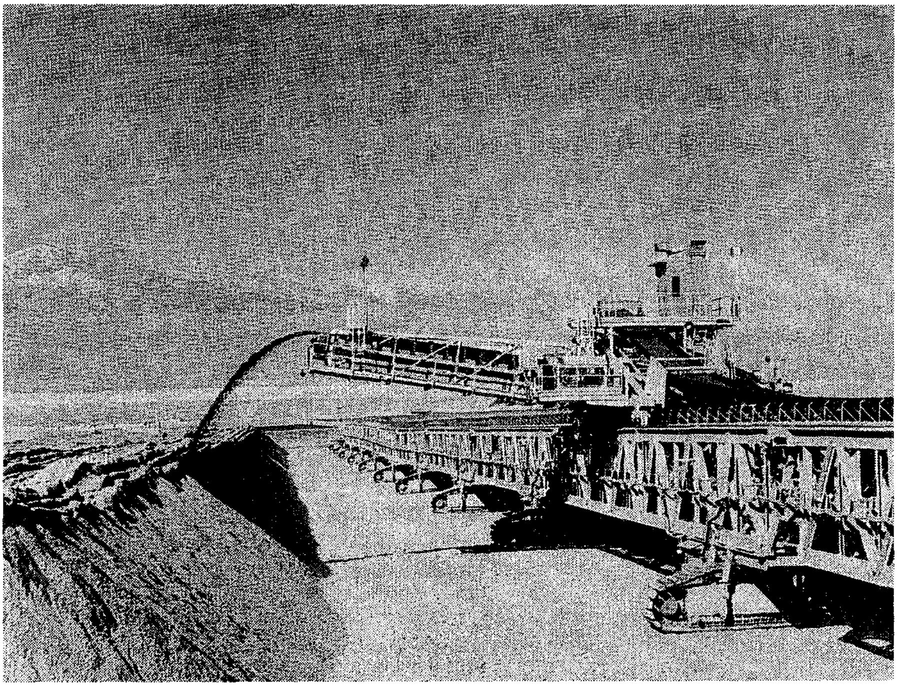

Figure 6.12: The Rahco mobile conveyor installed at the Cyprus Amax Mineral/Codelco El Abra mine stacks leachable ore to a depth of 6 m at a rate of 8600 st/hr. The conveyor's position is established and controlled by Global Positioning Satellite data to an accuracy of ±4 cm.

Table 6.3: Heap leaching of pyrite ore.

	Analysis of ore		Analysis of leach solution	
	Before leaching %	After leaching %		g/L
Cu	1.25	0.4	Cu	1
Pb	1.50	1.28	Pb	0
Zn	2.0	0.9	Zn	1
As	0.5	0.3	As	0.1
Bi	0.05	0.01	Bi	0.001
Fe	42.0	41.75	Fe(II)	8
S	47.5	48.0	Fe(III)	1
SiO_2	5.0	3.75	H_2SO_4	10
H_2O	—	≈ 3.0	—	—

Copper ores

The process was applied for leaching stock piled waste rock containing small smounts of copper too small to be recovered by any other means. It was so economical that many heaps of low-grade copper ores were constructed and leaching applied. Later, even high-grade copper oxide ores were treated in the same way provided however that the acid-consuming gangue is not excessive, e.g., at Miami, Arizona. Leaching copper oxides ores in heaps is different from that of sulfides. In the former case, air is not necessary for leaching and the temperature of the heap does not rise appreciably, while in the latter case air is essential for leaching and the temperature rises due to the oxidation reactions involved.

Uranium ores

In a typical dump leaching of uranium ores, a low-grade ore containing 0.05% U_3O_8 is leached with dilute sulfuric acid (35%). In about 8 days uranium is solubilized by the combined action of air and acid; water is then sprayed at the top of the heap to leach the uranium out of the bed. Uranium in solution is about 0.2–0.6 g/L, and the recovery is about 88%.

Gold ores

The Cortez Gold Mines in Nevada has been leaching successfully low-grade limestone gold ore by this method. About 0.7 million tons of ore containing less than one ppm gold is treated in this way every year. The leaching agent, 0.03% NaCN solution at pH 10.5, is sprinkled at the top of the heaps, and the pregnant solution is collected at the bottom in rubber-lined canals. It takes about three months to terminate a leaching cycle. Finely ground gold ores are also leached by this method; however, agglomeration prior to leaching is essential to permit percolation of the solution during leaching. For this purpose, the ore is mixed with a certain amount of cement then water is added to form a paste which is the allowed to agglomerate in a standard rotating disc or rotating drum. After few days the pellets formed are strong enough to be handled for leaching. Naturally, this agglomeration method applies only to alkaline leaching agents such as the cyanide solution since cement is attacked by acids.

PERCOLATION OR VAT LEACHING

This process is suited to cases where the material is porous and sandy, and is inapplicable to material which tends to pack into impervious masses. Regularity in the size of the particles rather than their actual size is the chief factor governing good percolation. The idea is that where the particles are of unequal size, the small ones pack in the openings between the larger ones, thereby clogging the channels. Extraction becomes slow, and channelling of solutions through the bed takes place. The method is therefore unsatisfactory if much slime is present.

The material to be leached is placed in a tank equipped with a false bottom covered with a filtering medium (Figure 6.13). The leach solution is added at the top of the tank and is allowed to percolate through the material. These tanks are usually arranged **so** that a countercurrent system is employed and thus a continuous operation is achieved; the new solids being added to the last tank and the weak liquid to the first and pumped successively from one tank to another till it reaches the last tank. Tanks having a capacity of 12 000 tons of ore are in common use (Figure 6.14). When leaching is finished, the tanks are emptied by mechanical shovels, and a new batch is introduced. Leaching time varies from 2 to 4 days. The method is used for leaching gold, copper, and uranium ores. Its advantages are minimum reagent consumption, the production of high-grade pregnant solution, and elimination of the use of expensive thickeners or filters.

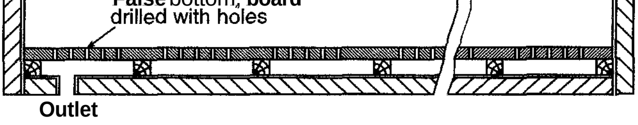

Figure 6.13: Percolation **tank.**

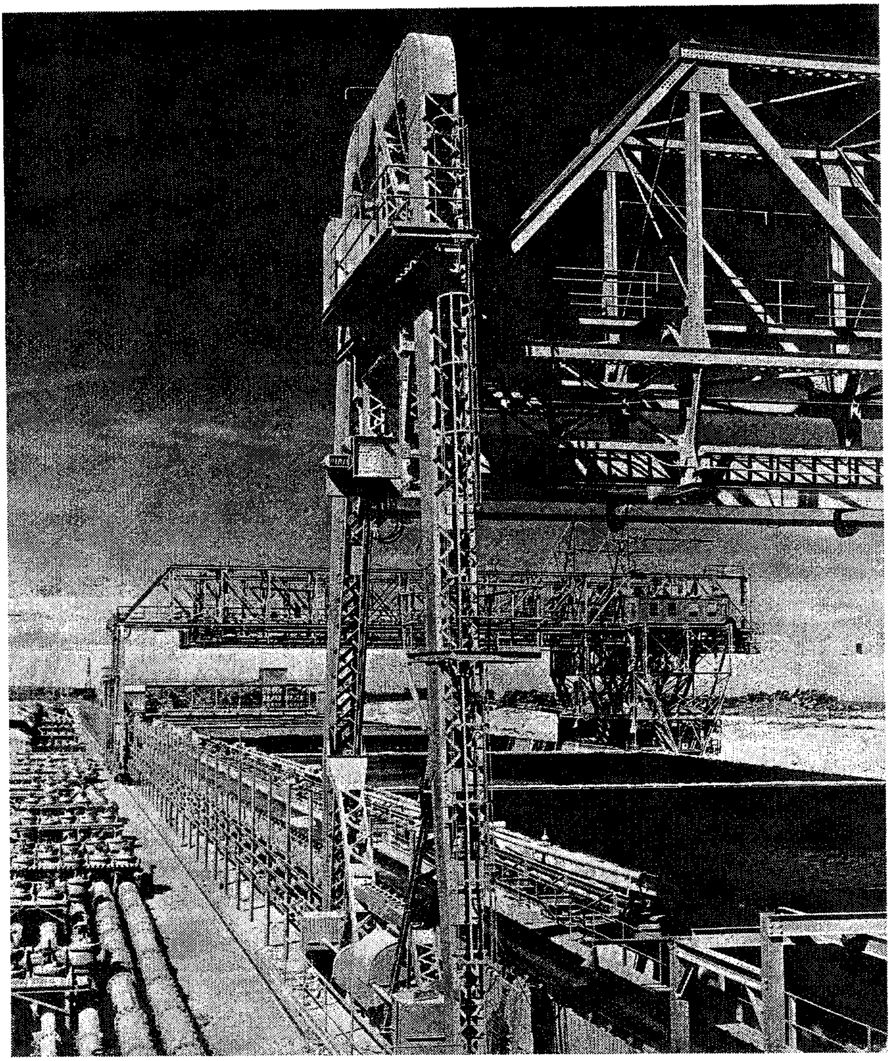

Figure ***6.14:*** Vat leaching plant at Chuquicamata, Chile.

Thin layer leaching

Vat-leaching of copper oxide ore was improved by adopting the so-called "Thin Layer Leaching". In this method, the finely crushed moistened ore is sprayed with a limited amount of concentrated H_2SO_4 in a rotating drum to permit agglomeration. The agglomerated material is then charged in the vat and left to cure for some time. This is then followed by normal heap-leaching by spraying dilute acid on the top.

AGITATION OR PULP LEACHING

In this method, the leaching agent is added to the finely ground raw material such that the mixture forms a pulp that has to be agitated continuously to prevent the solids from settling, and to terminate the leaching process in the shortest possible time. It is generally used under the following conditions:

- Raw material is of moderate or high grade.
- The metal values are of fine grain size and disseminated in the host rock therefore extensive crushing and grinding are necessary before leaching to expose the maximum surface of the solids to the solution.
- The metal values are difficult to dissolve and that is why intensive agitation is needed to increase the rate.

The equipment used are numerous and expensive, and high recoveries are mandatory. Leaching conditions may be mild using dilute solutions at ambient conditions or it may be severe using concentrated solutions (either acidic or basic) and at high temperature and pressure.

Methods of agitation

Agitation may be accomplished in two ways:

- Mechanical. In this case motor-driven impellers are used. Equipment are expensive and require high maintenance cost.
- Pneumatic. In this case compressed air or high-pressure steam is used. This has the advantage of low initial cost and low maintenance cost because there are no moving parts. Steam is used instead of air when heating is desired.

Ambient pressure

Leaching at ambient pressure may be conducted in the following ways:

- In open or closed vessels at ambient or moderate temperature.

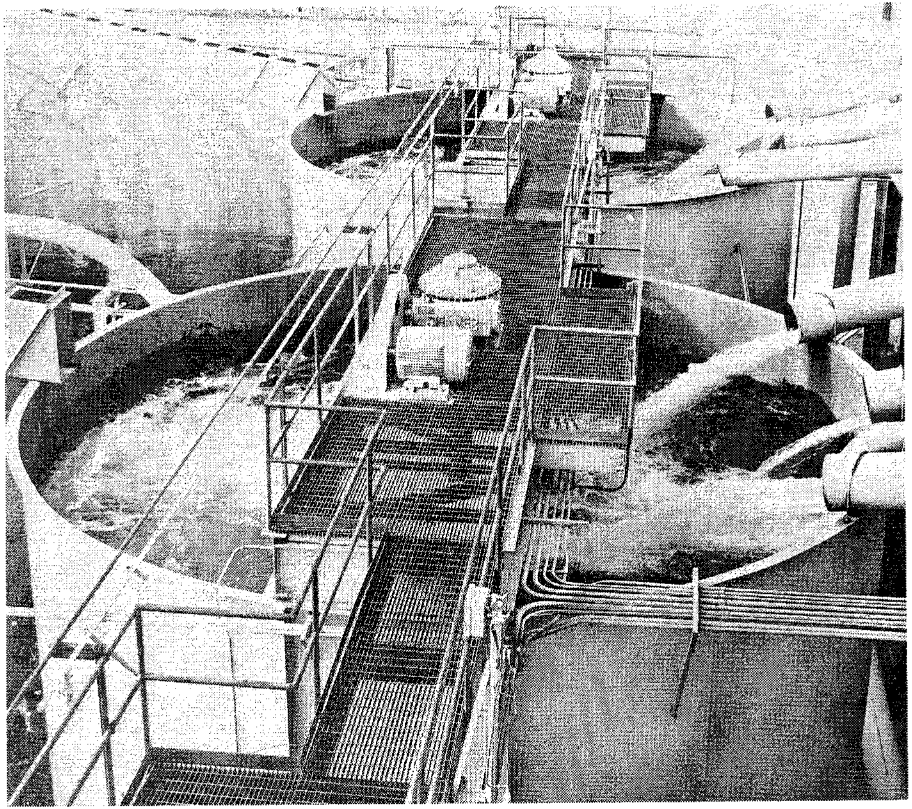

Figure 6.15: Open vessel, mechanically agitated leaching tanks.

- At a temperature near the boiling point of the solution with a reflux condenser installed on the reactor lid to prevent the loss of vapors. Agitation in this case is usually conducted mechanically.

Mechanically agitated tanks should be cylindrical with vertical axis, the bottom may be flat, dished out, or a shallow cone. They vary in size from small to large tanks, 10 m diameter x 10 m high (Figures 6.15–6.16). Square or rectangular tanks are not used because it is often difficult to secure adequate fluid motion in the corners. The tanks may be equipped with a jacket for heating or cooling (Figure 6.17) may be made of mild steel or alloy steel, titanium, or other corrosion-resistant material such as fiber glass. Steel tanks may also be rubber-, glass-, or brick-lined (Figure 6.18).

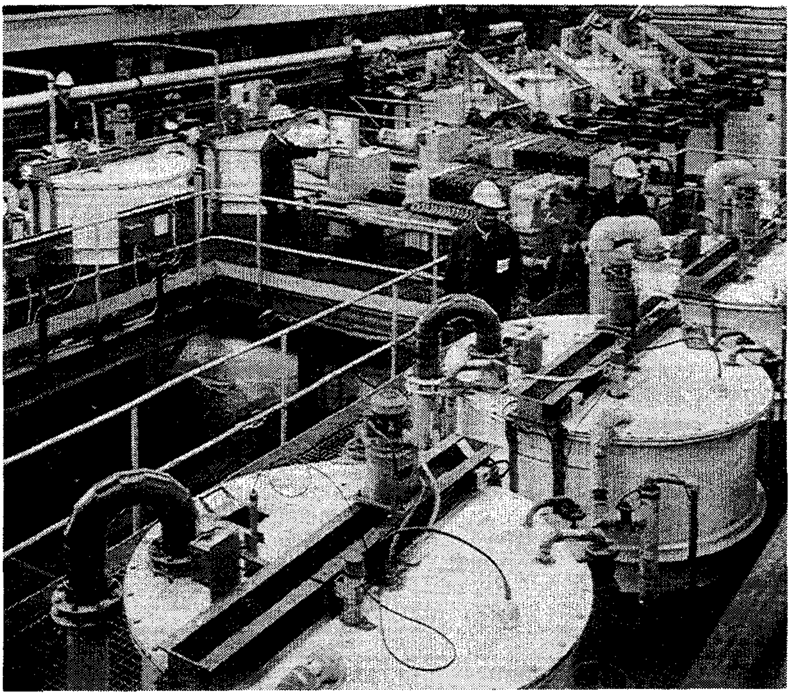

Figure 6.16: Closed vessel, mechanically agitated leaching tanks.

Figure 6.17: Mechanically agitated leaching reactor with heating jacket.

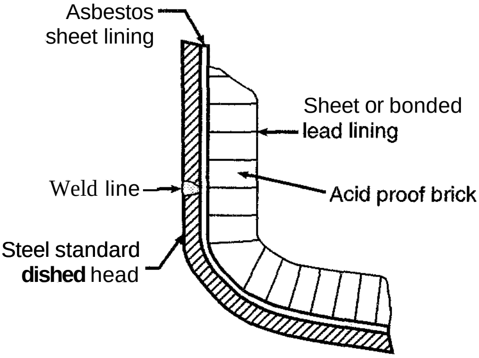

Figure 6.18: Acid-proof brick lining with impervious lead interliner for a leaching tank.

Pneumatically agitated tanks are known as Pachuca tanks which are named after a small mining town in Mexico where it was first used. Pachuca tanks (Figure 6.19) consist of a cylindrical tank of about 3.5 m in diameter and 14 m high, with a 60° conical bottom and are made of wood or rubber-lined steel. A central vertical tube open at both ends is provided through which compressed air is introduced when the tank is charged with the pulp, causing circulation of the materials up the central tube and down the annular space so that the solids are kept in suspension.

High pressure

High-pressure leaching necessitates the use of pressure reactors (or autoclaves). One should distinguish between two types of pressure leaching:

- *In absence of air or oxygen.* In this case the rate of leaching at ambient or moderate temperature is low and a temperature higher than the boiling point of the solution must be used. Consequently the reaction must be conducted in a closed vessel to prevent the escape of vapors. The pressure generated is the result of the vapor pressure of the solution. Table 6.4 shows the vapor pressure of water as a function of temperature. This method is mainly used for leaching bauxite, scheelite, ilmenite, and laterites.

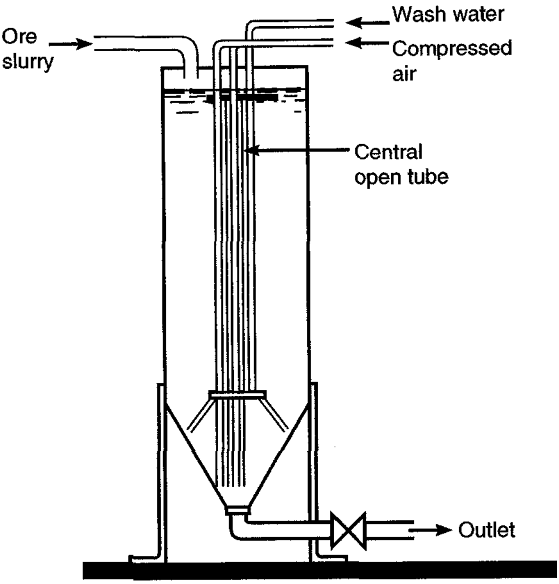

Figure 6.19: Pachuca tank.

Table *6.4:* Vapor pressure and boiling points of water.

Pressure		Temperature
atm	kPa	°C
1	98.1	100.0
6	588.6	159.2
10	981	180.3
16	1,580	201.9
20	1,962	213.0

- *In presence of air or oxygen.* In this case leaching at ambient or moderate temperature is not possible unless air or oxygen is present as oxidizing agent. In both cases, it is the oxygen partial pressure that has the controlling factor on the rate of leaching. At a certain temperature the rate increases with increasing oxygen partial pressure. The use of oxygen instead of air is more advantageous because for the same oxygen requirement the total pressure in the autoclave is low, and as a result the autoclave design will be less demanding, or decreased in size. When ammonium hydroxide is used as a leaching agent, the vapor pressure due to the volatility of NH_3 should be taken into consideration (see chapter 4). This method is mainly used for leaching sulfides, selenides, and tellurides.

Autoclaves

According to their shape, autoclaves may be in form of cylinders vertically mounted or horizontally laid, spherical, or in form of a long horizontal tube. Method of agitation in an autoclave may be effected by injecting high-pressure steam, mechanically, or by rotating the whole autoclave. Vertical autoclaves are usually steam-agitated, sometimes mechanically agitated, the horizontal are agitated mechanically by impellers and sometimes rotating, while the spherical are agitated by rotating the whole autoclave slowly around its horizontal axis. Some horizontal autoclaves are also agitated by rotation. Steam-agitated and rotating autoclaves have minimum maintenance costs while autoclaves agitated by mechanical impellers are usually expensive to maintain because of the rotating shafts. Industrial autoclaves have volumes of 10 to 70 m^3 and operate at 2500–5000 kPa. When the operating media are corrosive, the parts of the equipment are constructed of special steel alloys, titanium, and other high-grade materials. In some instances the interior surface of the autoclaves are lined with rubber or ceramic material. Autoclaves are usually connected in series to achieve continuous operation. When laid horizontally they are usually mounted on a slope of about 8° to provide flow by gravity from one to the next.

Nozzles for autoclaves are expensive and difficulties are encountered in their design, particularly with a lead and brick lined vessel. It is therefore advisable to minimize their number even to the extent of multiple services per nozzle. It is also desirable to locate as many of the nozzles as possible in the vapor phase; liquid-phase nozzles are subject to plugging. Dip-pipes extending into the liquid phase from vapor phase nozzles are used. Where liquid-phase nozzles are necessary, it is advantageous to provide means of back-flushing while in operation. In rotating autoclaves, solutions or slurries are introduced through a pipe in a hollow trunion.

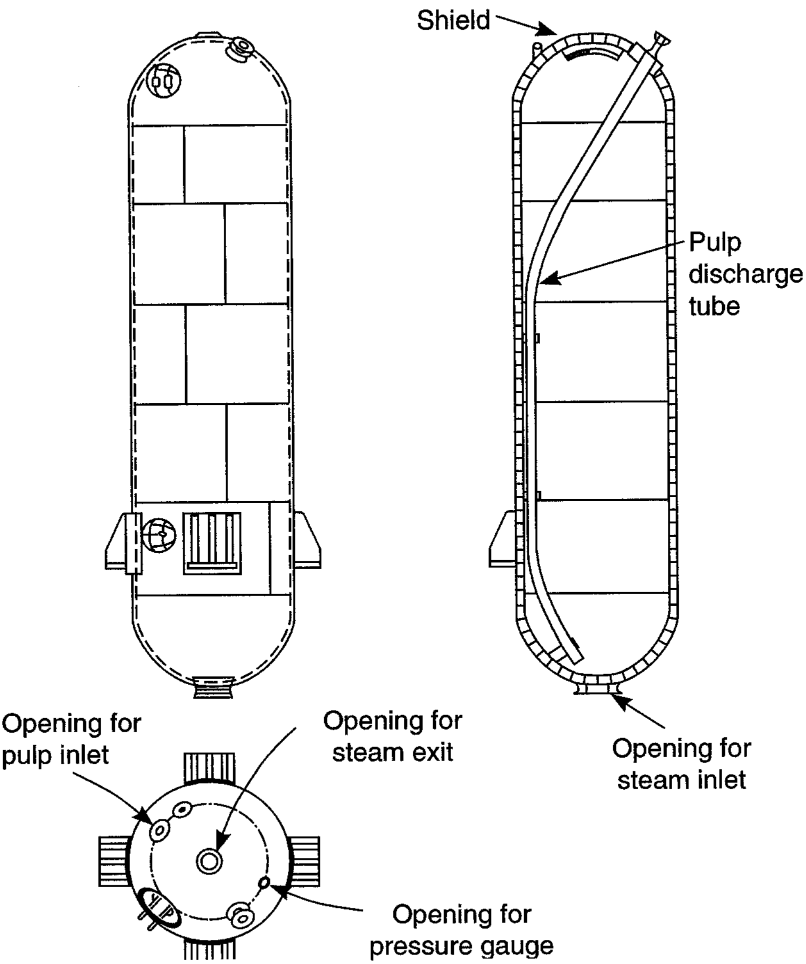

Figure 6.20: A 30 cubic meter vertical autoclave for leaching bauxites (Maslenitsky et al., 1969; Habashi, 1971).

Steam-agitated autoclaves. This is the simplest type and is used for leaching a material that requires no aeration, e.g. bauxite. An autoclave for this purpose is simply an insulated vessel capable of withstanding the operating pressure and is supplied with the necessary openings for introducing and discharging the pulp. These are usually fabricated from welded steel cylinders with spherical ends. Diameters vary from 1.5 to 2 m and heights from 6 to 12 m. In the upper part are located apertures for admission of pulp, a manometer, safety valve, and a discharging pipe. Steam is fed through the bottom for heating and mixing. On their outside surface, the autoclaves have a layer of insulation. Such equipment is used mainly for leaching bauxite by NaOH usually at 140–150 °C and 2500–3500 kPa. A typical design is shown in Figure 6.20.

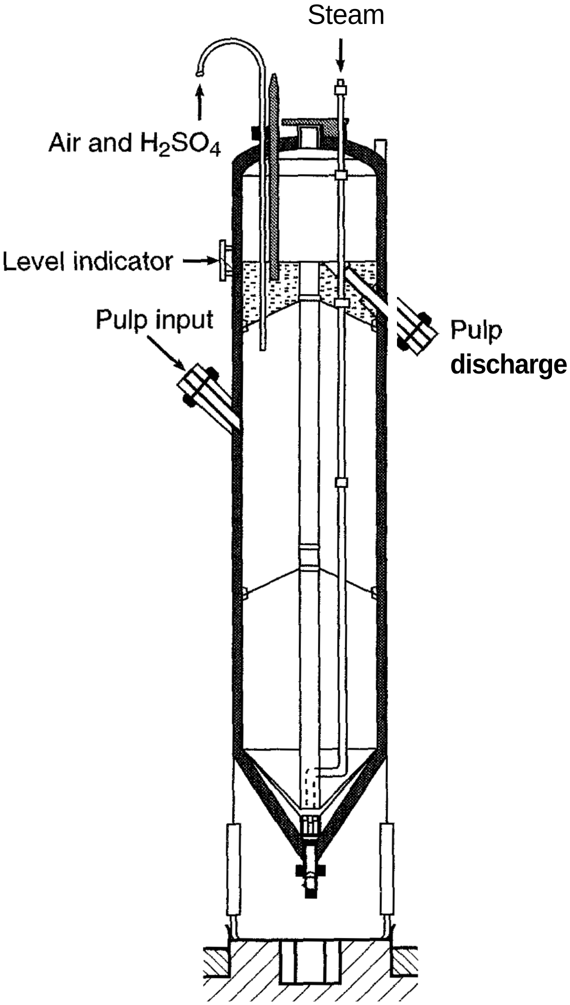

Figure 6.21: A 70 cubic meter vertical autoclave for leaching laterites at 250 °C and 4000 kPa (Maslenitsky et al., 1969; Habashi, 1971).

Autoclaves of similar design but with acid-resistant brick lining are used for leaching oxidized ores, e.g., laterites, by concentrated H_2SO_4 at 250 "C and 4000 kPa. In the Moa plant, Cuba, the steel shell is first lined in the inside with 6 mm lead (Figure 6.21). Protective brick lining consists of acid-proof brick and of carbon brick. Under the usual operating conditions, the acid-resistant brick is subject to cracking. Carbon brick, on the other hand, does not. In this way, the carbon brick protects the acid-resistant brick from corrosion and erosion. All interior parts of the autoclave and also the connecting pipes are made of titanium. Stainless steel is used only in areas where the temperature is lower than 100 "C.

Vertical, mechanically agitated autoclaves. Sometimes these autoclaves are used, e.g., in leaching uranium ores (Figure 6.22).

Horizontal autoclaves. When oxygen is essential for conducting a reaction in an autoclave, it is necessary that a high rate of gas–liquid interaction is achieved. This is met in mechanically agitated autoclaves. These autoclaves are cylindrical vessels, horizontally laid, that are divided in the inside by partitions. In each chamber is an electrically driven turbine mixer from the top. The body of the autoclave can be lined with lead, with alloy steel, or with rubber. Feed slurry is pumped into one end of the autoclave and cascades from one compartment to the next. The average degree of filling is 65–70% static to allow sufficient disengagement space for the exhaust gases and to reduce the possibility of plugging the relief valve nozzle. The maximum diameter in Canada is about 3.3 m to enable shipment of the finished vessel by rail (Figure 6.23). Larger diameter vessels may be employed but they have to be fabricated on the plant site. Compartment length is usually equal to four times the diameter; thus the length of a four-compartment 3.3 m diameter autoclave would be 13.2 m. At 65% filling, such an autoclave has a static operating volume of 77.3 m^3. Horizontal autoclaves are usually designed with four compartments, since too much volume will be lost in providing the static head required for the flow of slurry from one compartment to the next.

A major advance took place recently in the design and construction of the horizontal autoclaves. Some of these reactors are 4.6 meters diameter and 30 meters long, divided into 5 partitions each equipped with an agitator. The autoclave is constructed of a 5 cm thick carbon steel shell lined with a 6 mm lead sheet, and two layers of acid resisting brick having a total thickness of 17 cm (Figures 6.24 and 6.25).

Oxygen or air for leaching is always injected at a point under the bottom impeller to utilize the impeller for dispersion. Ammonia and other reagents are injected into the liquid phase. Slurry is discharged from the autoclave through a dip-pipe or by overflow through a nozzle located at the desired operating level.

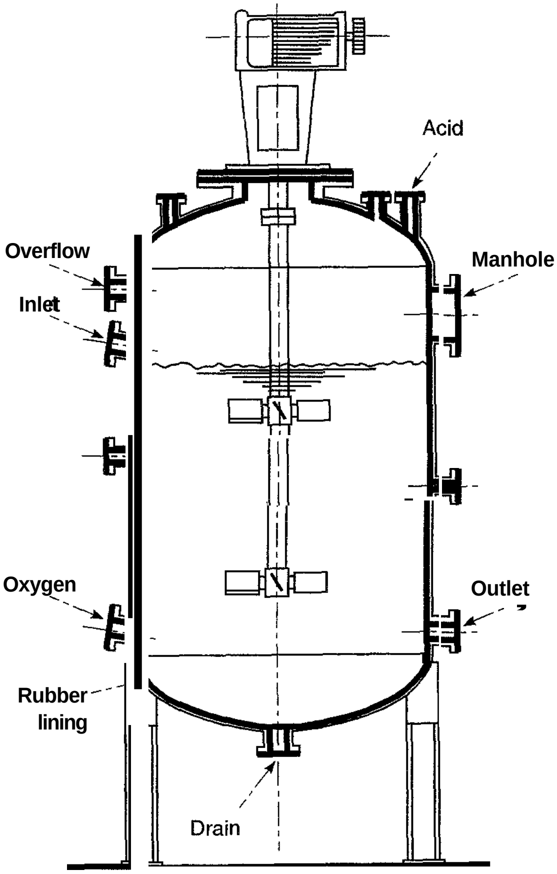

Figure 6.22: Vertical, mechanically agitated autoclave, **3** m diameter and 6 m high. Unmarked openings are for instruments.

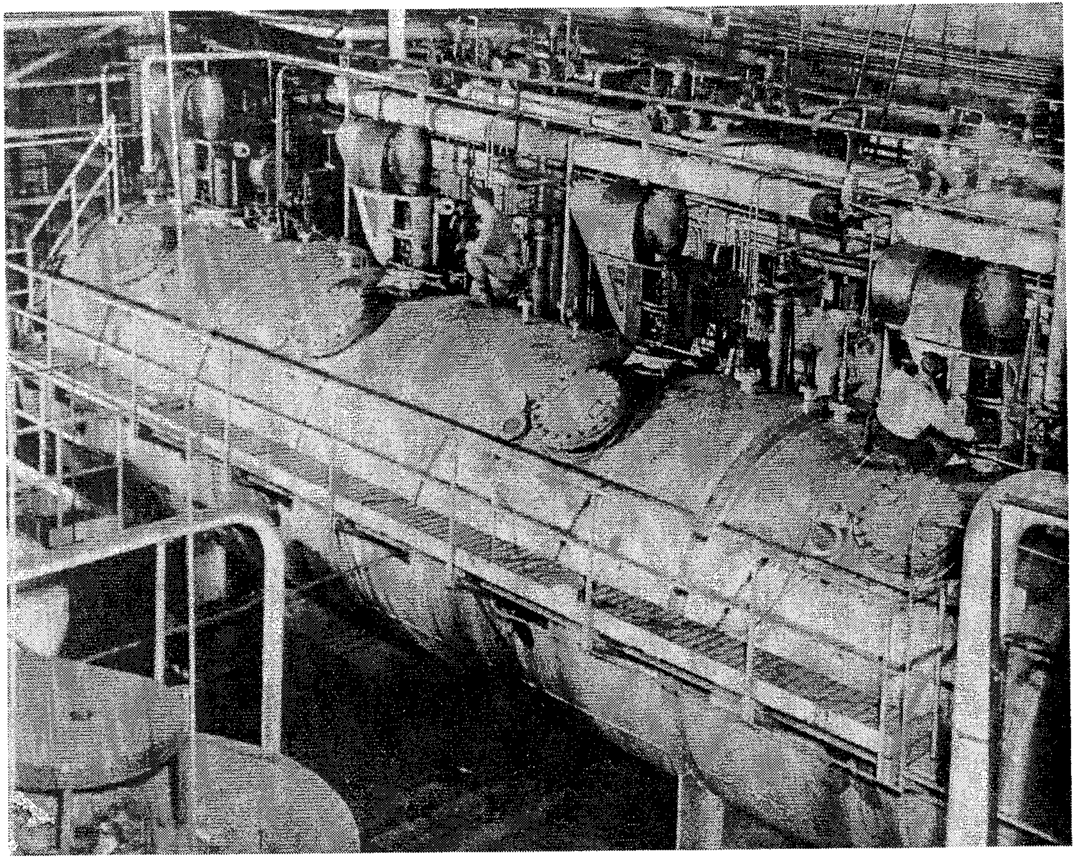

Figure 6.23: A horizontal autoclave 3.3 m (× 1[illegible] m long. of For[illegible]
Saskatchewan, Alberta, Canada.

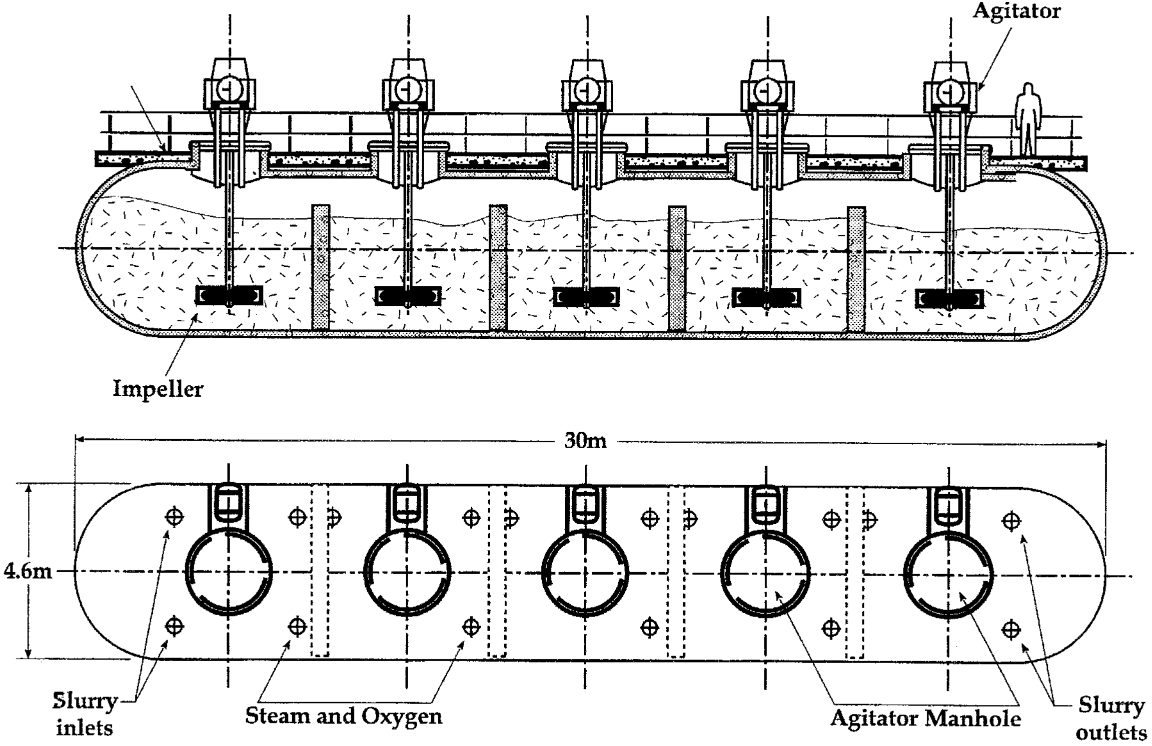

Figure 6.24: A large industrial autoclave 4.6 m diameter and 30 m long, lined with acid-resisting bricks, used for the oxidation of pyrite and arsenopyrite to liberate gold prior to cyanidation.

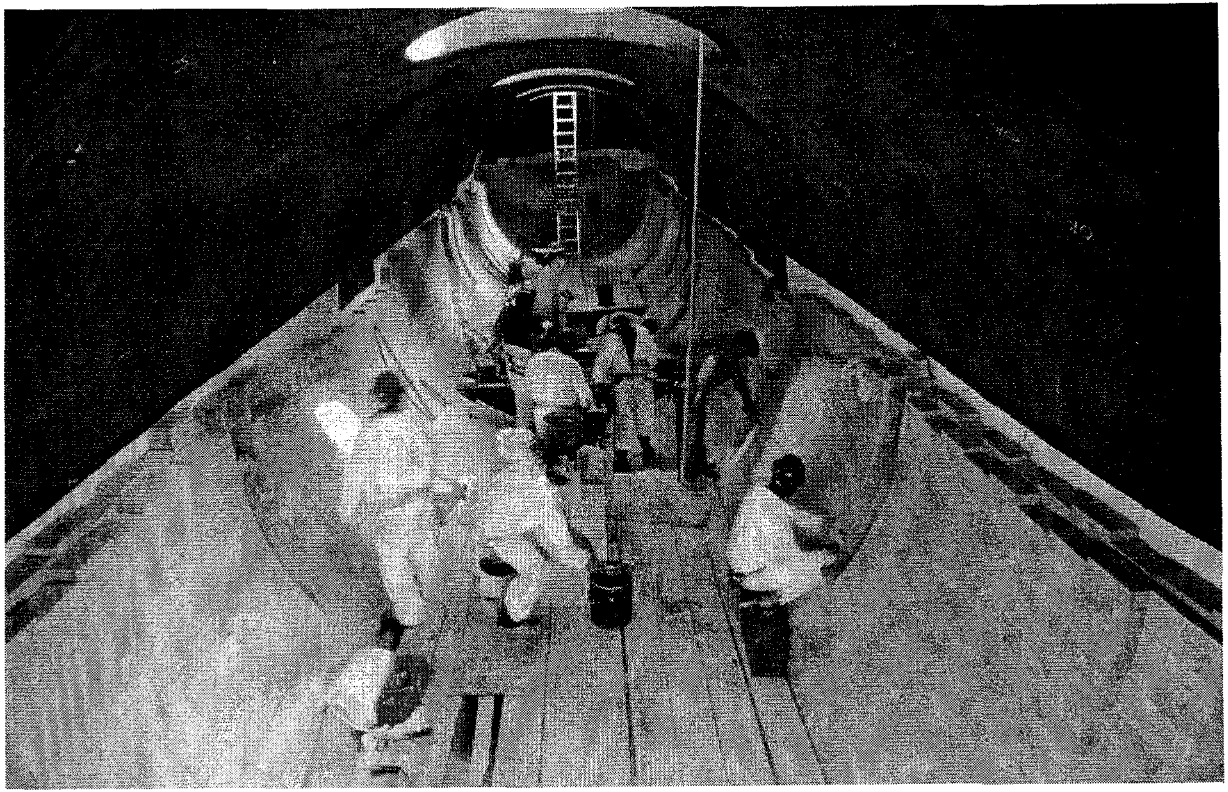

Figure *6.25:* Autoclave interior lining, 15 ft. diameter x 82 ft. length, five-agitator, 2-inch thick carbon–steel shell, 0.25-inch lead membrane, 2 layers of acid-resistant brick, 9 inches total thickness, capacity 415 cubic meters (courtesy Barrick).

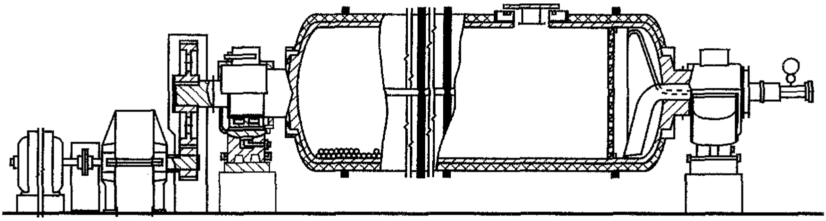

Figure *6.26:* A 10 cubic meter rotating autoclave for leaching tungsten and molybdenum concentrates (Maslenitsky et ai., 1969; Habashi, 1971).

Rotating autoclaves. These may be cylindrical or spherical in shape, constructed of steel with the proper lining. They turn on heavy pivots at a speed of 8–15 rpm. Through one of these pivots the loading and unloading of the pulp and the admission of steam are carried out. Through the other, the driving and turning of the autoclave is accomplished. These autoclaves are usually partially filled with steel balls; this type is used in cases where an insoluble reaction product is formed on the surface of mineral particles that impedes the penetration of the leaching agent. The rotation and the impact of the balls result in breaking the impervious crust thus accelerating the leaching. Figures 6.26 and 6.27 show rotating cylindrical autoclave used for leaching tungsten and molybdenum concentrates at 225 °C and 2500 kPa pressure, while Figure 6.28 shows a rotating spherical autoclave used for treating titanium ores.

Tube autoclaves. In tube autoclaves, the slurry is pumped through one end and is discharged through the other. The system has been applied in Germany and in Czechoslovakia in the 1960s for the continuous leaching of bauxite. The slurry is pumped into an externally heated thick-walled tube about 30 cm in diameter and 30 to 50 m long (Figures 6.29–6.30). The major part of the heat is supplied by the slurry leaving the tube. Only at the extreme end of the tube, steam from an outside source is used for heating. The development of diaphragm-piston pumps that are able to reach 10 000–20 000 kPa made possible the application of this reactor. The system is characterized by extremely short residence time 2–3 minutes, high thermal efficiency, and low capital investment.

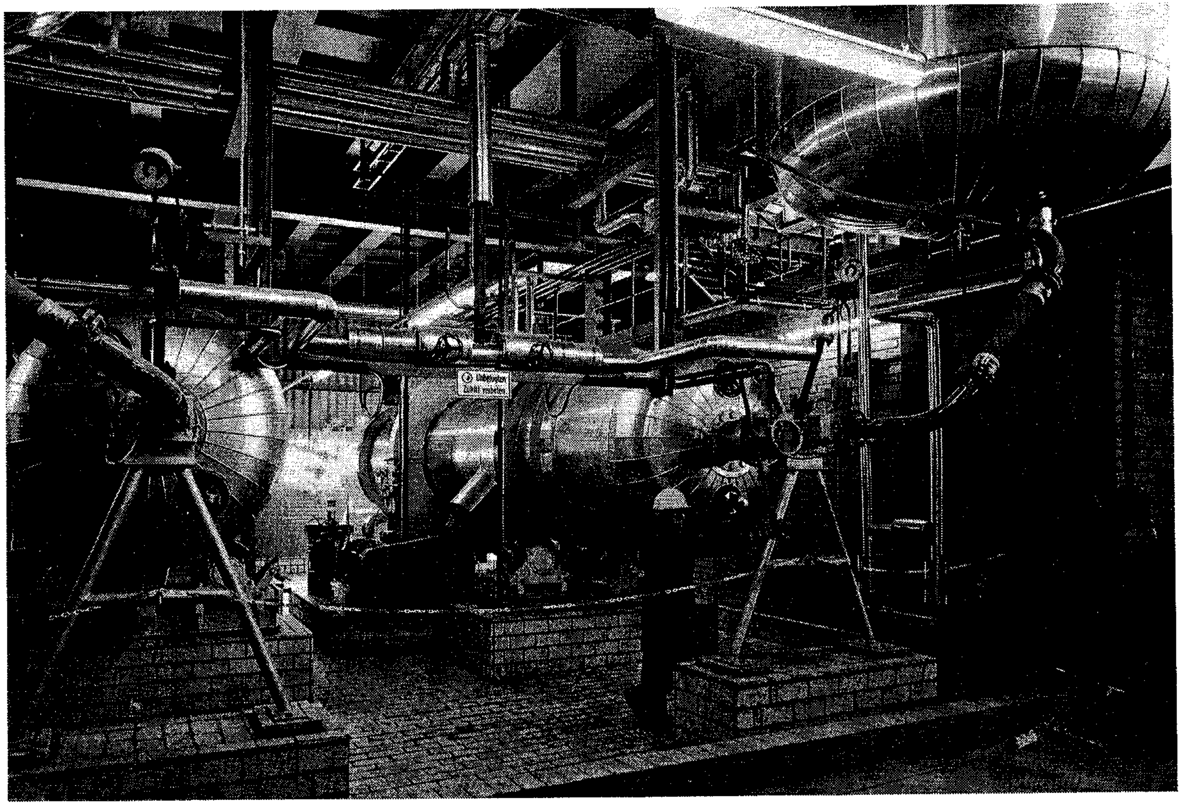

Figure 6.27: Rotating horizontal autoclaves for leaching scheelite concentrate with Na_2CO_3 solution at Bergla, Austria (Lurgi).

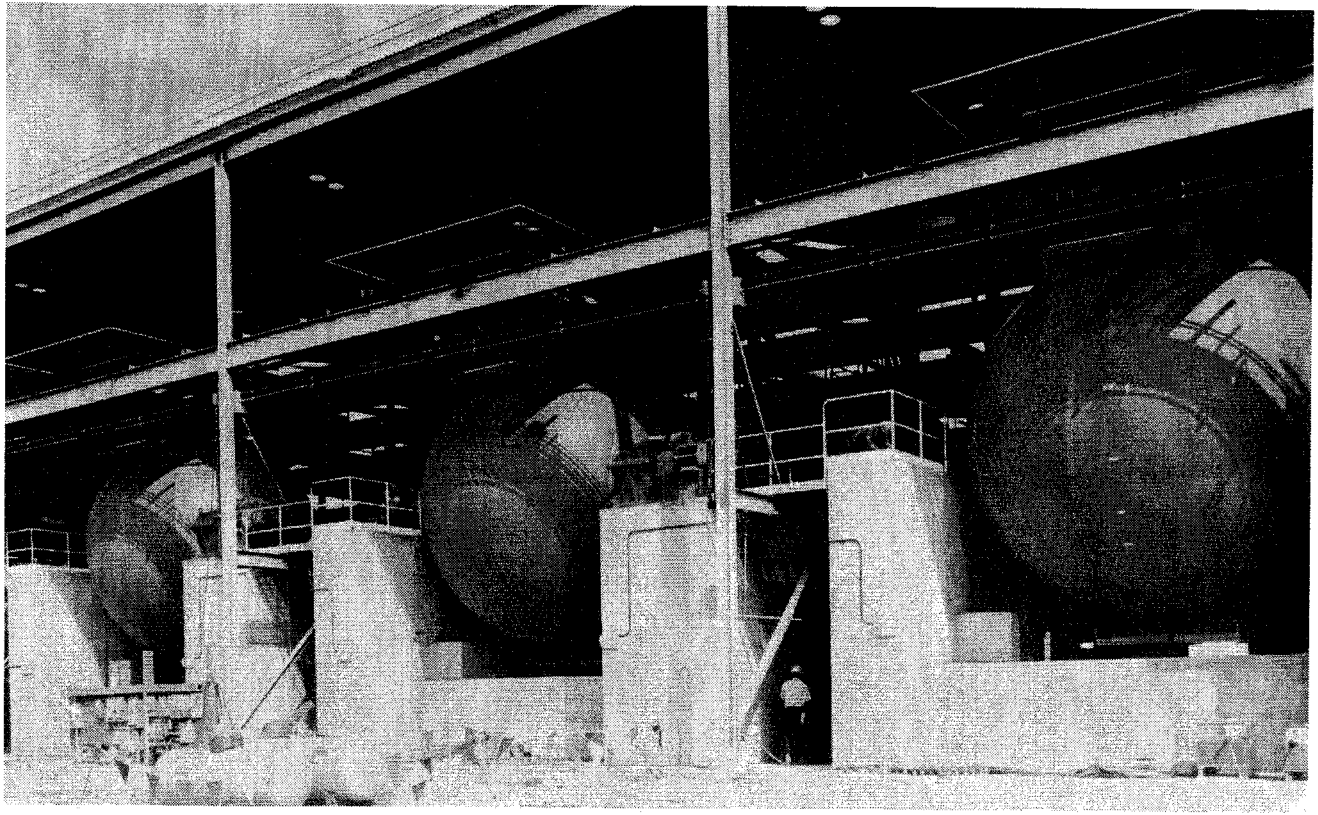

Figure 6.28: Spherical rotating autoclaves installed in plant (United McGill).

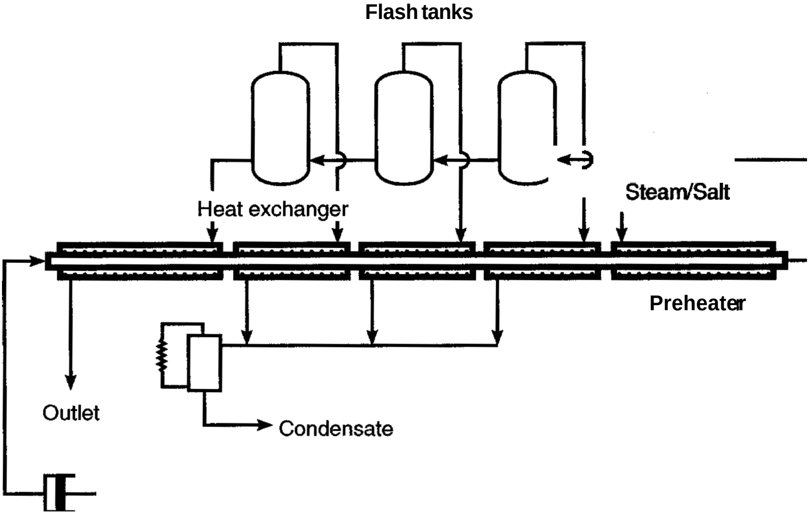

Figure 6.29: Tube autoclave unit (Lurgi)

BAKING PROCESS

This process is supplied when agitation leaching becomes impossible because the ore slurry solidifies to a thick mass in the early stages of leaching. Consequently the solidified mixture is allowed to react without agitation at a temperature around 200 °C hence the term ***baking*** is used. The reaction may be conducted in digesters, in rotary kilns, or in pugmills.

Digesters

These are large tanks about 10 m high and 4 m in diameter with a 15 cm discharge opening at the bottom and a similar opening at the top. They are made of mild steel with acid-resisting brick lining, or concrete with lead lining and acid-resisting brick. They are used, for example, in leaching ilmenite or titanium slag with concentrated H_2SO_4. The finely divided solid (about 18 tons) is mixed with the acid (about 23 tons) and the mixture heated with high pressure steam to about 180 °C to start the reaction. Once this temperature is reached, the material reacts vigorously since the reaction is exothermic but after few moments it solidifies and agitation becomes impossible.

As a result, it is left in the reactor for about 13 hours until the reaction is complete by its own heat. After cooling, dilute H_2SO_4 or water is added to dissolve and discharge the cake.

Rotary kilns

These are long horizontal brick-lined cylinders slightly inclined to the horizontal to permit the gradual descent of solids at the upper end (Figure 6.31). They are heated by burning a carbonaceous fuel at the lower end. They are used, for example, in the treatment of monazite sand with concentrated H_2SO_4. The raw material is made into a paste with the acid then charged to a kiln fired to about 200 °C. The solid product discharged from the other end of rhe kiln is then leached with water.

Pugmills

These are horizontal shallow tanks equipped with numerous rotating blades that are capable to move a thick paste or cut their way through a solidified cake (Figure 6.32). This method was suggested for the treatment of sulfide concentrates with concentrated H_2SO_4. The pugmills may be heated by a steam jacket.

SUMMARY

Table 6.5 gives a summary of the different methods of leaching and the equipment used.

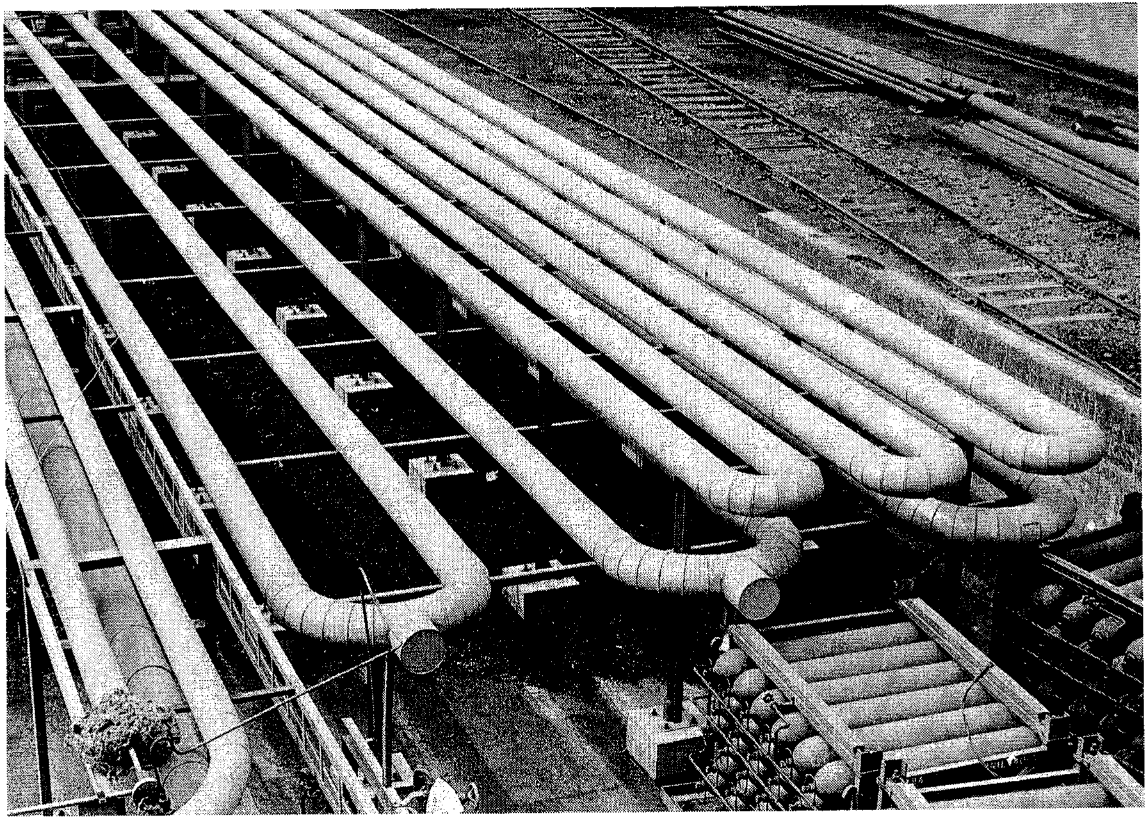

Figure 6.30: Tube autoclave made of titanium for leaching n pressure at the Vereinigte Aluminium Werke-Lipperwerk, Lünen, Germany (Lurgi).

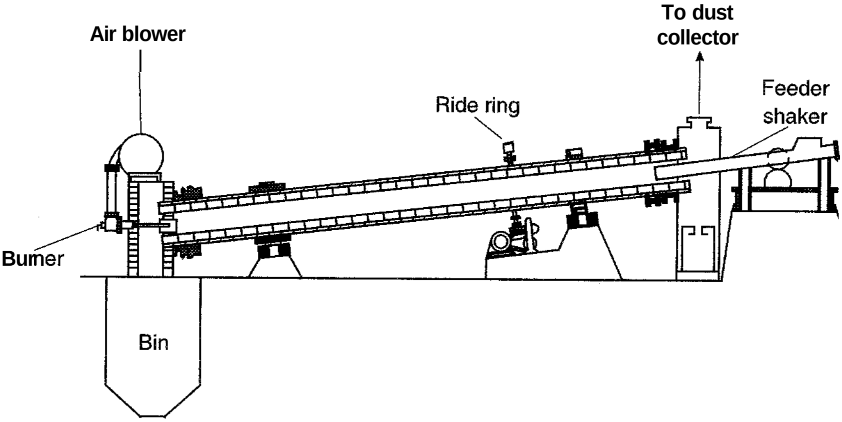

Figure 6.31: A **rotary kiln.**

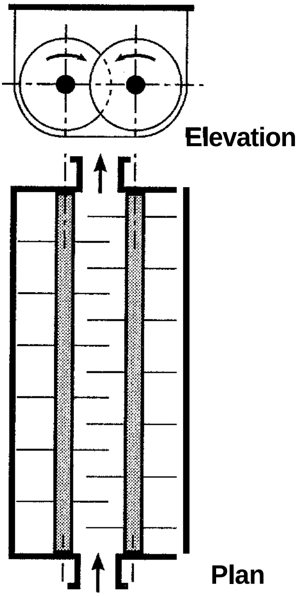

Figure *6.32:* A **pug** mill.

Table 6.5: Leaching methods and equipment.

Method	Pressure kPa	Temperature °C	Agitation	Ore size	Time of leaching	Equipment	Examples
Leaching in place[a]	Ambient	Ambient	None	Lumps	Years	None	Copper, uranium
Heap or dump leaching	Ambient	Ambient	None	Lumps	Months	None	Copper, uranium, gold
Percolation or vat leaching	Ambient	Ambient	None	Sandy	Days	Vats with false bottom	Copper, uranium, gold
Agitation or pulp leaching	Ambient	< 100	Mechanical, compressed air	Fine	Hours	Pachuca tanks, Dorr agitators, tanks	Copper, gold, ZnO, phosphates
	1,000–1,200	110–200	Mechanical, high-pressure steam, rotation	Fine	Hours	Autoclaves	Bauxite, laterites, nickel sulfide, scheelite
Baking	Ambient	≈ 200	None	Fine	Hours	Digesters, rotary kilns, pugmills	Anodic slimes, monazite sand, ilmenite

a. *Also* known as leaching in-situ or solution mining.

Chapter Seven

Engineering Aspects

General Principles 163
Recovery 163
Rate 164
Batch and continuous processes 166
Materials of construction 168
Pumping 168
Agitation and Mixing 169
Heat Transfer and **Economy** 170
Heating and cooling 170
Heat exchangers 171
Vacuum evaporators 172
Flash evaporators 174
Slurry preheater 175
Filtration and Washing 176
Thickening 180
Filtration 181
Residue disposal 187
Regeneration and Recycle of Leach Solution 188
Water Treatment 189
Impurities in water 189
Removal of impurities 189
Plant Layout 190

GENERAL PRINCIPLES

In conducting a leaching process certain factors must be considered since they directly influence the cost of operation.

Recovery

For any leaching process. the percent recovery is a major concern. It is determined from a material balance based on the analysis of solids and solutions. For example. on leaching 2000 tons of an ore containing 0.8% Cu with dilute H_2SO_4, the solution obtained was 7200 cubic meters and contained 2 g/L Cu. From these data, it would be possible to make a material balance and calculate the recovery of copper (90%) as shown in Table 7.1.

Table 7.1: Typical material balance in a leaching process, e.g., copper ore.

	Weight or volume	Cu content	Total Cu tons	Distribution %
Feed	2,000 tons	0.8%	$2000 \times 0.8/100\% = 16$	100
Solution	7,200 m^3	2 g/L	$7200 \times 2 \times 10^{-3} = 14.4$	90

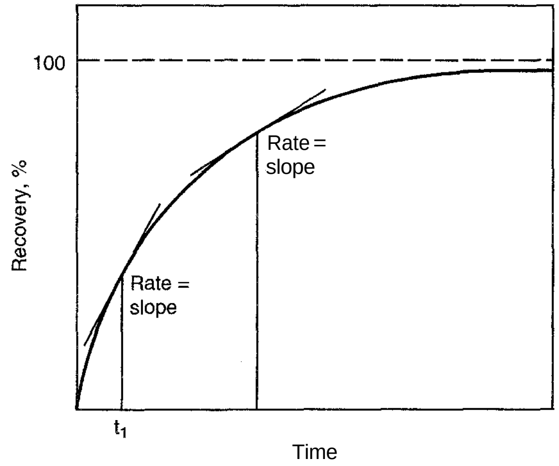

Figure 7.1: Recovery and rate of leaching.

Rate

The rate of a leaching process is followed by knowing the percent recovery as a function of time (Figure 7.1). The rate at any moment is the quantity of metal recovered per unit time. It is the slope of the curve at that moment. It can be seen that at the beginning of the process the rate is high and then it decreases gradually with time. Therefore, a compromise should be made between the percent recovery and the residence time in the reactor to achieve maximum productivity. The rate of leaching depends on the following factors:

Particle size. The rate increases with decreased particle size of solids, i.e., increased grinding since the smaller the particles, the larger is the surface area per unit weight. However, increased grinding is not only a costly item, but also may cause a filtration problem. Extremely fine particles are sometimes difficult to settle and to filter.

Concentration of leaching agent. Increased concentration of leaching agent increases the rate of leaching. But, it may also cause the dissolution of undesirable minerals thus leading to increased reagent consumption and increased impurities in solution.

Agitation. Increased agitation usually increases the rate of leaching. But, this again may be a costly item due to increased capital cost of the agitator and operating cost due to the power consumed to effect agitation.

Pulp density. Rate of leaching increases with decreasing pulp density, i.e., when a large volume of leaching agent is added to a small weight of solids. But this will result in dilute solutions that will make handling and recovery more difficult. High pulp density results in concentrated solutions, but, on the other hand, is usually associated with high erosion of equipment, e.g., pumps, agitators, etc.

Temperature. Rate of leaching increases with increased temperature (Figure 7.2). However, increased temperature may result in increased dissolution of other minerals thus causing increased reagent consumption and increased impurities in solution.

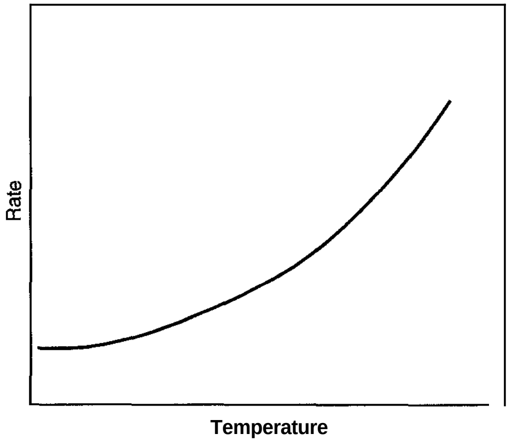

Figure 7.2: Increased rate of leaching with increased temperature.

Therefore, a compromise is always made between the increased rate of leaching and the negative effect of any of the factors influencing this increase.

Batch and continuous processes

A leaching process may be conducted batchwise or continuously (Figure 7.3). In a batch process, the solids and the solution are charged in a reactor and agitated for a certain time until reaction is complete. The slurry is then discharged for filtration and washing, and the process is repeated, i.e., charging, agitation, and discharging. In a continuous system (Figure 7.4), a number of reactors must be available through which the solids and the solutions flow from one to the other continuously. The number of the leaching tanks is such that in the last reactor the reaction should be complete. In a batch process the capital investment is therefore low but the operating cost is high while in a continuous process the reverse is usually true. In general, for large plants, continuous processes are usually more economical because the reactors are effectively utilized: no time is lost in charging and discharging, the possibility of fully automating the circuit, and a minimum of manpower will be required.

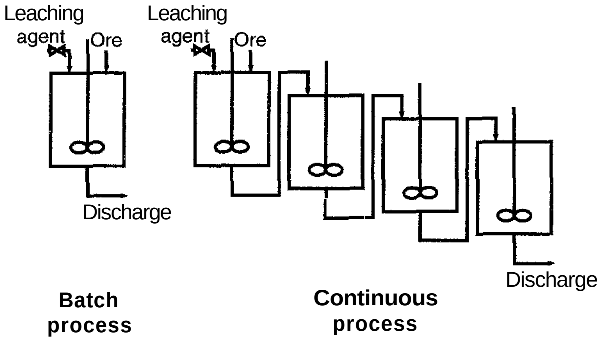

Figure 7.3: Batch and continuous leaching.

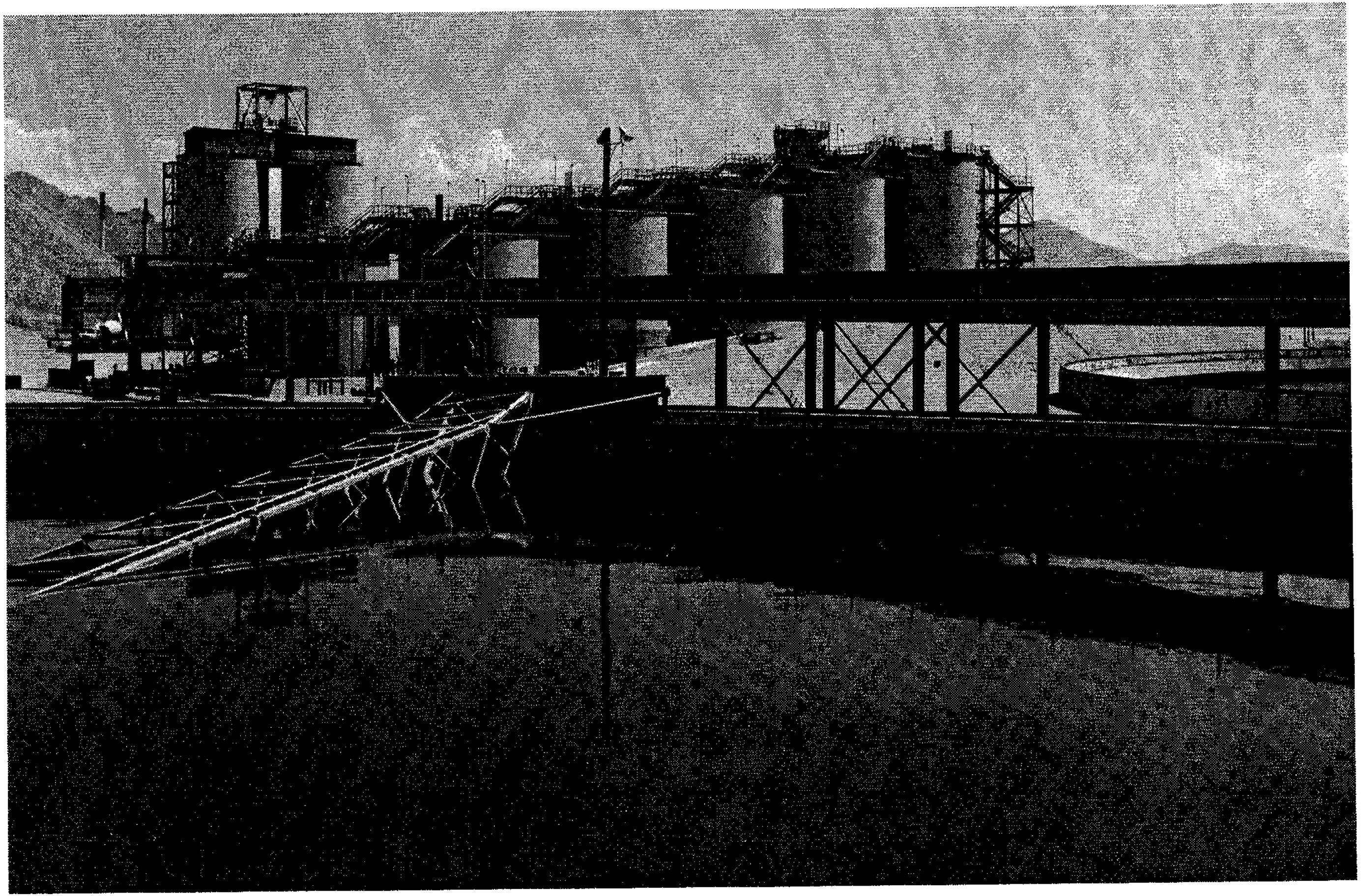

Figure 7.4: A continuous leaching plant.

Materials of construction

Corrosive and erosive conditions are usually encountered in leaching processes and consequently, the proper selection of materials of construction is an important factor in the design. Table 7.2 gives some data on this problem. Besides, many other corrosion-resistant materials are finding application, for example, Teflon, reinforced epoxy resins, Haveg, Ni-Hard, polypropylene, Dur-Iron, Stellite, and many of the ceramic materials. It should be noted, however, that impurities in leach solution may drastically change the corrosion-resistant properties. For example, stainless steel is well-suited to boiling nitric acid but deteriorates rapidly when the acid contains small amounts of chlorides or fluorides.

Table 7.2: Materials of construction in hydrometallurgical plants.

Medium	Material of construction
Ammonia leaching	Stainless steel clad vessel, mild steel or stainless steel agitators.
Ammonia + ammonium sulfate	Stainless steel clad, stainless steel agitators.
Dilute sulfuric acid in oxidizing atmosphere	Stainless steel clad, or butyl rubber and brick-lined vessels depending on temperature: stainless steel agitators.
Strong sulfuric acid in oxidizing atmosphere.	Butyl rubber or lead and brick-lined vessels, stainless steel, titanium, or Hastalloy agitators.
Hydrochloric acid	Titanium, brick-lined vessels.
Nitric acid	Stainless steel.

Pumping

Transferring of solutions and slurries may be conducted by gravity flow when possible, but in most cases **pumps** are used. High-pressure membrane piston pumps (Figure 7.5) are used for introducing pulps into autoclaves. The pump is equipped with a flexible rubber membrane, a piston, and two ball valves. The space between the piston and the membrane is filled with oil (Figure 7.6). When the piston is in its downward stroke, the membrane expands outwards closing the lower valve and at the same time opening the upper valve, rhus forcing the slurry to move out, and vice versa, when the piston is into upward stroke, the membrane moves inwards, opening the lower valve and closing the upper valve thus sucking the slurry in. The advantage of this pump is that the piston does not come in contact with the slurry which can be abrasive.

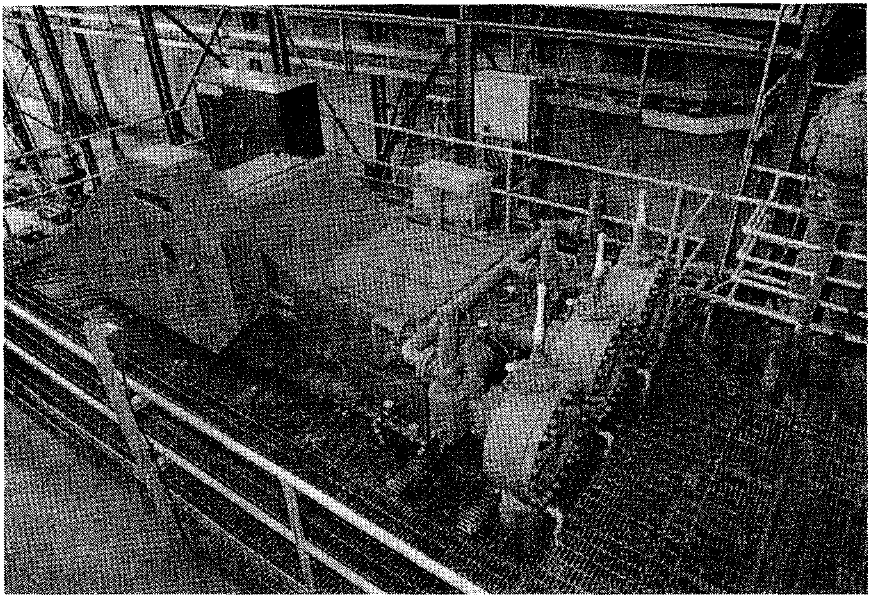

Figure 7.5: Typical installation of a high-pressure membrane piston pump for pumping ore slurry into autoclaves.

AGITATION AND MIXING

Agitation and mixing of solids in a solution may be conducted mechanically or pneumatically. In the first case an impeller causes the fluid motion while in the second case compressed air or high-pressure steam is used. Impellers are usually made to be about $^1/_4$ to $^1/_2$ the tank diameter, and if only one is on a shaft, it is placed no more than one impeller diameter from the bottom. When the impeller is in the center of the tank the motion is rotary and there is vortex formation. The liquid and solids are not forced sideways or vertically and as a result there is little mixing. This is especially the case for low pulp density slurries. To eliminate the formation of vortex two methods are commonly used:

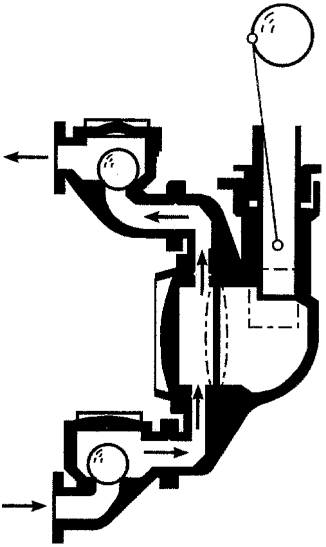

Figure *7.6:* Membrane piston pump (section).

- Off center mounting of impeller either in axial or angular position.
- Introducing baffles at the wall of the vessel. This produces an axial flow which is also necessary to oppose the settling of the particles. Baffles usually extend $^1/_{12}$ the tank diameter from the wall.

HEAT TRANSFER AND ECONOMY

Most leaching processes are conducted at ambient temperature. Heat transfer and economy is important only for pressure leaching processes where temperature as high as 250 °C may be used.

Heating and cooling

For endothermic reactions, e.g., leaching of bauxite, heat is supplied to the autoclave during the whole leaching period. On the other hand, for exothermic reactions, e.g., leaching of sulfides, hear is usually supplied only to initiate the reaction, and once this is accomplished, cooling will be necessary. The initial heating stage is usually done by direct steam injection. Cooling, however, is conducted by several methods:

Jackets. An external jacket has the advantage that no nozzles in the pressure vessel are required, but this system suffers from the low heat transfer efficiency, insufficient heat transfer area, and formation of scales on the water side due to high surface temperature. For these reasons, cooling jackets are no longer used for pressure reactors.

Internal coils. This method is extensively used. The main disadvantage is the scaling on the cooling water side and treated water is usually used to overcome this difficulty.

External heat exchanger. This system has an improved overall heat transfer efficienty but suffers from excessive erosion when slurries are handled. It is especially effective when large amounts of heat have to be supplied or removed.

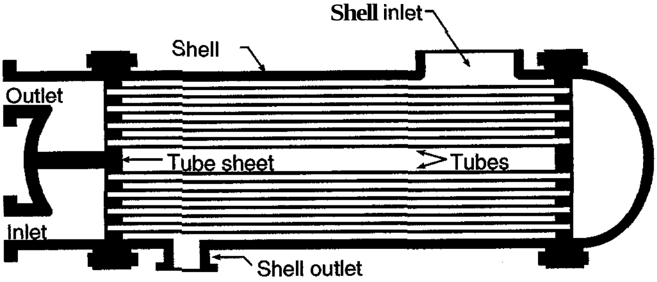

Figure 7.7: Heat exchanger.

Heat exchangers

These are equipment used for heating or cooling solutions or slurries and at the same time recovering a certain amount of heat which would be otherwise lost (Figure 7.7). In these systems the following rules are usually followed:

- The hot fluid should be inside the tubes so that the heat losses would be minimum.
- The fluid susceptible to form a scale should be inside the tubes so that cleaning could be done easily.
- Counter-current flow is more effective than parallel flow for two reasons:
  - Rate of heat transfer is a function of temperature difference: In parallel flow, the temperature difference at one end is high and

at the other end is low. In counter-current, the temperature difference is practically constant.

- In a counter-current flow, the hot fluid can be cooled to a lower temperature and the cold fluid heated to a higher temperature than in a parallel flow.

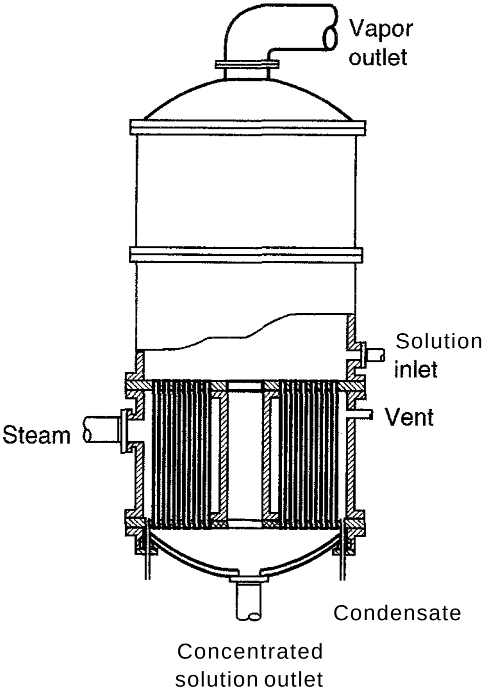

Figure 7.8: Single-effect evaporator.

Vacuum evaporators

Sometimes it is necessary to concentrate a solution by evaporation, e.g., phosphoric acid obtained by leaching phosphate rock, or solutions that will be subjected to crystallization, or recycled leach solutions as in the aluminum industry. For this purpose, single or multiple effect evaporators are used (Figures 7.8–7.9). In this system, steam generated in the first evaporator is used to heat the charge in the second evaporator, and that from the second is used to heat the charge in the third. To decrease the boiling point of the solution and thus economize in the heat requirement, evaporation is conducted under vacuum. Vacuum is usually generated by condensing steam from the last evaporator, and is maintained by a column of water 10 meters high. A water-jet venturi for evacuation is shown in Figure 7.10.

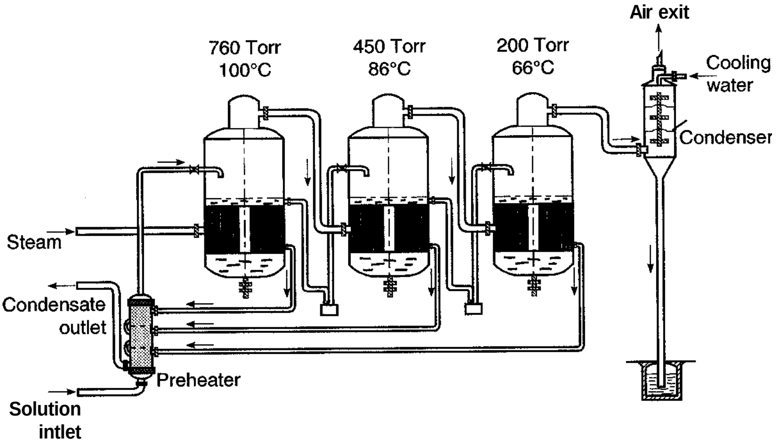

Figure 7.9: Multiple-effect evaporator.

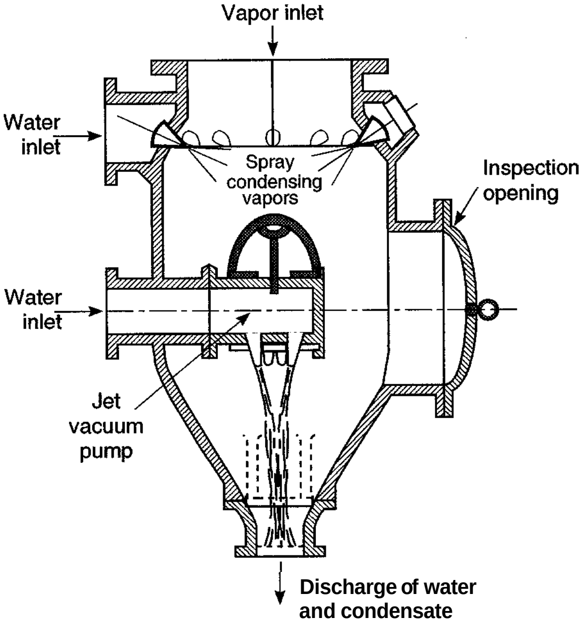

Figure 7.10: A water jet venturi in the barometric condenser for creating vacuum.

Flash evaporators

These are large vertical tanks usually installed after an autoclave. Figure 7.11 shows two designs. In one, the hot slurry is introduced through a tube directed towards the bottom of the tank where protective baffles are installed to minimize the erosion of the tank due to impact. In the other design, the hot slurry is introduced tangentially at the bottom of the tank to form a vortex which enhances the disengagement of steam. This equipment serves three purposes:

- Decreasing the pressure and temperature of the slurry.
- Recovery of heat in form of low-pressure steam.
- Concentration of the solution as a result of the flash evaporation of water.

Figure 7.12 shows industrial installations for flash evaporators.

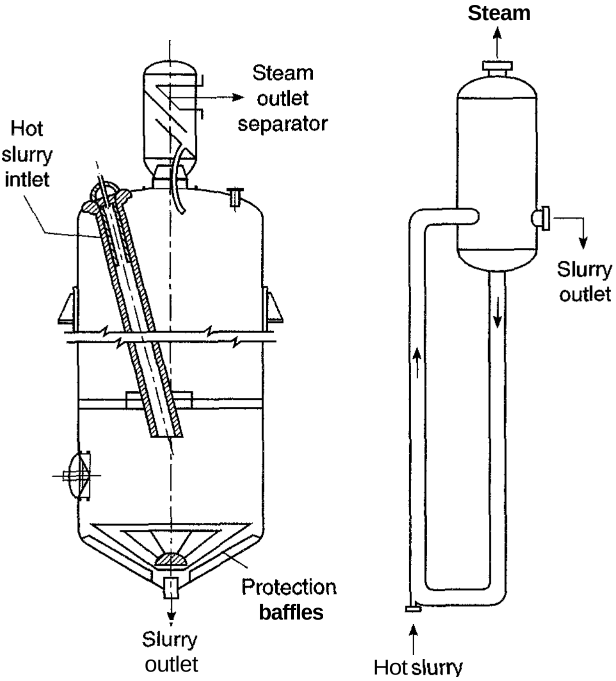

Figure 7.11: Flash evaporators (Maslenitsky et al.).

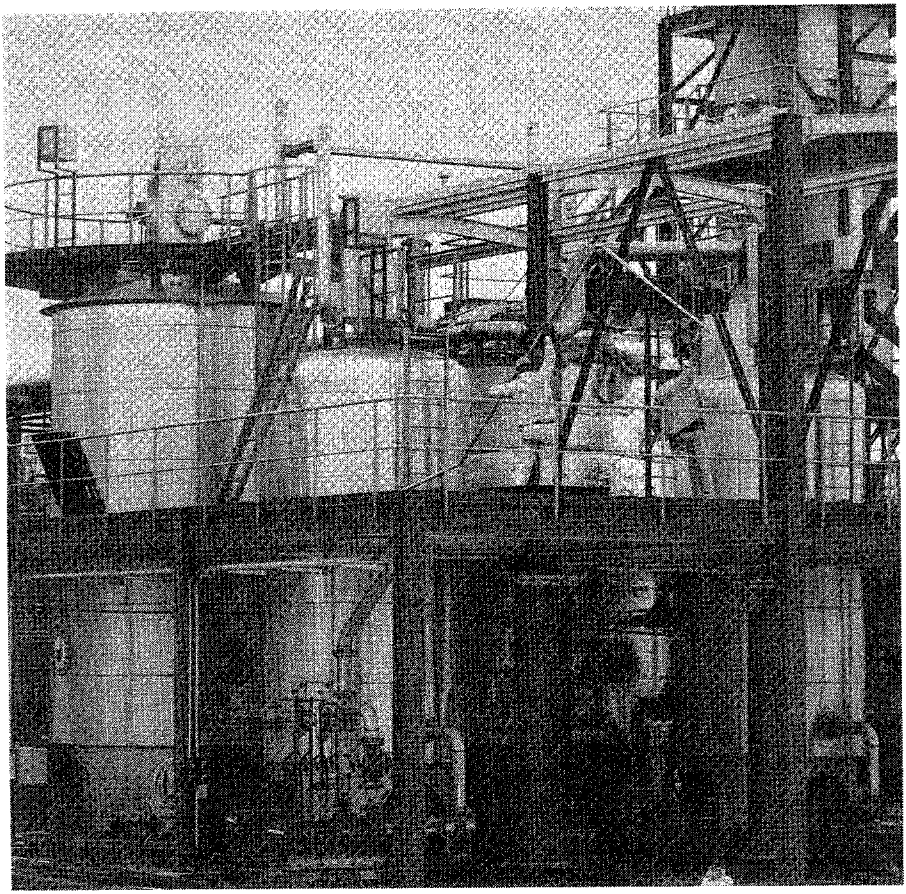

Figure 7.12: Flash evaporator (Lurgi).

Slurry preheater

Slurries to be introduced in an autoclave are usually preheated by the steam generated in the flash evaporator. A typical design is shown in Figure 7.13.

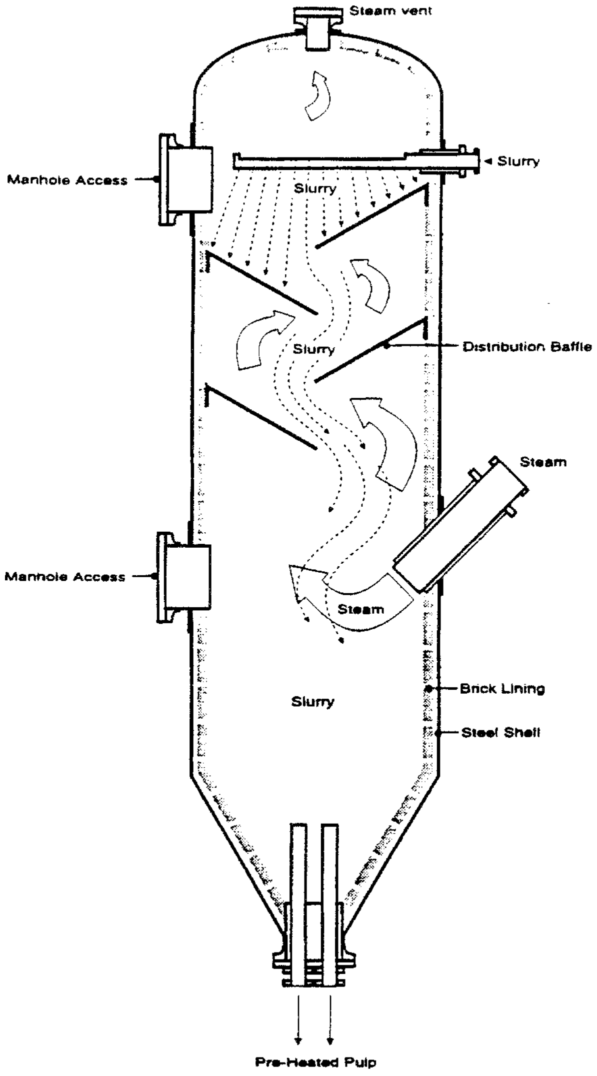

Figure 7.13: Slurry preheating by direct contact with steam.

FILTRATION AND WASHING

Slurries obtained after leaching are usually filtered to recover the leach solution then washed to remove entrained solution. Very clear solutions can only be obtained if sophisticated and expensive solid–liquid separation plant is installed. The finer the grind required either to liberate the metal values or to increase the rate of leaching the more expensive is the filtration plant. In a conventional gold or uranium ore leaching plant, for example, the clarification and filtration steps account for a significant proportion of the overall operating cost. The following procedures are usually practiced:

- When the undissolved material is small as that obtained in leaching concentrates, it is usually washed directly on the filter (Figure 7.14). Intensive washing increases the recovery of soluble metal values but decreases their concentration and also results in large volumes of solutions to be handled. Therefore a compromise must be made between the metal recovered and the cost of washing.
- When the undissolved material is moderate in volume, the slurry is filtered, the filter cake is repulped in water, and the solids separated while washing counter-currently in thickeners. This is usually the case of leaching zinc oxide calcines (Figure 7.15).
- When the undissolved material is voluminous as that obtained in leaching low-grade ores, extensive washing is necessary. This is usually conducted in the following ways:
  - Counter-current washing in thickeners followed by filtration. This is usually the case of gold, copper oxide, and oranium ores (Figures 7.16–7.17).

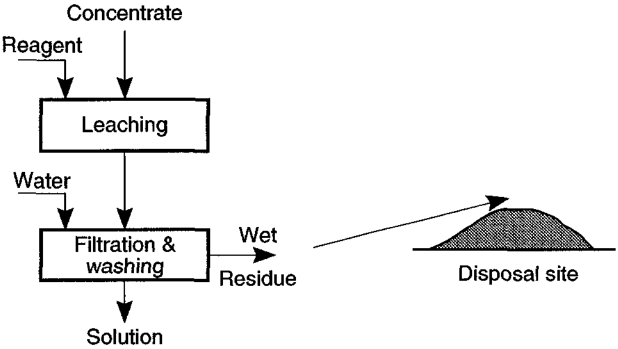

Figure 7.14: Leaching, filtration, and washing of concentrates.

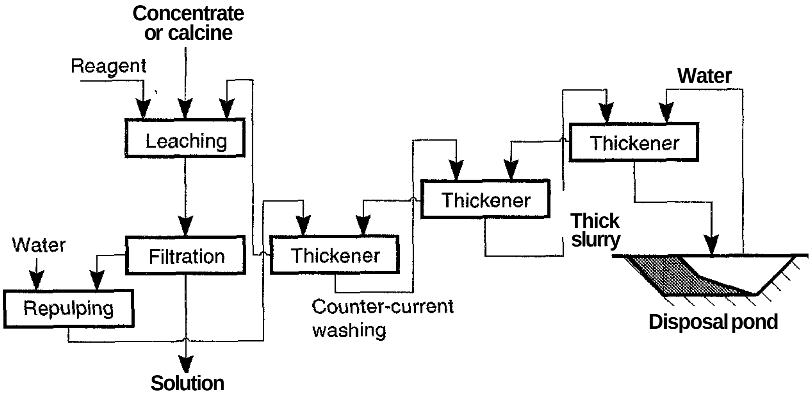

Figure 7.15: Leaching, filtration, and washing of high-grade raw material with repulping.

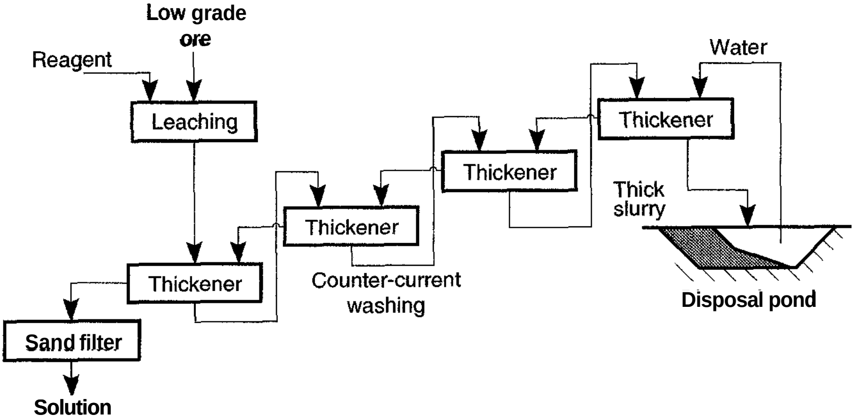

Figure 7.16: Filtration and washing of low-grade ores.

- Separation of the slurry by means of a hydrocyclone into two fractions: sand and slimes. This is done because washing of sand is faster and cheaper than washing slimes. Sand is washed in rake classifiers while the slimes in thickeners. In both cases counter-current washing is used (Figure 7.18).

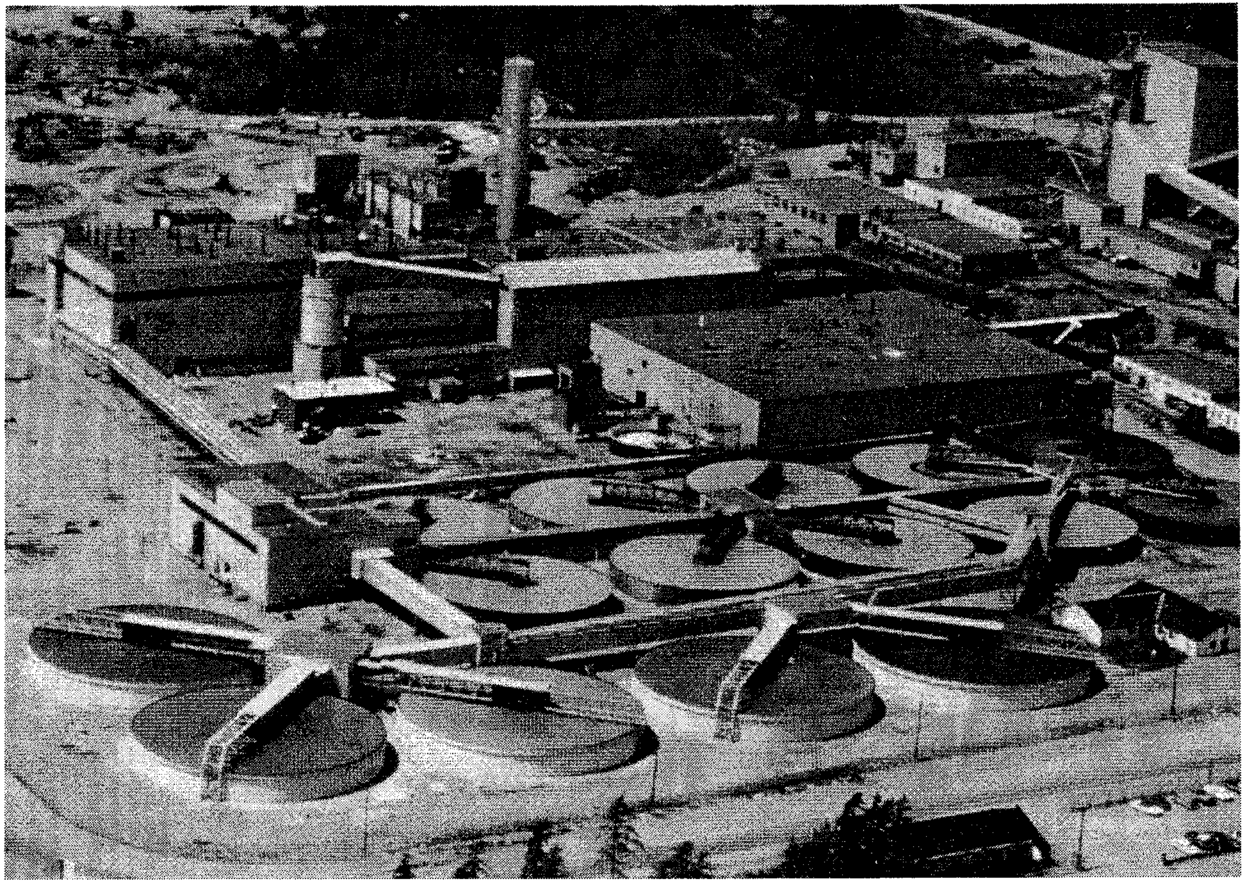

Figure 7.17: Counter-current thickeners for washing uranium residues at Elliot Lake, Ontario.

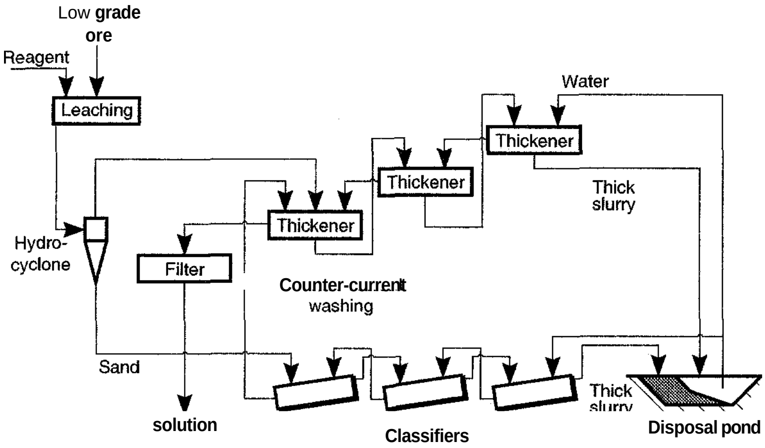

Figure 7.18: Filtration and washing of low-grade ores containing slimes.

Thickening

The thickener consists of a flat-bottomed tank of large diameter as compared with the depth (Figure 7.19). It has a central shaft on which slowly revolving arms with plow scrapers are fixed. The slurry from agitators is fed to a central well at the top of the shaft. Clear liquid containing the soluble matter overflows into a channel around the circumference of the tank. The solids separate at the bottom of the tank and are gradually removed by the scrapers to the center, where they are withdrawn. Organic coagulating agents such as glue are sometimes added to facilitate the settling of fine slimes.

Thickeners are usually installed at graded elevation so that the overflow moves by gravity from one thickener to the other (Figure 7.20) while the underflow is pumped by a slurry pump and moves from one thickener to the other in a counter-current direction until finally discharged in disposal ponds. Slurry pumps are generally mounted on the edge of the thickener. Overflow from the thickeners may contain about 500 ppm solids; these are removed in sand filters to obtain a clear solution suitable for further processing, for example, when ion exchange, solvent extraction, or precipitation are used.

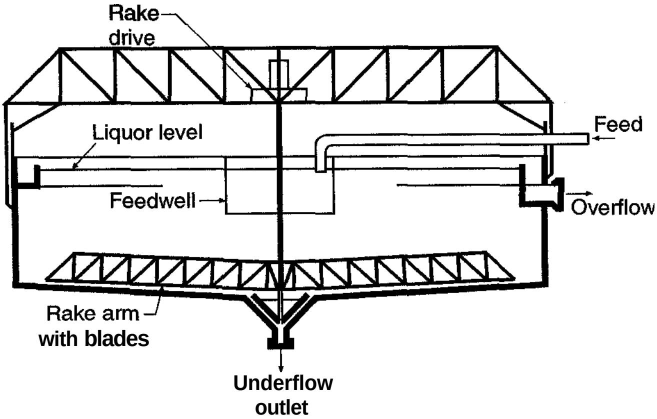

Figure 7.19: A thickener.

Filtration

Filtration is the process of removing solids from solutions; there are many types available. The simplest type is the sand filters shown in Figure 7.21. These are cheap equipment used for removing small amounts of suspended matter from leach solutions. The turbid solution is passed over a bed of granular sand where the suspended matter is retained. When the rate of percolation decreases, the bed is regenerated by back-washing with water to expel the suspended matter out.

The bulk of industrial filtration is accomplished by means of woven fabric, either of cloth, metal, or glass, supported on a rigid surface. The suspension is forced through the membrane either by positive pressures greater than atmospheric or under vacuum.

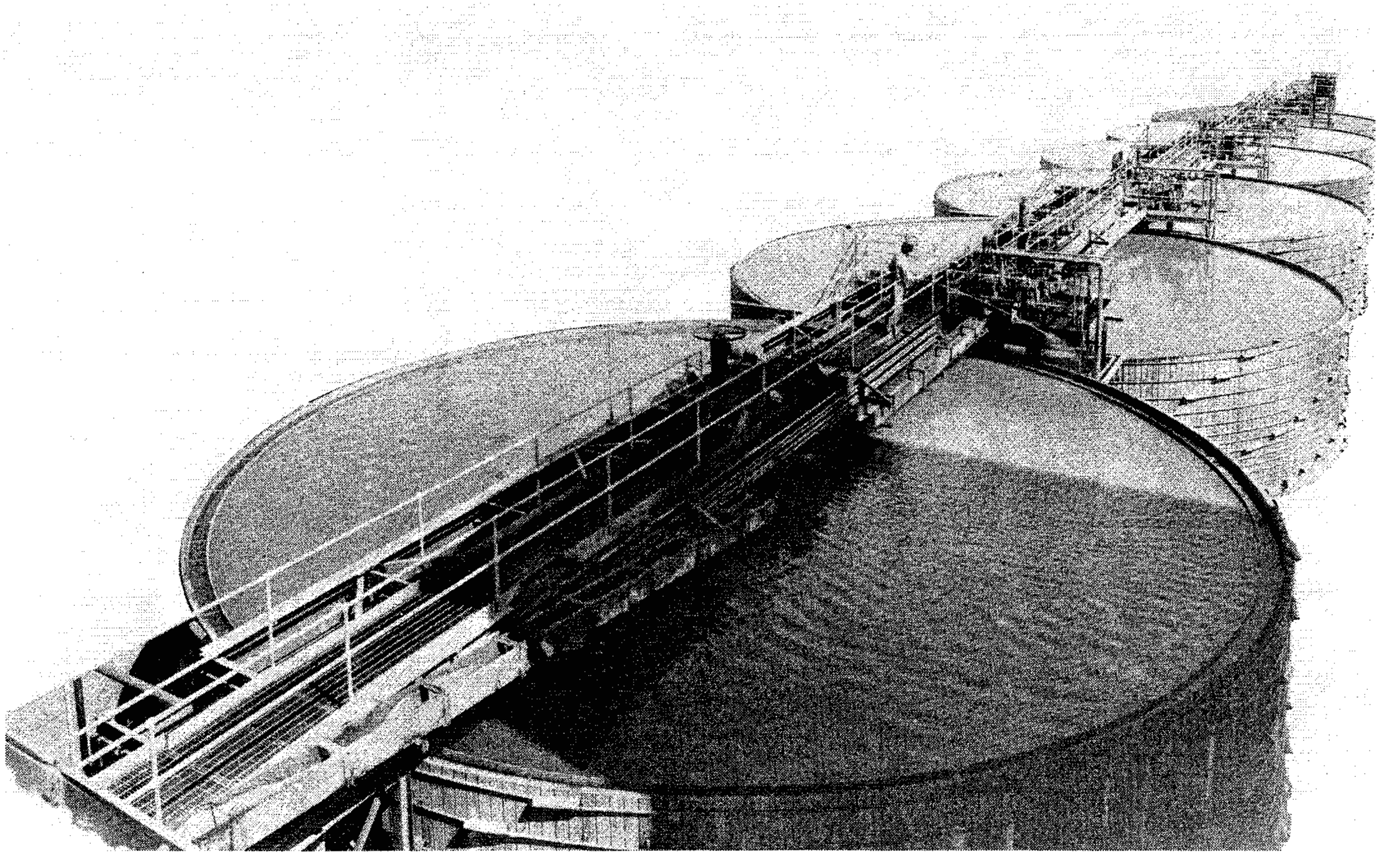

Figure **7.20:** Thickeners operating in a counter-current decantation system.

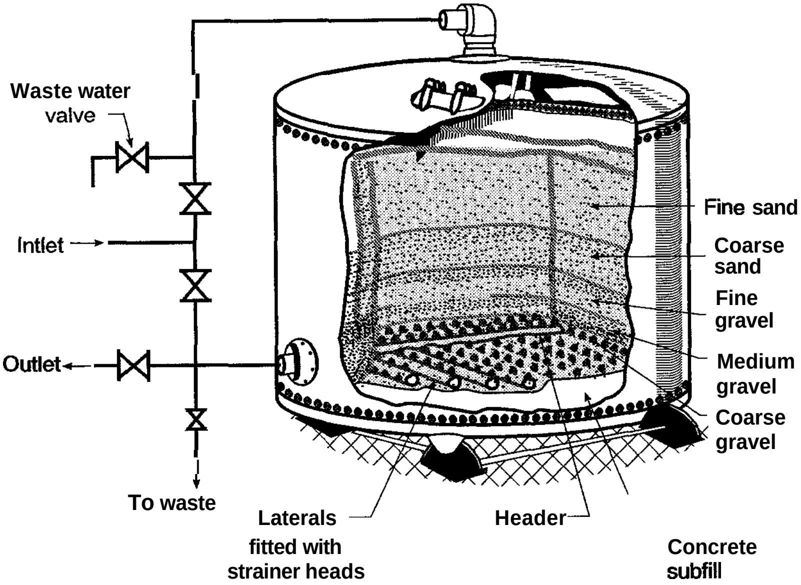

Figure 7.21: A sand filter.

Pressure filters. A typical unit of this type is the filter press shown in Figure 7.22. It is intermittent in operation. A filter press is essentially a series of shallow compartments whose vertical walls are lined with fabric. The suspension is pumped into these compartments under pressure; the solids are either retained on the walls as a thin layer or constitute a cake filling the whole compartment; and the filtrate runs down the solid walls behind the fabric and escapes through openings at the bottom of the press. These compartments are made up either by covering a number of recessed plates with cloth and pressing them together or more commonly by employing cloth-covered flat plates and interposing between them frames of the same area, pressing the whole firmly between a fixed and a movable head. The cloths serve as packing material to prevent leakage. The plates and frames are supported and aligned by projections resting on side rails.

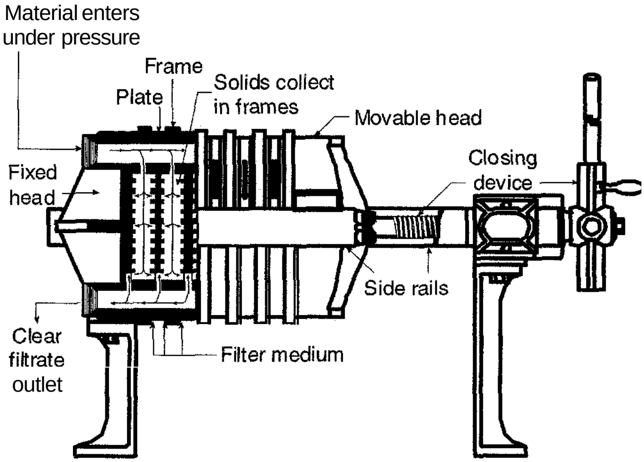

Figure *7.22:* A filter press.

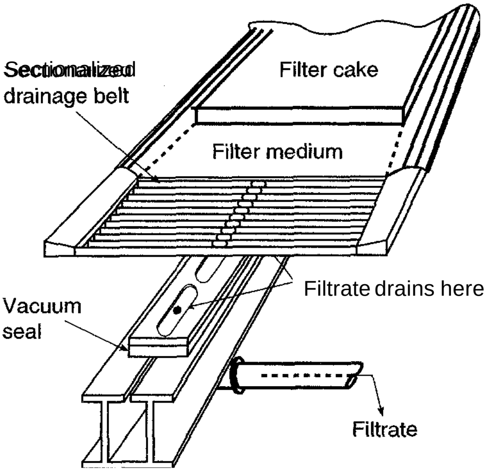

Figure *7.23:* Belt filter.

Vacuum filters. These filters operate continuously. The simplest type is the belt filter shown in Figure 7.23. **A** moving belt covered with a filter medium rests on a perforated vacuum compartment. The filtrate drains through and the cake remains on top and is discharged when the belt ends its turn.

- In the ***rotary*** *drum filter* (Figures *7.24–7.25)* the entire surface of a horizontal drum, except each end, is perforated and covered with cloth reinforced by spirally wound wire, or is made of heavy and fairly closely woven wire screen. Beneath this perforated surface are several separate parallel compartments, each connected to a cored shaft. **A** circular tank equipped with agitators holds the suspension, and in this the filter drum is partly immersed. The cycle of filtering, washing, drying, reversal of air current to loosen the cake, and discharge by scrapers characterizes this type of filter.

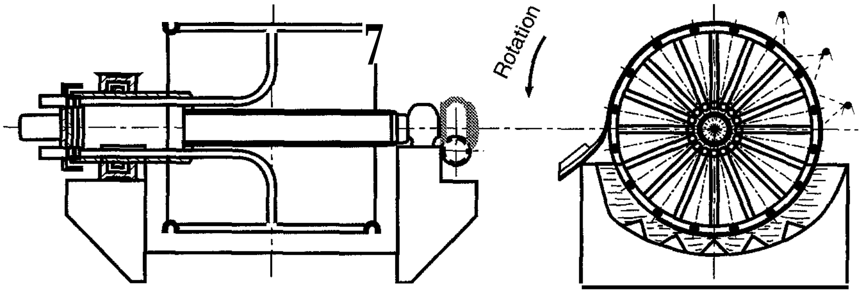

Figure *7.24:* Rotary drum vacuum filter; elevation and side view.

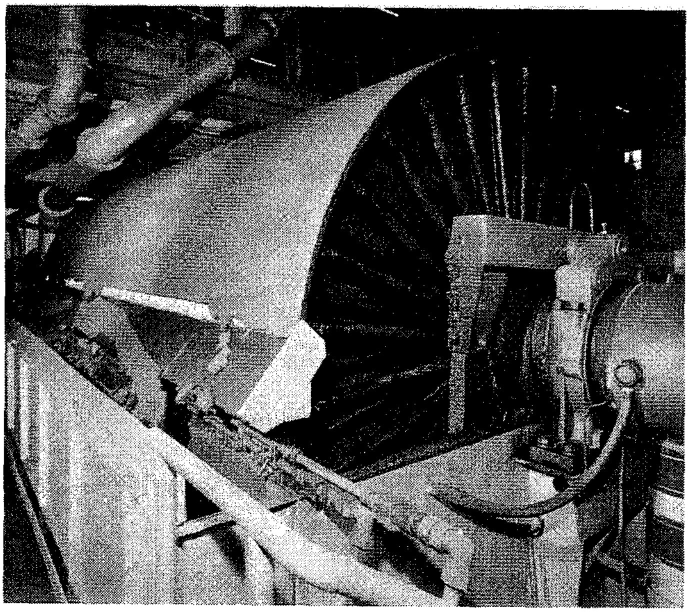

Figure *7.25:* Rotary drum vacuum filter in operation.

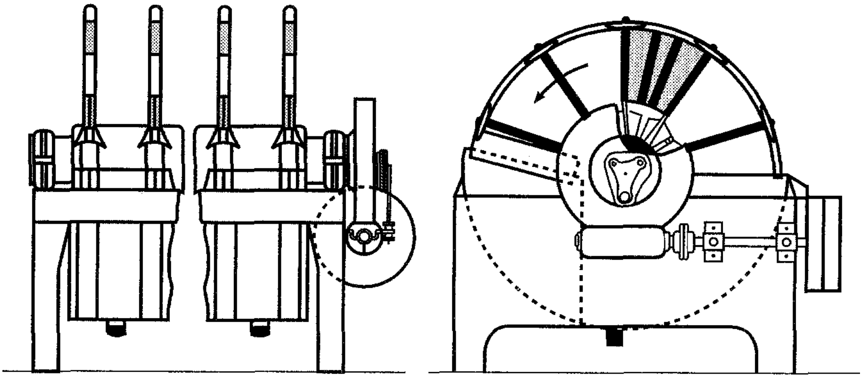

Figure 7.26: Rotary leaf filter.

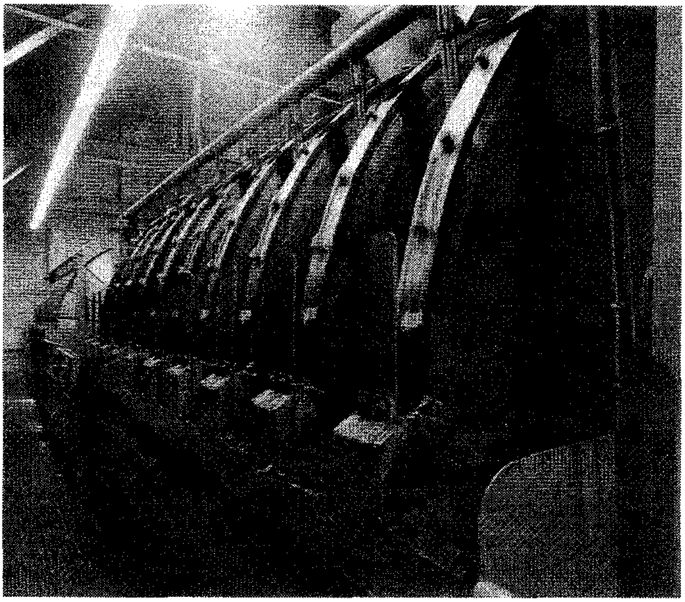

Figure 7.27: Rotary leaf filter in operation.

- In the *rotary leaf filter* (Figures 7.26–7.27) several fan-shaped leaves make up continuous disks, but each leaf is separately connected to the proper channels in a hollow shaft and functions individually. The disks turn in a tank of special shape containing the suspension. Suction is applied to those that are below the surface, and this is continued as the leaves rise from the tank. Water is sprayed on the cake, the channel now being connected to a separate opening in a disk valve at the end of the cored shaft. Air is drawn through the cake, and, as the leaves approach the surface of the suspension, a reverse current loosens the adhering solids and they are scraped off and discharged.

- In the dipping leaf filter also known as *Moore filter*, a leaf is made up of a cloth bag stretched over a frame of perforated pipe and reinforced by separating strips. A number of leaves in a single frame and connected by hose with a vacuum pump are dipped into a tank containing the suspension. Atmospheric pressure drives the liquid through the cloth, and the solids accumulate in a cake on the outside. When a sufficient thickness has been attained, the unit is lifted out and placed in a second tank of water for washing. The leaves are finally swung out over a discharge hopper, air is drawn through to bring about partial drying, and the current is then reversed to cause the cake to drop off.
- A *tilting pan vacuum filter* is shown in Figure 7.28. In this system multistage washing is possible before the cake is discharged.

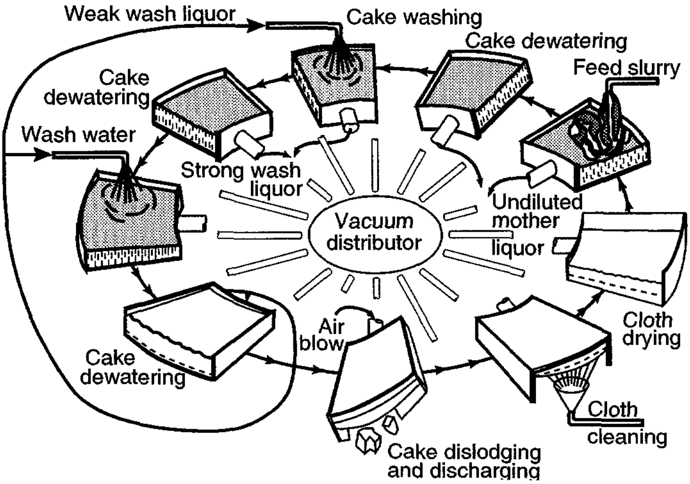

Figure 7.28: A tilting pan vacuum filter.

Residue disposal

Solid residue, usually wet, is transported by conveyer belts or trucks to disposal site. Thick slurry from the last thickener underflow is pumped to large disposal ponds where long-term settling takes place. Clarified water is pumped back to the washing circuit.

REGENERATION AND RECYCLE OF LEACH SOLUTION

In many leaching operations, it is desirable and is usually possible to regenerate the leaching agent after the metal recovery step. The following examples may be cited:

- After leaching a copper oxide ore with dilute sulfuric acid, copper is usually recovered from the solution by electrolysis. During this process, dilute acid is formed according to:

  Cathodic reaction: $Cu^{2+} + 2e^- \rightarrow Cu$

  Anodic reaction: $H_2O \rightarrow 2H^+ + {}^1/_2O_2 + 2e-$

  This acid is usually recycled to the leaching step. Since only copper was precipitated at the cathode, other metal ions remain in solution. Therefore, when the leaching agent is recycled, impurities will accumulate in the circuit and may contaminate the product. To keep a certain safe limit of impurities in the recycled solution, a part of the solution is usually discharged to waste; it is known as *bleed solution* (Figure 7.29). A similar situation exists in the treatment of gold ores by cyanide solution. Measures should be taken to prevent polluting the environment by this solution.

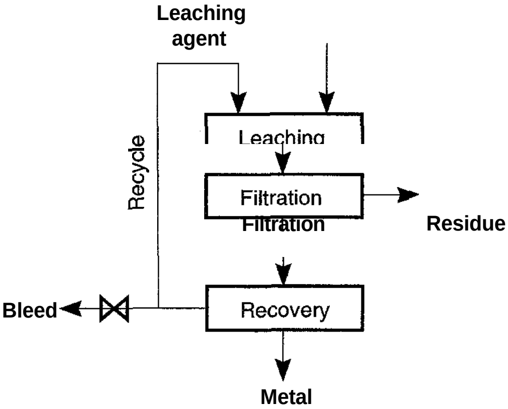

Figure 7.29: Maintaining the impurity level in a leaching circuit by bleeding.

- In some cases, the solution must be concentrated by evaporation before recycling. This is usually the case when the metal values are precipitated by hydrolysis, e.g., in treatment of bauxite by NaOH.
- In leaching ilmenite by hydrochloric acid, the acid is regenerated from the ferrous chloride solution by oxyhydrolysis (see p. 76).

WATER TREATMENT

Hydrometallurgical processes require large volumes of water for leaching and washing. Natural waters contain dissolved salts and must be treated prior to utilization to remove these salts to avoid contamination of the circuit.

Impurities in water

Impurities in water vary widely depending on its origin. This is due to the geologic formations the water came in contact with and the amount of atmospheric CO_2 that dissolved in it. As a result, natural waters usually contain appreciable amounts of Ca^{2+} and Mg^{2+} in form of bicarbonates and sulfates as well as suspended matter, and other impurities depending on the locality, e.g., Fe^{2+}, Mn^{2+}, and Cl^-.

Removal of impurities

Removal of impurities from water is usually achieved in three steps:

- *Lime–soh addition.* The purpose of this treatment is to remove the major amounts of calcium bicarbonate, calcium sulfate, and magnesium bicarbonate. Slacked lime removes the bicarbonates but not the sulfate. Consequently, a dosed mixture of $Ca(OH)_2$ and Na_2CO_3 is added to precipitate Ca^{2+}:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaHCO_3$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

$$Mg(HCO_3)_2 + Na_2CO_3 \rightarrow MgCO_3 + 2NaHCO_3$$

- *Filtration.* The finely divided precipitate is allowed to settle then filtered in a sand filter. To facilitate the settling, a small amount of aluminum sulfate is added which precipitates to form a gelatinous hydroxide:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$$

- *Ion exchange.* The clear and purified water is then passed over a bed of natural or artificial zeolite which are hydrated sodium aluminum silicates with characteristic properties to remove traces of Ca^{2+}, Mg^{2+}, and other ions by exchanging them for Na^+. When the bed is nearly saturated with the sorbed ions it is regenerated by passing a solution of NaCl then washing with water. This is discussed in chapter 20; Figure 7.30 shows an ion exchange water treatment plant.

If the water is colored due to organic compounds, it is purified by passing on a bed of activated charcoal.

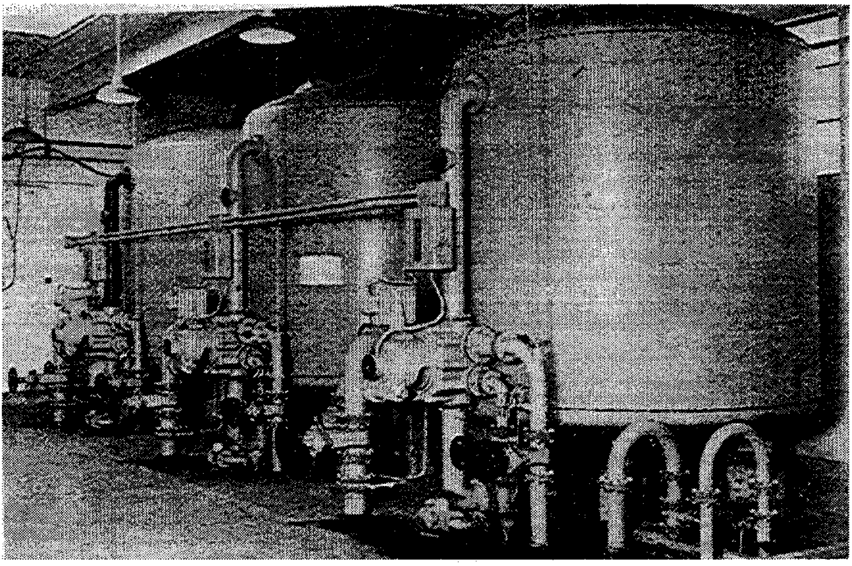

Figure 7.30: Base-exchange water–softeners for treating an industrial water supply.

PLANT LAYOUT

Hydrometallurgical plants are usually located in remote areas where the ore deposit is found, for example, gold and copper oxide leaching operations. In some cases, however, the ore or the concentrate are shipped long distances to the treatment plant, for example, bauxite and sulfide concentrates. Plant design should follow some prearrangement plan based upon requirement, selection of equipment according to processing flows, plant location, and future expansion.

Both building and equipment should be designed to give the most efficient production with a minimum of handling of material in process. Provision should be made for storage, for expansion to fit in with the original arrangement without disturbing the flow of work, and for the most favorable and economical conditions of operation of each piece of equipment with respect to all variables. Design is centered about problems of rates of mass and energy transfer and of chemical change. Other factors that should be considered in the design of building and equipment arrangement include possible hazards of fire, explosion, chemical injury, and injury to health, the welfare of the worker, economical distribution of process steam and power, and expansion of production.

Figure 7.31 shows layout for a typical atmospheric leaching plant including counter-current washing system while Figures 7.32 and 7.33 show a pressure leaching plant housed indoors.

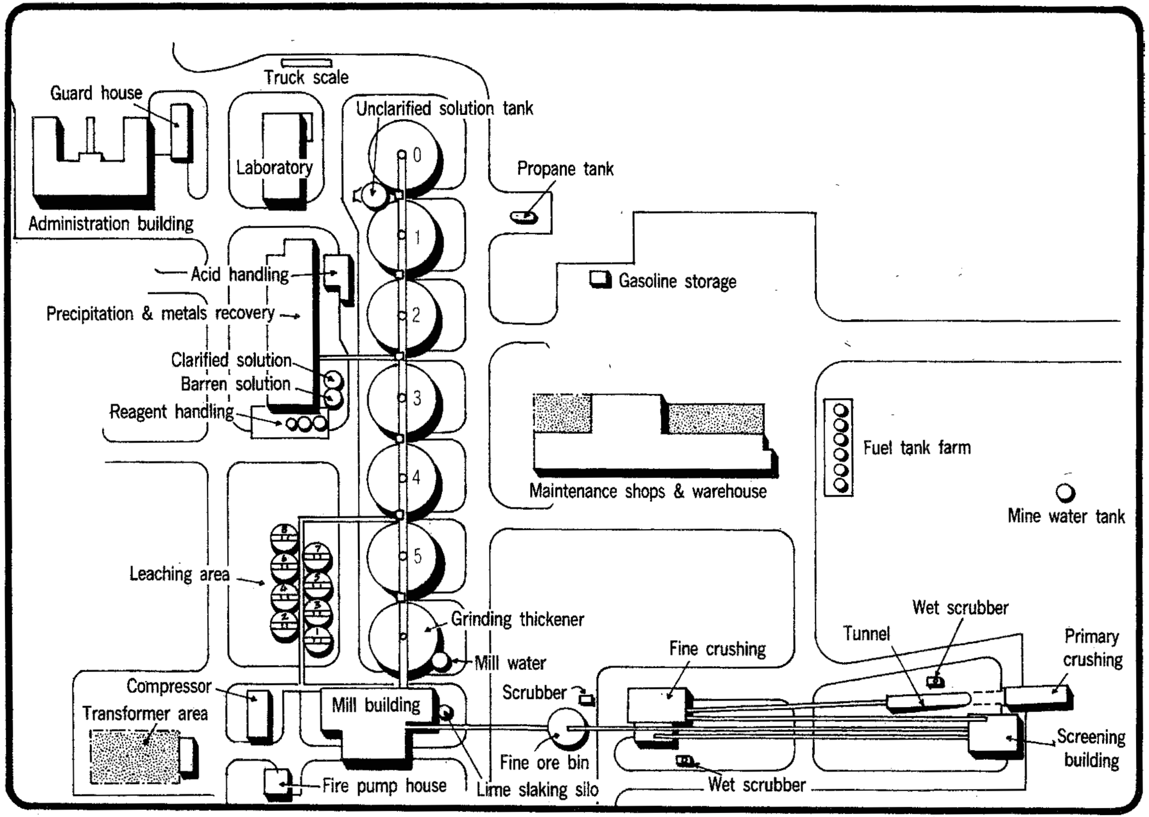

Figure 7.31: Plant layout for a gold leaching and precipitation operation (Paradise Peak, Nevada).

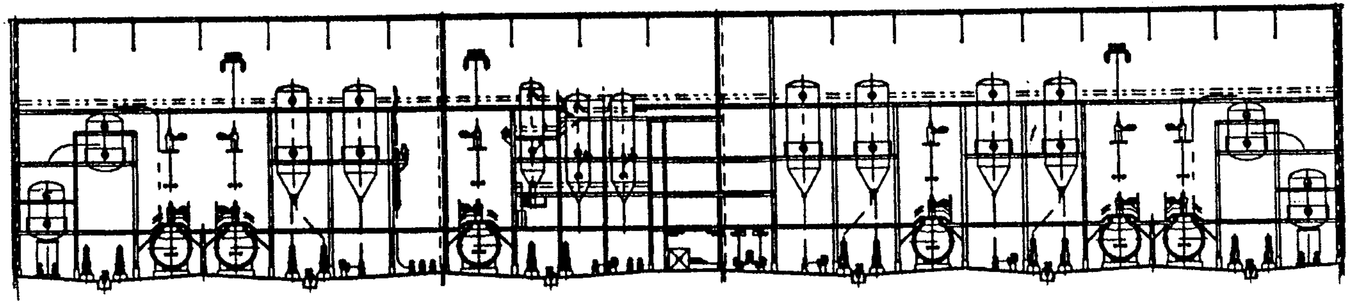

Figure 7.32: Pressure leaching plant (elevation).

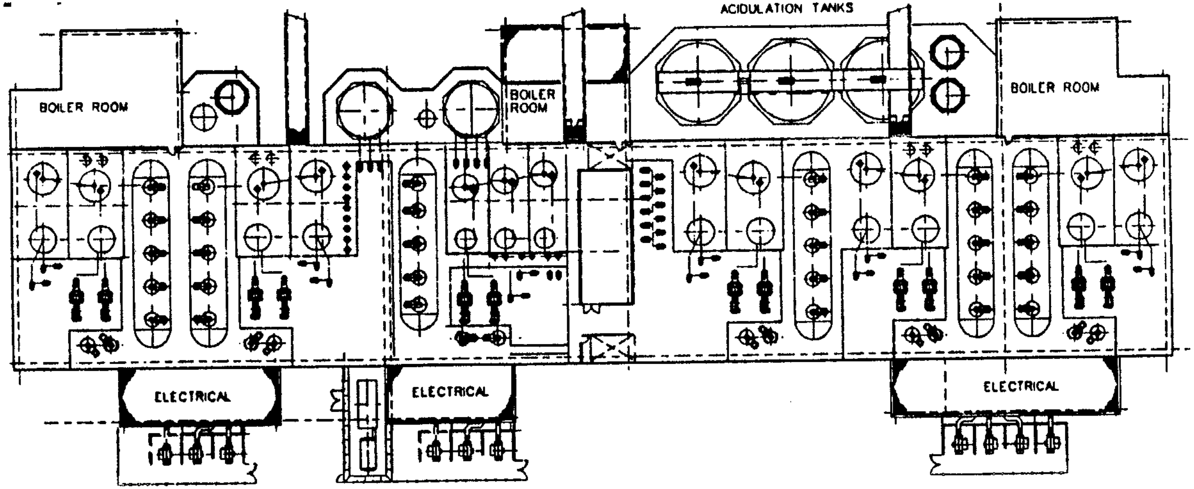

Figure 7.33: Pressure leaching plant (plan).

Chapter Eight

The Role of Microorganisms

Autotrophic Bacteria 195
Characteristics 197
Applications 198

AUTOTROPHIC BACTERIA

Certain microorganisms known as *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* isolated from mine water and others isolated from sulfur-bearing hot springs are capable of accelerating the rate of dissolution of sulfide minerals. Little or no solubilization of the metal sulfide results when sterile solutions are used under the same conditions. These bacteria can also accelerate the oxidation of elemental sulfur, ferrous ion, sulfite ion, and thiosulfate ion. There are also bacteria that reduce sulfates to sulfides, others oxidize H_2S to sulfur, nitrogen to nitrates, etc. Many sedimentary ore deposits are supposed to have been formed by the action or microorganisms.

Bacteria are minute, unicellular microscopic organisms 0.5–2 mm in **size** that reproduce by binary fission. They are widely distributed in soil, air, and water. They are divided into two classes according to their energy source:

- *Autotrophic.* These are organisms that live on inorganic matter.
- *Heterotrophic.* These are organisms that live on organic matter.

Bacteria can also be divided into two groups according to their utilization of oxygen:

- *Aerobic.* These utilize oxygen for growth, e.g., microorganisms that live on sulfides.
- *Anaerobic.* These do not need oxygen for their growth, e.g., microorganisms that live on sulfates, nitrates, and carbohydrates.

Bacterial action may be twofold:

- Enzymic processes. Enzymes generated in the bacterial cells are responsible for catalyzing the attack of minerals.
- Nonenzymic processes. Metabolic products such as acids and bases react with the mineral.

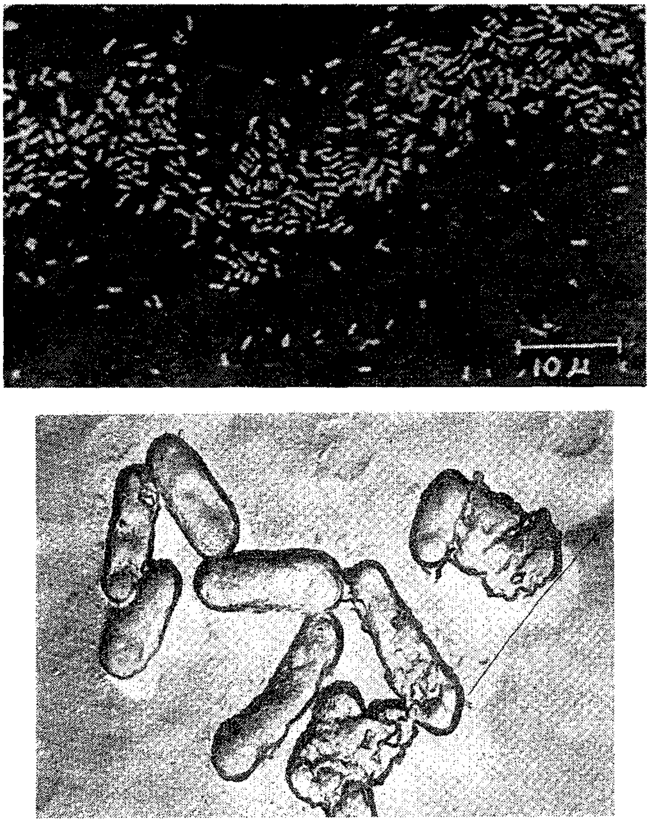

Figure 8.1: *Thiobacillus ferrooxidans*. Top: Magnification 900 × (Sutton and Corrick, 1961). Bottom: Magnification 40 000 × (Trud-inger, 1971).

T. thiooxidans and *T. ferrooxidans* are autotrophic aerobic bacteria (Figure 8.1). In industrial leaching operations where the continuous flow of leach solutions provides nutrient and a balanced environment, they multiply following the logarithmic law:

$$n = n_0 e^{kt}$$

where n_0 is their initial number, n their number at time t, and k is a constant. A leach solution in a copper dump leaching operation may contain as many as 10 million microorganisms/mL.

Characteristics

Autotrophic bacteria have the following characteristics:

- They must have oxygen to carry out their function, i.e., the oxidation of mineral substances with release of energy which is necessary for their growth.
- They utilize CO_2 as the principal source of carbon required for the synthesis of organic compounds composing the cell. In this respect they resemble plants. If CO_2 is removed from air supplied to bacteria, no growth will be observed. Rather than utilizing organic matter such as fats, carbohydrates, or proteins as a source of energy, these organisms cannot even tolerate their presence. They are unable to grow in agar, and obtain their energy solely by the oxidation of inorganic materials.
- They absorb certain nutrient from solution, e.g., PO_4^{3-} ions that are necessary for their metabolic function.
- They have resistance to high concentrations of metal ions in solution, e.g., Cu^{2+} which are usually extremely toxic to most other forms of life.
- They adapt to live and grow in strongly acidic environments (pH 1.5–3).
- They are destroyed by light, particularly ultraviolet light. Total darkness has a positive effect on their action. In shallow ponds bacterial action is inhibited during day light.
- Their maximum activity occurs at a certain temperature. For *Thiobacillus ferrooxidans*, for example, this occurs at 35 °C while for those isolated from sulfur-bearing hot springs (the thermophilic bacteria), the temperature may be as high as 85 °C. Below these temperatures they are dormant while above, they are destroyed.
- They manufacture enzymes and with their aid they catalyze the oxidation process:

$$MS_{(s)} \rightarrow M^{2+}_{(aq)} + S^{2-}_{(aq)}$$

$$S^{2-} + 20, \rightarrow SO_4^{2-}$$

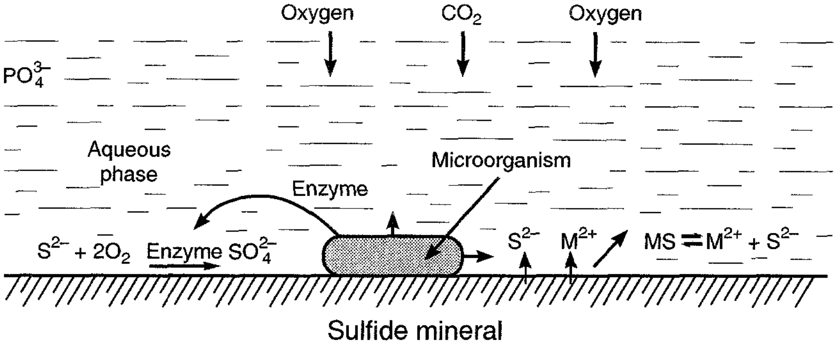

Figure 8.2: Schematic representation of the action of microorganisms adhering on the surface of a sulfide mineral.

The adherence of the microorganisms on the sulfide surface makes possible the rapid oxidation of S^{2-} ions liberated by the mineral and catalyzed by the enzymes (Figure 8.2). This is supported by the fact that the rate of dissolution of sulfides in presence of microorganisms is proportional to the solubility product of the sulfide.

- They catalyze the oxidation of any elemental sulfur generated during the chemical dissolution of sulfide minerals:

$$MS + 2H^+ + {}^1/_2O_2 \rightarrow M^{2+} + S + H_2O$$

$$S + {}^3/_2O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}$$

Hence there is no possibility of obtaining elemental sulfur during bacterial leaching.

- They catalyze the oxidation of any ferrous ion generated during the leaching of pyrite:

$$FeS_2 + {}^7/_2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$2Fe^{2+} + {}^1/_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O$$

Applications

The catalytic action of microorganisms in the oxidation of sulfides is exploited industrially in *in situ* and in dump leaching operations. The natural conditions are usually favorable for bacterial growth. Typical applications are for the recovery of copper, for the oxidation of pyrite to liberate locked-in gold, or to generate acid to dissolve uranium minerals associated with the pyrite, and for the elimination of pyrite from coal. The process is cheap but slow and may generate excessive amounts of sulfuric acid that have to be neutralized before disposal. However, it is highly economic for leaching low-grade ores.

Part Three

Leaching Processes

Raw materials treated by hydrometallurgical methods vary from very low-grade ores such as gold ores (concentrations of 1 ppm) to high-grade concentrates. The chemical nature of the raw material may be metals, oxides, complex oxides, sulfides, etc., as shown below.

Raw material	Examples
Metals	Native: Au, Ag, Cu, Pt metals. By reduction of oxides: Cu, Ni, Co.
Oxides	Bauxite, laterites, copper oxide ores, uranium ores, zinc ores and calcines, maganese ores and nodules.
Complex oxides	Chromite, niobite, tantalite, pyrochlore, ilmenite, wolframite, scheelite.
Sulfides	Mainly of the primary metals: Cu, Pb, Zn, Ni.
Selenides and tellurides	Anodic slimes of copper electrolysis.
Arsenides	Cobalt and nickel arsenide ores and speiss.
Phosphates	Phosphate rock, monazite sand.
Silicates	Clays, nepheline–syenite, beryllium ores, serpentine.
Chlorides and sulfates	Halite, potash, pyrite cinder.
Carbonates	Trona.
Borates	Borax.

Chapter Nine

Metals

Gold and Silver[1] 204

Sources 204

The cyanidation process 205

Effect of foreign ions 212

Destruction of cyanide ion 218

Recent advances 218

Refining 224

Low-gold alloys 224

High-gold alloys 227

Platinum Metals 228

Sources 228

Leaching and recovery 229

Copper, Nickel. and **Cobalt** 232

Applications 235

Selenium[2] 237

Summary 239

Metals commonly leached may come from one of the following sources:

- Occurring in nature in the native state. e.g., gold. silver. platinum metals. and copper.
- Produced by reduction of an oxide ore. e.g., copper. nickel. and cobalt.
- Crude metals **to** be refined. e.g., gold. silver. and platinum metals.
- Produced as by-product of a metallurgical process. e.g., selenium.

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[1] References to original literature can be found in F. Habashi. *Kinetics and Mechanism of Gold and Silver Dissolution in Cyanide Solution.* Bulletin 59. Montana Bureau of Mines. Butte. Montana 1967.

[2] Although selenium is a metalloid. it is included here for convenience.

GOLD AND SILVER

Sources

Gold and silver almost always occur together in the native state. They are recovered from the following sources:

Alluvial or placer deposits. These are formed by mechanical processes from the weathering and disintegration of mineral-bearing rocks and veins, followed by the transportation and concentration of the freed mineral by the action of running water. Metallic and nonmetallic minerals which are highly resistant to weathering become separated from their more easily weathered parent rock. The main agents which bring about the disintegration are variations in temperature, the expansion of water on freezing, erosion due to the movement of water, and the sandblasting action of the wind. The best conditions for the concentration of gold in auriferous gravels are when the river gradient is moderate, under balanced conditions of erosion and deposition. Sometimes large nuggets weighing tens of kilograms are found. These deposits may be concentrated further by gravity methods. Gravity concentrates are usually melted and refined. When this is not possible they are leached.

Veins associated with quartz and various sulfides. These are also known as reefs and are the parent ore body of alluvial deposits. They must be crushed and finely ground to liberate the minerals prior to leaching. Sometimes economic grinding is not enough to liberate gold from certain sulfides. In such cases the sulfides are chemically treated to liberate the gold prior to leaching, e.g., by thermal oxidation or by aqueous oxidation (see chapter 12).

Refining residues of nonferrous metals. Gold is usually a by-product of copper and nickel refining while silver is a by-product of lead refining.

Beside the native metals, gold telluride and silver sulfide are also found in nature in important deposits. Ocean water contains 1 ppb gold; gold from this source is estimated at 64×10^9 tons. Major gold producers are: Republic of South Africa, Russia, Canada, and USA.

Chlorine water or bleaching powder acidified with dilute sulfuric acid were used as early as 1848 to leach gold from its ores; the process was known as the *Plattner Process* after its inventor. In this process, a solution of $AuCl_3$ was obtained, from which gold was precipitated by ferrous sulfate or activated charcoal. Another process, known as the *Patera Process*, was also used at about the same time especially for silver ores. In this process the ore was roasted with sodium chloride to convert silver to silver chloride, and was then leached with water to remove base-metal chlorides. Sodium thiosulfate solution, $Na_2S_2O_3$, was then applied to dissolve silver chloride in a way similar to its use in developing a photographic film. Both processes became obsolete at the beginning of this century as a result of the introduction of the *cyanidationprocess*, i.e., the process in which an alkali cyanide is used as a leaching agent. Recently, there has been interest in substituting sodium cyanide by an equally inexpensive but nontoxic reagent. For example, thiourea, $N_2N–CS–NH_2$, in presence of oxygen, extracts gold from its ores faster than cyanide. Ammonium polysulfide, $(NH_4)_2S$, is also a good solvent for gold. None of these reagents, however, are used in commercial practice yet. Mercury was at one time used to recovery large particles of gold prior to cyanidation by *amalgamation*. This practice was, however, abandoned in the 1960s because of the toxic nature of mercury, except illegally in the Amazon region in Brazil.

The **cyanidation process**

The dissolution of gold and silver in cyanide[1] solutions was one of the puzzles that faced metallurgists for many years for two reasons:

- Gold, the most noble metal that dissolved only in aqua regia, dissolved readily in a very dilute solution of sodium cyanide.
- Although gold did not tarnish in air, air was essential for its dissolution.

This puzzle was solved when it was recognized that the dissolution of gold is an oxidation–reduction process in which cyanide ion forms a strong complex with Au^+ ion and the reduction of oxygen on the

---

[1] Cyanide is derived from Greek κυανος meaning blue, because hydrocyanic acid (blue acid) was derived for the first time from Prussian blue pigment when heated with sulfuric acid.

surface of metal may take place partially to the hydrogen peroxide stage or completely to hydroxyl ion as follows:

Oxidation: $Au \rightarrow Au^+ + e^-$

Complex formation: $Au^+ + 2CN^- \rightarrow [Au(CN)_2]^-$

Reduction: $O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Overall reaction:

$$2Au + 4CN^- + O_2 + 2H_2O \rightarrow 2[Au(CN)_2]^- + H_2O_2 + 2OH^-$$

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4[Au(CN)_2]^- + 4OH^-$$

Similar equations can be also written for the dissolution of silver. The first equation agrees with experimental facts (Table 9.1) and the second equation takes place only to a minor extent:

- For every 1 equivalent of metal dissolved, 2 moles of cyanide are consumed.
- For nearly every 2 equivalents of metal dissolved, 1 mole of oxygen is consumed.
- For nearly every 2 equivalents of metal dissolved, 1 mole of H_2O_2 is produced.

According to this stoichiometry, 1 gram mole of oxygen and 4 gram moles of NaCN should be present in solution. At room temperature and at atmospheric pressure, 8.2 mg O_2 are dissolved in 1 liter of water. This corresponds to 0.27×10^{-3} mol/L. Accordingly, gold dissolution should occur at a concentration of NaCN equal to $4 \times 0.27 \times 10^{-3} \times 49 = 0.05$ g/L or 0.005%. Thus a very dilute sodium cyanide solution would be enough for dissolving gold. The fact that oxygen was necessary for dissolution was not readily recognized because as seen from the above calculations, oxygen in solution as a result of air solubility is enough to bring about the reaction.

Table 9.1: Stoichiometry of cyanidation:
A) Consumption of cyanide;

Time [hours]	Amount of gold dissolved		Observed consumption of cyanide		Molar ratio [KCN/Au]
	mg	equivalent ($\times 10^{-3}$)	mg	moles ($\times 10^{-3}$)	
0.5	0.96	4.86	0.62	9.52	1.96
1.0	2.01	10.2	1.26	19.4	1.90
3.0	7.49	38.0	4.94	76.0	2.00
7.0	15.91	80.9	10.50	162.0	2.01
10.0	18.77	95.1	12.46	192.0	2.01
				Average	2.0

B) Consumption of oxygen;

Time minutes	Ag dissolved equivalent ($\times 10^{-5}$)	O_2 consumed moles ($\times 10^{-5}$)	$[Ag]/[O_2]$
10	2.96	1.45	2.05
20	7.76	3.07	2.50
30	9.36	4.17	2.25
40	12.42	5.40	2.30
120	36.06	16.00	2.25
		Average	2.2

C) Formation of hydrogen peroxide.

	Metal dissolved		H_2O_2 formed		Metal equiv./ moles H_2O_2
	mg	equivalent ($\times 10^{-5}$)	mg	moles ($\times 10^{-5}$)	
Gold	57.3	29.0	5.11	15.0	1.93
	47.6	24.1	4.02	11.8	2.04
Silver		2.96		1.43	2.06
		7.76		3.09	2.50
		9.36		4.00	2.24
		12.42		5.51	2.26
		36.06		14.76	2.44
				Average	2.3

Effect of cyanide and oxygen concentration

Since both cyanide and oxygen are necessary for the reaction it would, therefore, be expected that the rate of dissolution would depend on the concentration of both. However, it was found in practice that the rate of gold dissolution increases linearly with increasing cyanide concentration until a maximum is reached, beyond which a further increase in cyanide had no effect (Figure 9.1). These curves were contrary to common experience since the rate of dissolution of a metal, for example, iron in an acid increased with increasing acid concentration. Further, when the oxygen pressure was varied and its effect on the rate was studied, it was found that at low cyanide concentration, the rate of dissolution depends only on the cyanide concentration as shown in Figure 9.2, while at high cyanide concentration, the rate is independant of the cyanide concentration, and depends only on the oxygen pressure. An explanation for these curves was made possible by the electrochemical mechanism of dissolution, i.e., when the oxidation–reduction processes taking place are considered: The slowest reaction controls the whole process. Thus, at low cyanide concentration (and high O_2), it is the oxidation-complex formation reactions that control. At high cyanide concentration (and low O_2), it is the oxygen reduction reaction that controls.

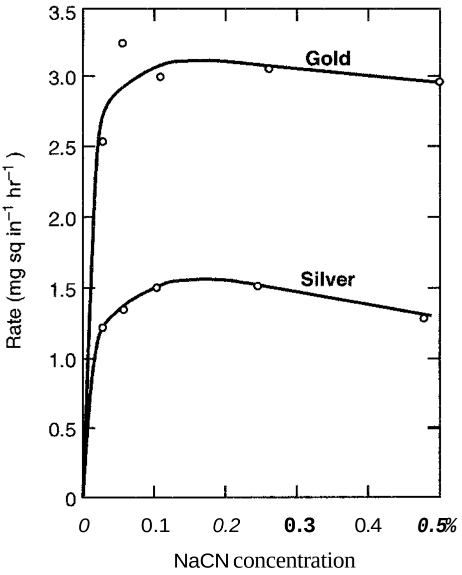

Figure 9.1: Effect of cyanide concentration on the rate of dissolution of gold and silver in air-saturated solution (Maclaurin, 1893; Barsky et al., 1934).

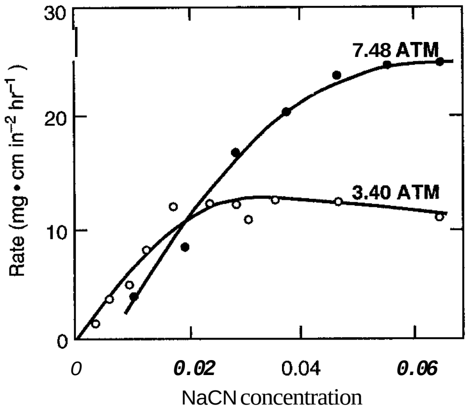

Figure *9.2:* Rate of dissolution of silver at different O_2 pressures and different NaCN concentrations at 24 °C (Deitz and Halpern, 1953).

From the technical point of view neither the concentration of dissolved oxygen alone (i.e., degree of aeration of the solution) nor the concentration of free cyanide alone are of importance, but it is the ratio of the two concentrations. Therefore, if much effort is spent to achieve ideal aeration while the solution is deficient in free cyanide, this effort is wasted. And the reverse is also true: If excess cyanide is added while the oxygen content of the solution is below the theoretical value, this excess cyanide is wasted.

Effect of hydrogen ion concentration

It is essential that the cyanide solution be kept alkaline during leaching to prevent the formation of HCN (Figure 9.3) which is extremely poisonous gas. Hydrogen cyanide may form as a result of absorption of atmospheric CO_2:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + CN^- \rightarrow HCN + HCO_3^-$$

High alkalinity, however, decreases the rate of dissolution as shown in Figure 9.4. The natural pH of a 0.1% KCN solution is 10.5 due to hydrolysis:

$$CN^- + H_2O \rightarrow HCN + OH-$$

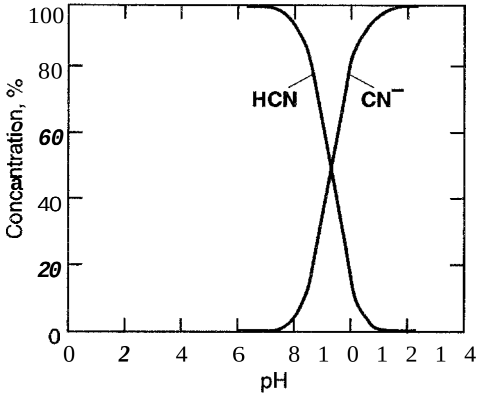

Figure **9.3:** Species present in cyanide solution as a function of pH.

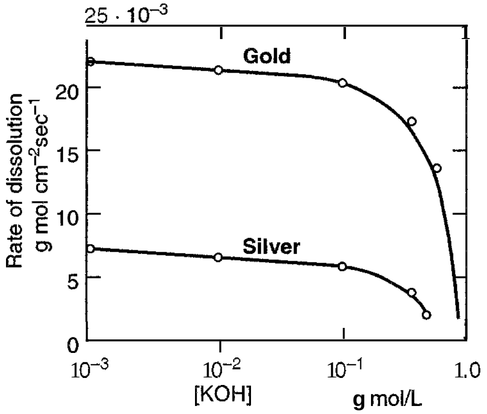

Figure 9.4: Effect of high alkalinity on the rate of dissolution of gold and silver in cyanide solution (Kakovskii and Kholmanskikh, 1959, 1960).

The alkalinity of cyanide solutions should, therefore, be carefully controlled to achieve high dissolution rates. In practice, the pH usually ranges from 11 to 12. Solutions kept alkaline by $Ca(OH)_2$, when compared to others at the same pH kept alkaline with KOH, show a remarkable retarding effect in the case of lime, as shown in Figure 9.5. The retarding effect is supposed to be due to the formation of calcium peroxide layer on the surface of the metal which prevents the reaction with cyanide. Calcium peroxide was considered to be formed by the reaction of lime with H_2O_2 accumulating in solution, according to:

$$Ca(OH)_2 + 2H_2O_2 \rightarrow CaO_2 \text{ t } 2H_2O$$

Lime is one of the reagents commonly used in industry to adjust the pH of the pulp. Its use must, therefore, be carefully considered.

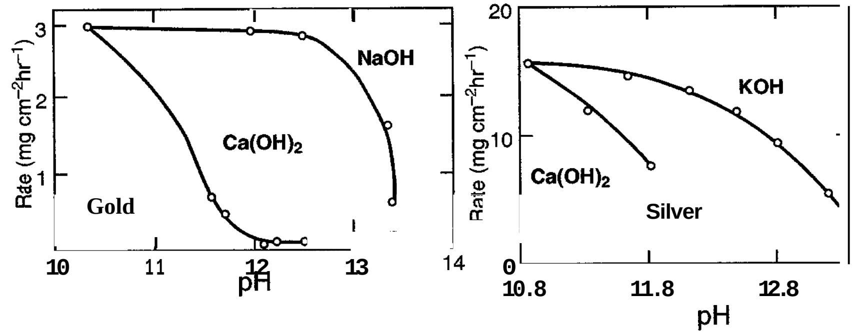

Figure 9.5: Retarding effect due to calcium ions at high alkalinity (Gold: Barsky et al., 1934; Silver: Deitz and Halpern, 1953).

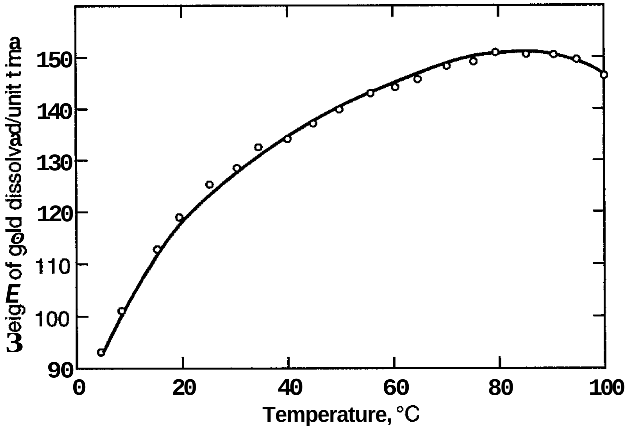

Figure 9.6: Effect of temperature on the rate of dissolution of gold in 0.25% KCN (Julian and Smart, 1921).

Effect of temperature

Increasing the temperature increases the rate of dissolution. On the other hand, the oxygen content of the solution decreases with increasing temperature. Therefore, there should be an optimum temperature for the maximum rate. This was found to be at about 85 °C as shown in Figure 9.6. The activation energy of dissolution of ranges from 2–5 kcal/mole, which is typical for processes controlled by diffusion.

Effect of agitation

The rate of dissolution increases with increased agitation, which is also typical of diffusion-controlled processes.

Effect of foreign ions

Most gold occurs as native metal, nearly all alloyed with various amounts of silver. Certain minerals are characteristically associated with gold, and the most important are pyrite, galena, zinc blend, arsenopyrite, stibnite, pyrrhotite, and chalcopyrite. Various selenium minerals and magnetite may also be present. In Witwatersrand, South Africa, uraninite, and to a lesser extent, thucholite are associated with the gold ore; uranium is recovered as a by-product of gold milling. Carbonaceous matter is associated with some gold ores. The most common gangue minerals are quartz, feldspar, micas, garnet, and calcite. Although the gangue minerals are insoluble in cyanide solution, some metallic minerals are soluble to some extent. Carbonaceous matter in gold ore is a source of trouble, because it adsorbs gold cyanide complex.

With the exception of a few ions such as Na^+, K^+, Cl^-, NO_3^-, and SO_4^{2-} which have no effect on the rate of dissolution of gold and silver in cyanide solution, ions may have an accelerating or a retarding effect. Lead(II) ions may have either an accelerating or a retarding effect, depending on their concentration in solution. The study of the effect of these foreign ions on cyanidation is complicated because the dissolution process is composed of two simultaneous reactions: The oxidation reaction involving the formation of the auro- or the argentocyanide ion and the reduction of oxygen as mentioned above. Which of these reactions is affected by the foreign ion is usually difficult to say, and many contradictory statements are found in the literature. Data available were mainly obtained by studying the effect of foreign ion in the gold leaf test.

An approach to this problem is to study the effect of the foreign ion on the cathodic and the anodic reactions separately. This can be achieved by studying the change in potential-current density characteristics of the gold (or silver) electrode in two separate experiments :

- Gold electrode + $[Au(CN)_2]^-$ + CN^- + foreign ion, oxygen being excluded from the system.
- Gold electrode + O_2 + H_2O + foreign ion, in the absence of cyanide ion.

In the first experiment, the effect of the foreign ion on the reduction of oxygen on the gold surface can be studied, and in the second experiment, the effect of the same ion on the anodic reaction of gold dissolution in cyanide. The results of such tests should be interpreted with care, however, as the application of external emf to cause dissolution does not correspond to actual cyanidation practice. Thus, for example, under these conditions oxygen is reduced to OH^- and not to H_2O_2. Another approach involves the use of radioactive indicators of the ions being studied.

Accelerating effect

It has been reported that small amounts of lead, bismuth, thallium, and mercuric salts accelerate the dissolution. This was confirmed later by many researchers. From calculations of electrode potentials in cyanide solutions, it was concluded that gold metal can actually displace the ions of only these four metals. It was, therefore, suggested that the rapid dissolution of gold in the presence of these ions might be due to alteration in the surface character of gold by alloying with the displaced metals. Early researchers detected the presence of lead on the surface of gold when the cyanide solution contained Pb^{2+} ions, but did not identify its nature. It was only recently confirmed by electron microscopic studies that lead alloys with gold on the surface (Figure 9.7). The alloy then dissolves rapidly, hence lead acts as a catalyst.

The addition of lead salts to cyanide solutions is a common mill practice aimed also at counteracting the harmful effect of sulfides. Addition of excessive lead salts, however, may cause a retardation in the rate of dissolution of the gold, as will be described later.

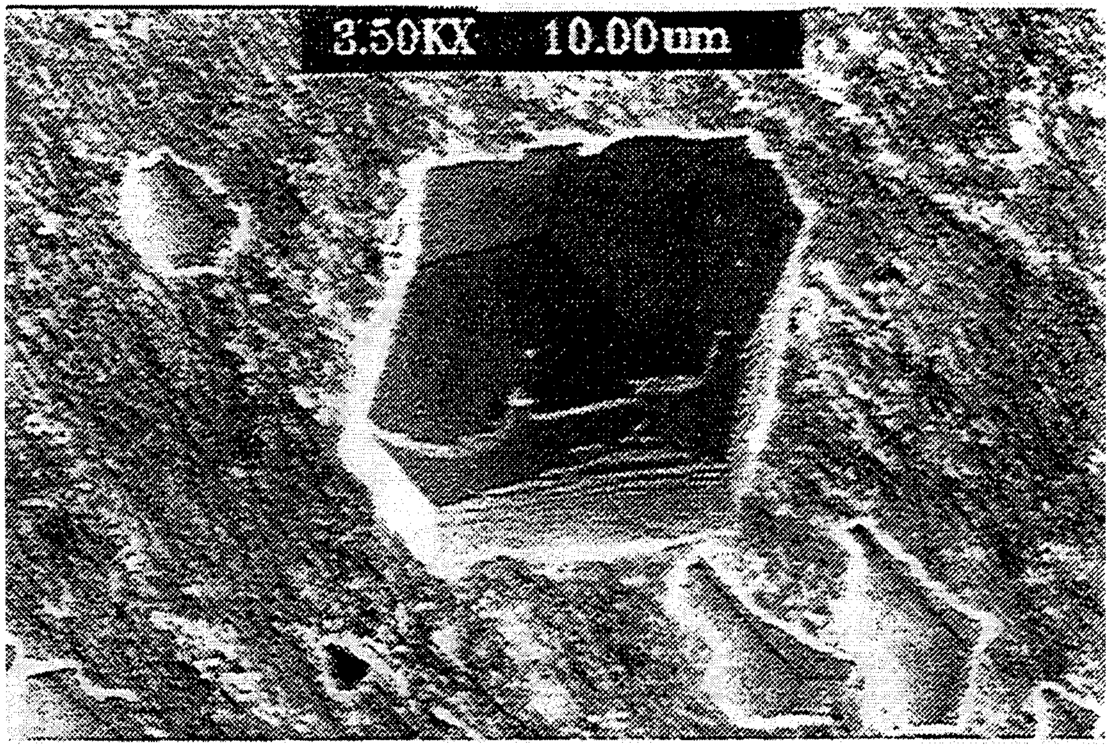

Figure **9.7:** Formation of a lead–gold alloy on the surface of gold undergoing cyanidation in presence of few milligrams of $Pb(NO_3)_2$ in solution (D. Mussati, J. Hager, and G. P. Martin, pp. *247–265* in *Aqueous Electrotechnologies*, edited by D. Dreisinger, TMS-AIME, Warrendale, Pennsylvania 1997).

Retarding effect

The presence of metallic cations such as Fe^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Ca^{2+}, and Ba^{2+} (the latter two only at high alkalinity) has a retarding effect. Lead(II) plays a unique role in cyanidation, and there has been much confusion regarding its effect on the rate of dissolution of gold. Besides the accelerating action already described, some reports describe a retarding effect. It can be concluded from those studies that when Pb^{2+} is present in very small amounts as compared to the CN^- ion, an accelerating effect is observed, whereas when the $[Pb^{2+}]/[CN^-]$ ratio exceeds a certain value there is a retarding effect.

It is also well known that the sulfide ion and certain flotation agents such as xanthate ion, which is sometimes used to concentrate the sulfides with which gold is associated have a retarding effect on the rate. The retarding effect may be due to one or more of the following reasons:

- *Consumption of oxygen from solution:* Because oxygen is necessary for gold dissolution, any side reactions in which the cyanide solution is deprived of its oxygen content will lead to a decrease in the rate. Pyrrhotite accompanying gold in some ores decomposes in alkaline medium forming ferrous hydroxide and sulfide ion:

  $$FeS + 2OH^- \rightarrow Fe(OH)_2 + S^{2-}$$

  In presence of oxygen, ferrous hydroxide is easily oxidized to ferric hydroxide:

  $$2Fe(OH)_2 + {}^1/_2O_2 + H_2O \rightarrow 2Fe(OH)_3$$

  while sulfide ion is partly oxidized to thiosulfate and polysulfide:

  $$2S^{2-} + 2O_2 + H_2O \rightarrow S_2O_3^{2-} + 2OH^-$$

  $$S^{2-} + H_2O \rightarrow HS^- + OH-$$

  $$2HS^- + {}^1/_2O_2 \rightarrow S_2^{2-} + H_2O$$

  thus contributing to the depletion of oxygen from solution.

- *Consumption of free cyanide from solution:*
  - Formation of complex cyanides: Some copper, zinc, and iron minerals that may be associated with gold ore dissolve in cya-

nide solution and therefore deplete the solution of its cyanide content, e.g.:

$$ZnS + 4CN^- \rightarrow [Zn(CN)_4]^{2-} + S^{2-}$$

  - Formation of thiocyanate: Sulfide ion liberated, when the ore contains sulfide minerals, reacts with cyanide and oxygen to form thiocyanate ion, which has no action on gold:

$$S^{2-} + CN^- + {}^1/_2O_2 + H_2O \rightarrow CNS^- + 2OH^-$$

  - Adsorption on gangue material: Auriferous ores and concentrates may contain quartz, aluminosilicates, or other silicates which, if finely divided in an aqueous alkaline medium, form colloidal silica and alumina; if iron sulfides are present in the ore, ferric hydroxide is also formed. These gangue materials have a strong adsorptive capacity for potassium cyanide.

- Film formation on the surface of the metal:
  - Sulfides: The retarding effect of the sulfide ion in the cyanide solution is well-known. As little as 0.5 ppm of the sulfide ion retards the dissolution. This cannot be accounted for by the depletion of the solution of its cyanide or oxygen contents, as the leaching solution usually contains excess oxygen and excess cyanide. It is believed that an insoluble aurous sulfide film is formed on the gold, which protects it from dissolution.

    The effect of sulfide ion on the electrode potential of gold in KCN solution in the absence of oxygen is negligible, while its effect on the electrode potential of gold in the absence of KCN but in the presence of oxygen is great. It appears that the trace sulfide poisons the gold surface toward the cathodic reduction of oxygen but does not affect the anodic reaction.

  - Peroxides: Calcium ion has no effect on gold dissolution. At $pH > 11.5$, however, the rate of dissolution is greatly reduced. At the same pH, solutions kept alkaline by $Ca(OH)_2$ show a remarkable decrease in the rate of gold and silver dissolution when compared with others kept alkaline with KOH. It was suggested that the decrease may be due to the formation of calcium peroxide on the metal surface, which prevents the reaction with cyanide. Calcium peroxide was thought to be formed by the reaction of lime with H_2O_2 accumulating in solution according to:

$$Ca(OH)_2 + H_2O_2 \rightarrow CaO_2 + 2H_2O$$

It was possible by chemical analysis to identify the precipitate formed as calcium peroxide. This was confirmed later by means of X-ray diffraction analysis; $Ba(OH)_2$ behaves similarly. Lime is one of the reagents commonly used in cyanide mills to adjust the pH of the pulp and to help settling. Its use must therefore be carefully considered.

- Oxides: Ozone when added *to* cyanide solution decreased the rate of dissolution of gold. Apparently a layer of gold oxide, which caused a visual change of the gold to brick red, produced the retarding effect. However, potassium cyanide is also oxidized by ozone according to:

  $$3KCN + O_3 \rightarrow 3KCNO$$

- The rate of dissolution decreases with the addition of as little as *0.4* ppm of potassium ethyl xanthate. When flotation is used to concentrate the sulfides with which gold is associated, prior to cyanidation, difficulties are frequently faced. The gold surface was reported to turn reddish. A gold xanthate film was probably formed. This was confirmed by using potassium xanthate marked with S^{35}.

The accumulation of impurities in solution retards dissolution. The effectiveness of the cyanide solution is tested frequently by measuring the time required for a gold leaf to dissolve under prescribed conditions of shaking. The faster the gold leaf dissolves, the more effective is the cyanide solution. One way of minimizing such difficulties is by adding a lead salt such as lead oxide, nitrate, or acetate. This precipitates the sulfide ion as soon as it is formed in the form of insoluble lead sulfide. The addition of small amounts of potassium permanganate also eliminates this difficulty by oxidizing the sulfide ion to sulfate. Another way is to agitate the ore pulp in an alkaline medium using $Ca(OH)_2$ to decompose sulfide minerals, and form harmless precipitates:

$$FeS + 2OH^- \rightarrow Fe(OH)_2 + S^{2-}$$

$$2Fe(OH)_2 + {}^1/_2O_2 + H_2O \rightarrow 2Fe(OH)_3$$

$$S^{2-} + 20, \rightarrow SO_4^{2-}$$

$$SO_4^{2-} + Ca^{2+} \rightarrow CaSO_4$$

The sulfide-free pulp is then subjected to cyanidation. Figure 9.8 shows a modern cyanidation plant.

Destruction of cyanide ion

Bleed solutions containing cyanide cannot be thrown away in surface waters because of their poisonous nature. The following methods are used to render them harmless before disposal.

- *Acidification and recovery of HCN.* When SO_2 is bubbled in bleed solutions, HCN is formed: It can be collected and absorbed in a solution of NaOH to form NaCN for recycle:

  $$CN^- + H^+ \rightarrow HCN$$

  $$HCN + OH- \rightarrow CN^- + H_2O$$

  Any copper and iron present in solution as cyanides precipitate as copper ferrocyanide. Remaining metal ions in the acid solution can then be precipitated by $Ca(OH)_2$ and disposed of safely.

- *Oxidation to cyanate.* While the cyanide ion is highly poisonous, its oxidation product, the cyanate ion, is not. Chlorine is usually used as oxidizing agent for this purpose:

  $$CN^- + Cl_2 + 2OH^- \rightarrow OCN^- + 2Cl^- + H_2O$$

  Excess of chlorine oxidizes the cyanate ion further to CO_2 and nitrogen:

  $$2OCN^- + 3Cl_2 + 4OH^- \rightarrow 2CO_2 + N_2 + 6Cl^- + 2H_2O$$

Recent advances

Thiourea process

The solubilizing action of gold and silver in thiourea may be represented by the oxidation–reduction couple as follows:

$$Au \rightarrow Au^+ + e-$$

$$Au^+ + 2(NH_2)_2CS + [(H_2N)_2CS \cdot Au \cdot SC(NH_2)_2]^+$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

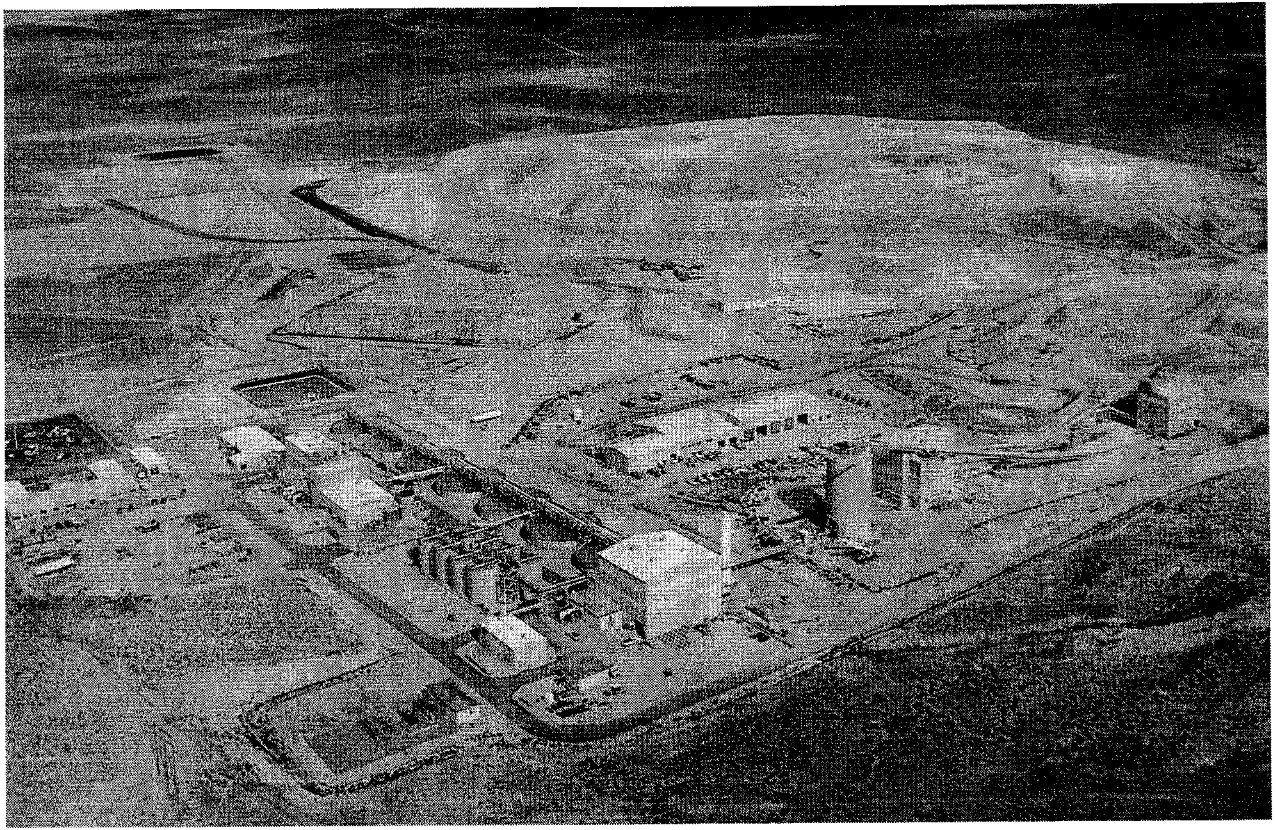

Figure 9.8: Gold and silver recovery plant at Paradise Peak mine near the town of Gabbs, Nevada.

This takes place in acid medium, is faster than cyanidation, and less toxic. However, thiourea undergoes appreciable decomposition during leaching.

Heap leaching

The increased price of gold in the 1970s made possible the leaching of old tailings containing as little as 1 ppm gold thanks to the newly developed heap leaching technology that was developed for the leaching of low grade copper and uranium ores. To improve the percolation of the leach solution in the bed, the fine tailings were sometimes agglomerated by slurrying with water and a small amount of cement which was allowed to set. The heaps were then constructed from the hard agglomerates and leached with the alkaline cyanide solution.

Treatment of refractory ores

A problem in gold metallurgy was the treatment of gold locked up in pyrite or arsenopyrite crystals and therefore unresponsive to cyanidation. Roasting followed by leaching was an expensive and polluting proposition. A hydrometallurgical approach proved to be a successful solution for this type of ores. Barrick Goldstrike now treats a pyrite ore–water slurry in autoclaves at high temperature and oxygen pressure. Horizontal autoclaves are used, each being 30 m long and 5 m in diameter, operating at 160–180 °C and 2000 kPa, with a retention time of 20 minutes (Figures 9.9 and 9.10). The autoclaves are made of carbon steel 8 cm thick, lined with as 6 mm lead membrane and two layers of acid-resisting brick 22.5 cm total thickness. After this treatment, the ore is then suitable for cyanidation. Table 9.2 gives data on some aqueous oxidation operations for refractory gold ores.

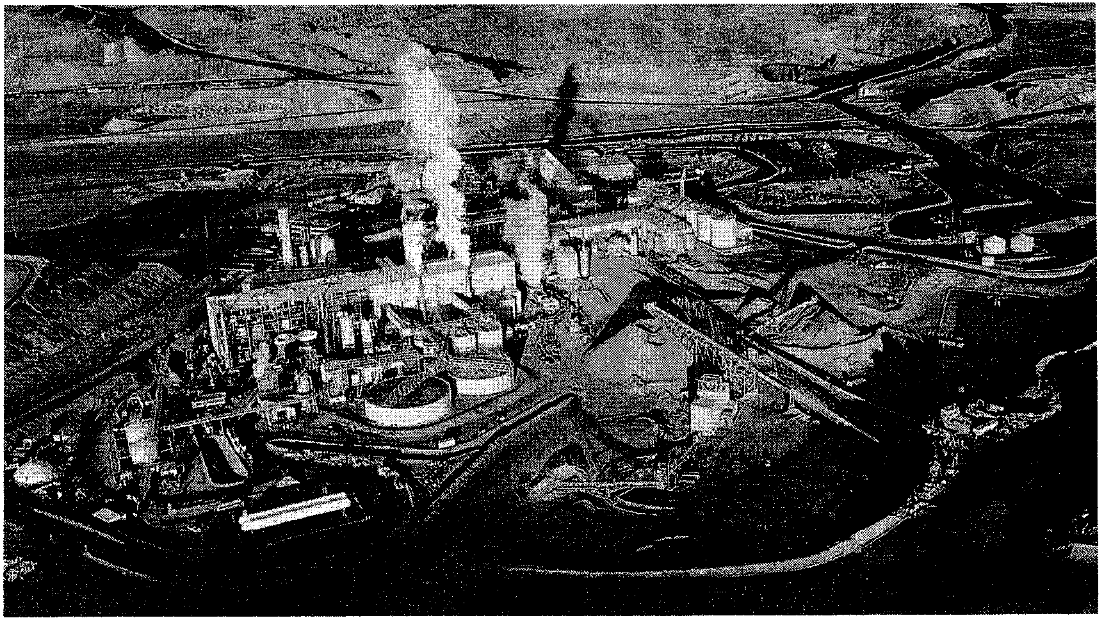

Figure 9.9: A large pressure leaching operation for gold ores prior to at Nevada (courtesy Barrick Goldstrike).

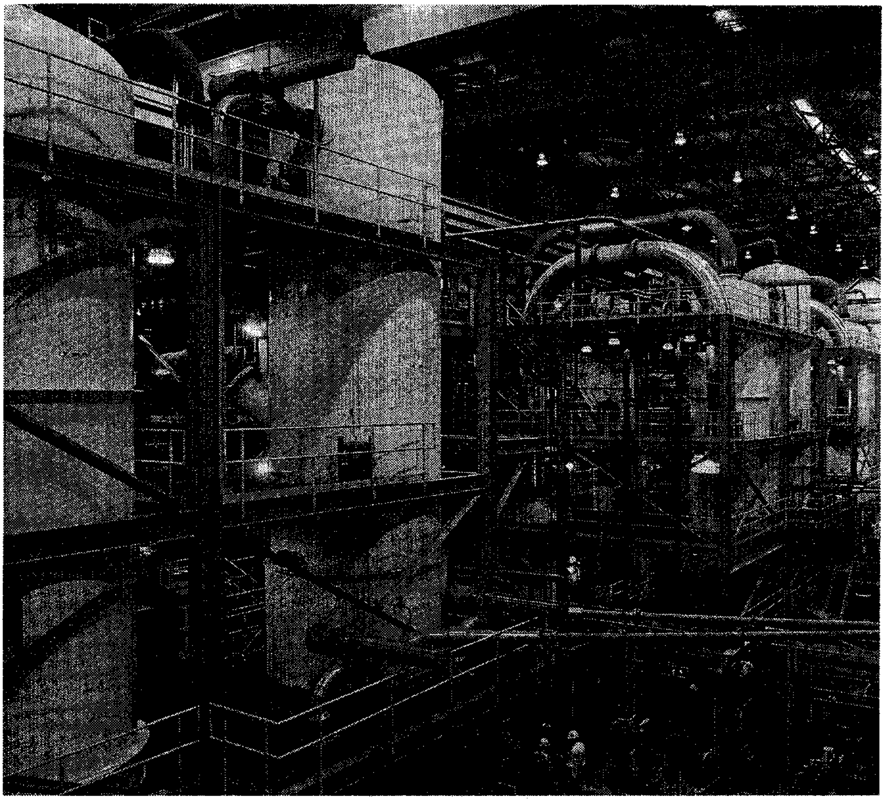

Figure 9.10: Inside the Barrick Goldstrike plant for pressure leaching of refractory gold ores prior to cyanidation.

Gold ores containing carbonaceous material are also known as refractory ores and are difficult to treat, not only because part of the gold is tied up with the organic matter but also because dissolved gold is adsorbed on the carbon present in the ore and therefore reports in the taillings. This problem was solved by aqueous oxidation using chlorine. Some of the gold may be solubilized by the chlorine water but the major function of the controlled chlorination is to oxidize organic matter before cyanidation. A plant at Carlin, Nevada, uses this technology. Another solution to this problem was found by using the carbon-in-leach process as described below.

Table **9.2:** Status of treatment of refractory gold ores by pressure hydrometallurgy.

Start up	Plant location	Owner	Feed	Medium	Capacity, t/d	Number of autoclaves
1985	McLaughlin, USA	Homestake, USA	ore	acid	2700	3
1986	San Bento, Brazil	Genmin, South Africa	concentrate	acid	240	2
1988	Mercur, Utah, USA	American Barrick, Canada	ore	alkaline	680	1
1989	Getchell, USA	First Miss Gold	ore	acid	2730	3
1990	Goldstrike, Nevada, USA	American Barrick, Canada	ore .	acid	1360	1
1991	Goldstrike, Nevada, USA	American Barrick, Canada	ore	acid	5450	3
1991	Pargera, Papua–New Guinea	Placer Dome, Canada	concentrate	acid	1350	3
1991	Campbell, Canada	Placer Dome, Canada	concentrate	acid	70	1
1992	Con, Lihir	Nerco Minerals	concentrate	—	90	1
1993	Goldstrike, USA	American Barrick, Canada	ore	acid	11580	6
1994	Pargera, Papua–New Guinea	Placer Dome, Canada	concentrate	acid	2700	6
Under study	Lihir, Papua–New Guinea	—	—	—	—	

Cyanidation under pressure

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

Refining

Separation of gold from silver and other impurities (Cu, Pt metals, etc.) is usually carried out by electrolysis or by chlorination. However, on a small scale, e.g., in mints, refining is done by selective leaching. The method used depends on the gold content as well as on the type of impurities present. While silver is soluble in both nitric and sulfuric acids, and gold is insoluble, yet these acids cannot be used to dissolve silver away from an alloy containing more than 25% Au. For high-gold alloys, aqua regia is therefore used. In such alloys, gold is leached, while silver forms an insoluble residue.

Gold is soluble in aqua regia, but a gold–silver alloy containing more than 8% Ag cannot be attacked due to the formation of an insoluble layer of AgCl. Therefore, the aqua regia leaching process is used only for refining high-grade bullions, where the silver does not amount to more than 8%, or to cases where the bullion contains enough copper to open it up to attack in spite of the silver present. A summary of these processes is shown in Table 9.3. In both cases, the bullion is first melted and poured in water to obtain granules suitable for leaching.

Pure gold is too soft and it is therefore alloyed with other metals, usually copper. The purity, known as fineness, is usually expressed in "carats" or "karats"[1]. Pure gold is 24 carats; an alloy containing 22 parts gold and 2 parts other metals is 22 carats, etc.

Low-gold alloys

In such alloys, silver is selectively leached. It is necessary to alloy the bullion with silver such that silver constitutes 75% of the alloy.

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[1] The carat in the diamond industry has a different meaning: it is a measure of weight. The international carat is 200 mg.

Such an alloy is known as *parting alloy.* In the nitric acid process (Figure 9.11), the reactions are:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 2H_2O + NO$$

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Table 9.3: Summary of gold refining processes by leaching (√ = attacked, × = not attacked).

	Alloy composition [%]		Attack by		Remarks
	Ag	Au	HNO_3 or H_2SO_4[a]	Aqua regia[b]	
Low-gold bullion	100	0	√	×	Bullion treated by HNO_3 or H_2SO_4.
	75	25	√	×	
	70	30	×	×	Bullion must be alloyed with Ag before treatment with HNO_3 or H_2SO_4.
	50	50	×	×	
	25	75	×	×	
	10	90	×	×	
High-gold bullion	8	92	×	√	Bullion treated by aqua regia.
	0	100	×	√	

a. Ag is soluble but Au is insoluble.
b. Au is soluble but Ag is insoluble due to the formation of AgCl.

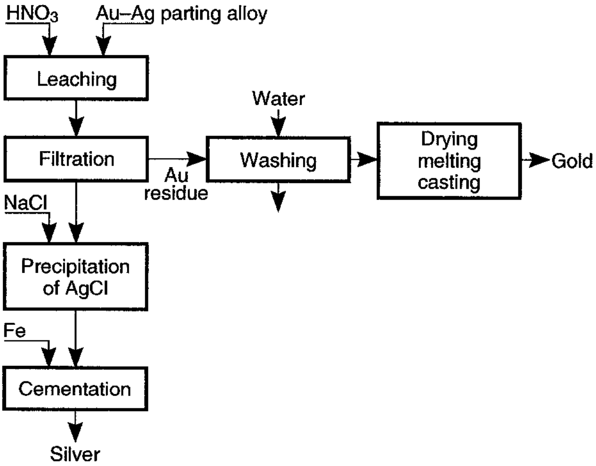


Figure 9.11: Nitric acid process for refining gold.

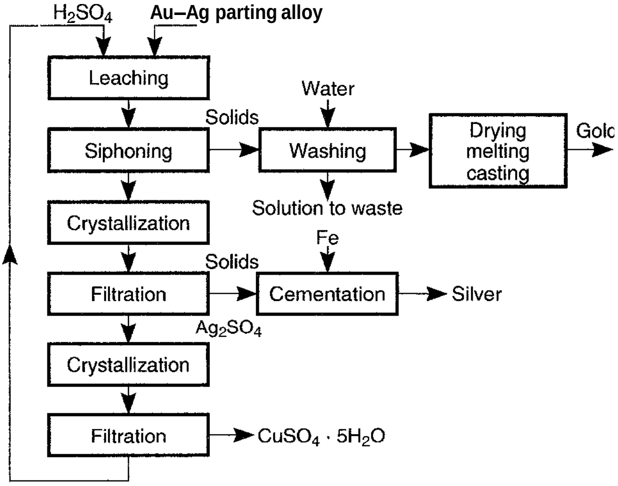


Figure 9.12: Sulfuric acid process for refining gold.

The reaction is carried out in stainless steel vessels, and nitric gases are oxidized and recovered as HNO_3. Silver and platinum will go into solution, while Au, Ru, Rh, and Ir are left behind as a finely divided black mud. Silver is recovered from the solution by precipitation as AgCl by adding NaCl. Silver chloride is then converted to metallic silver by contact with scrap iron. The gold residue is then washed, dried, melted, and cast.

The introduction of sulfuric acid as a leaching agent for refining gold reduced the cost greatly as compared with the nitric acid process. Cast iron vessels could be used, and copper in the bullion is converted to copper sulfate, which is a marketable product. The process is shown in Figure 9.12 and the reactions are:

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + 2H_2O + SO,$$

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2$$

Silver, copper, and part of the palladium are dissolved, while **Au,** Pt, Ru, Rh, and Ir are not. The gold residue is separated, washed, dried, briquetted, melted, and cast. The solution containing silver and copper is transferred to lead-lined tanks, diluted with water, and cooled to crystallize Ag_2SO_4. Silver sulfate is slightly soluble in cold water but dissolves readily in hot concentrated H_2SO_4. The crystals are separated, washed, reduced with scrap iron, melted, and cast. The mother liquor is evaporated and cooled to crystallize and separate $CuSO_4$. The residual sulfuric acid is recycled. This process cannot be used for bullions containing appreciable quantities of lead, because $PbSO_4$ will be left behind with the gold residue and considerable fluxing of the final product would be necessary to remove it.

High-gold alloys

As indicated earlier, aqua regia is used to attack high-gold alloys since both nitric and sulfuric acids are not effective. In this method, gold, copper, and other impurities go into solution while silver remains behind as silver chloride. The leaching equations are:

$$2Au + 3Cl_2 \rightarrow 2AuCl_3 \text{ (soluble)}$$

$$2Ag + Cl_2 \rightarrow 2AgCl \text{ (insoluble)}$$

$$Cu + Cl_2 \rightarrow CuCl_2 \text{ (soluble)}$$

The dissolving pans are made of stoneware, glass, or fused silica and have a capacity of about 250 liters. Each pan is filled two-thirds with HCl and heated by steam injection. The nitric acid is added at intervals to maintain a vigorous reaction. The dissolution of gold follows the equation:

$$4HCl + HNO_3 + Au \rightarrow HAuCl_4 + NO + 2H_2O$$

When the process is complete, the excess acid is boiled off:

$$HNO_3 + 3HCl \rightarrow NOCl + 2H_2O + Cl_2$$

The liquor is allowed to settle, and the supernatant solution is siphoned and treated with a reducing agent (e.g., $FeCl_2$, oxalic acid, SO_2) **to** precipitate gold, which is filtered off, washed, and melted (Figure 9.13). Silver chloride residues are washed with water, and the first washings (containing gold) are returned to the dissolving pan. The material is then reduced with scrap iron to metallic silver.

This process is of special value when refining platiniferous gold. Platinum and palladium are dissolved together with gold, while Rh, Ru, and Ir remain with the silver chloride. Gold is precipitated by $FeCl_2$, and then filtered, and Pt and Pd are recovered from the solution by the usual methods.

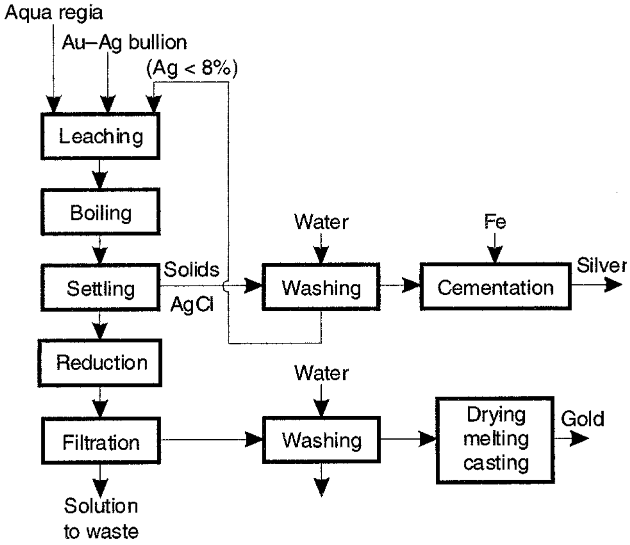


Figure 9.13: Aqua regia process for refining high-gold bullions.

PLATINUM METALS

Sources

There are three main sources for obtaining platinum metal concentrates:

Native platinum ores. Some concentrates are rich in platinum, others are rich in palladium, and a third type contains a high proportion of rhodium, ruthenium, and iridium. Gold and silver are present in most types of concentrates, together with nonferrous metals such as copper, nickel, lead, bismuth, and tellurium. For example, a concentrate containing 90% Pt metals is obtained from the placer deposits in Alaska by applying gravity and magnetic separation techniques to the ore. Large deposits of platinum-bearing ore are also exploited in Transvaal, South Africa, and the Urals in Russia.

Gold ores. During the electrolytic refining of gold, platinum metals are concentrated either in the electrolyte (Pt and Pd) or in slimes (Rh, Ir, and Ru). The Witwatersrand gold ores in South Africa are an important source of osmium.

Nonferrous metals sulfide ores. During the processing of copper or nickel sulfide ores, the platinum metals may be concentrated in any of the following fractions:

- In the magnetic fraction separated from the sulfide matte.
- In anodic slimes of copper or nickel electrolytic refining. Examples: Sudbury ore in Canada and the nickel–copper sulfide flotation concentrate obtained from the Rustenburg Platinum Mines in Transvaal.

Leaching and recovery

Due to the fact that only small amounts of platinum metals are processed, together with complex and costly separation methods, only a few places in the world are concerned with these operations. The solutions handled are usually highly concentrated, extremely valuable, and very corrosive. Handling is therefore carried out by employing the simplest possible methods, including siphoning and gravity draining. Use is made of glass-lined vessels, glass pipelines, and glandless pumps of chemically resistant materials (Figures 9.14–9.15).

The platinum metals concentrate or the gold sand from anodic slimes is dissolved in dilute aqua regia at 90 °C. Platinum, palladium, and gold go into solution, while Ru, Rh, Os, and Ir as well as Ag do not. A solution of ferrous sulfate is added to precipitate gold. The gold so obtained is filtered, washed free from acid, melted, and cast into anodes for electrolytic refining. The residue from the aqua regia treatment contains ruthenium, rhodium, osmium, and iridium: it is dried, ground, and screened.

Platinum and palladium remain in solution after gold reduction as Pt(IV) and Pd(II) respectively; Pd(IV) is already reduced to Pd(II) by ferrous sulfate. At first platinum is precipitated by NH_4Cl as ammonium chloroplatinate:

$$PtCl_4 + 2NH_4Cl \rightarrow (NH_4)_2[PtCl_6]$$

This is decomposed by heating to crude platinum sponge, which is further purified by aqua regia dissolution and NH_4Cl precipitation. The product of calcination is then a pure platinum sponge.

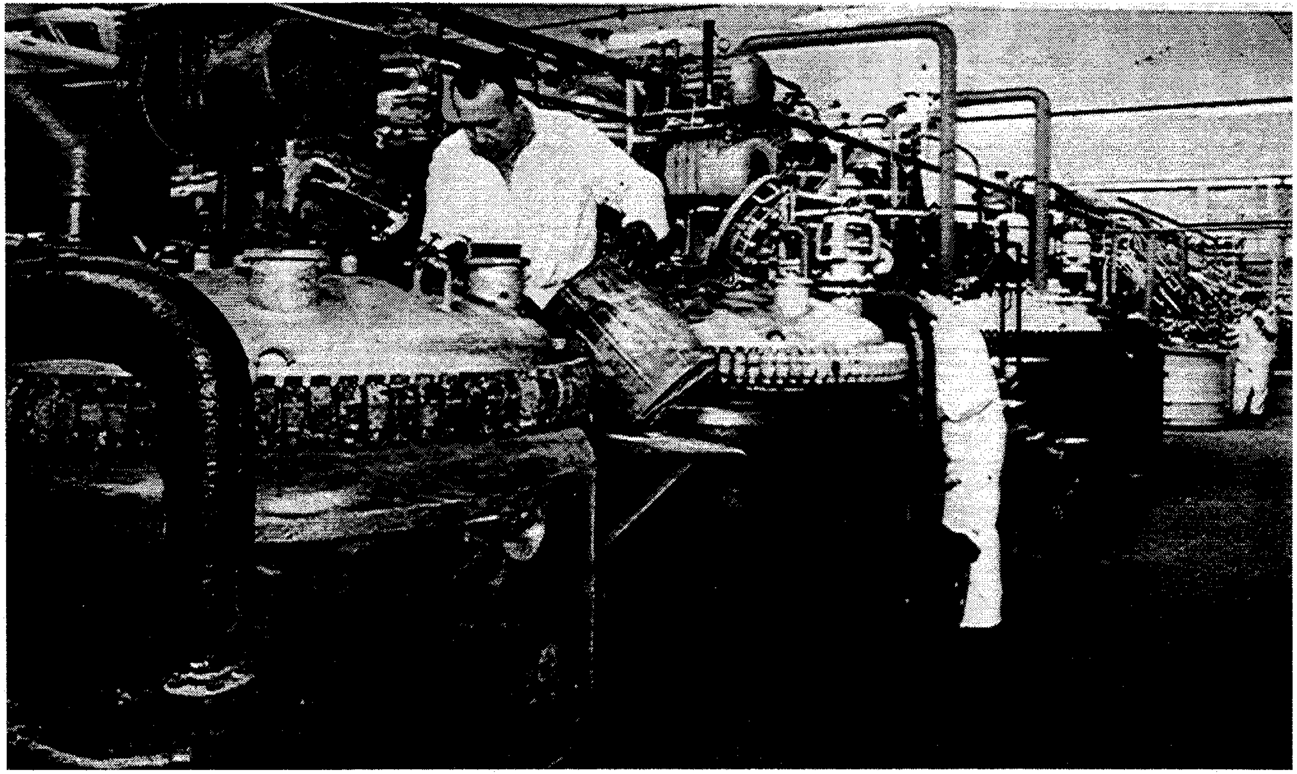


Figure 9.14: Digestion with aqua regia to dissolve platinum and palladium (Johnson Matthey Refinery).

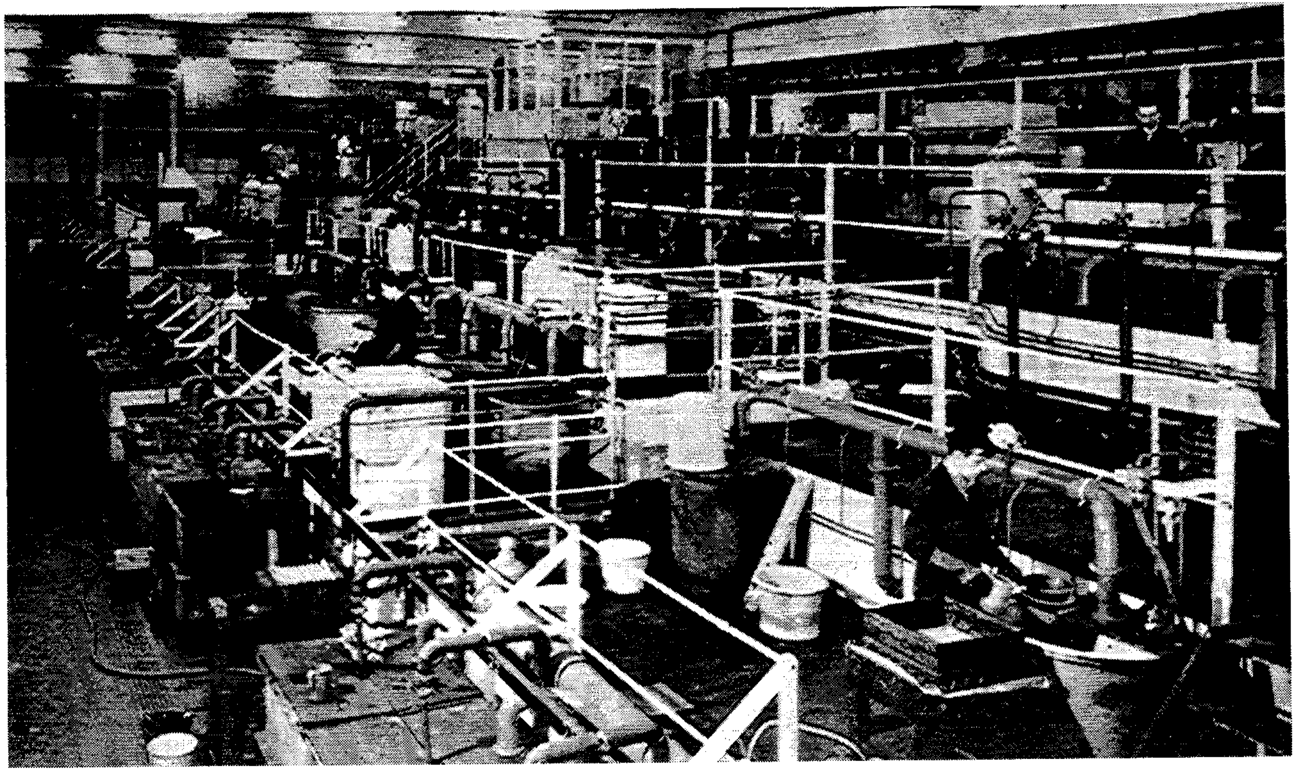


Figure 9.15: Cascade system to facilitate the movement of solutions (Johnson Matthey Refinery).

The filtrate from platinum salt precipitation is treated further with NH_4OH to convert Pd(II) into the tetraammine complex:

$$PdCl_2 + 4NH_3 \rightarrow [Pd(NH_3)_4]Cl_2$$

The tetrammine complex is converted to the insoluble diammine complex by adding HCl:

$$[Pd(NH_3)_4]Cl_2 + 2HCl \rightarrow [Pd(NH_3)_2]Cl_2 + 2NH_4Cl$$

The precipitate is filtered and treated similarly to recover pure palladium. Before discarding the filtrate, traces of residual palladium and platinum in solution are recovered by cementation with zinc. Ruthenium, rhodium, osmium, and iridium concentrate are then fused with a mixture of KOH and KNO_3, followed by dissolution in water and then distillation of ruthenium and osmium as volatile oxides. The solution remaining after distillation contains iridium and rhodium, which are recovered as sodium salts, followed again by precipitation of their complex ammonium compounds and calcination. **A** flowsheet is shown in Figure 9.16.

Recovery from automobile catalysts

A large amount of platinum, palladium, and rhodium are now used in the production of anti-pollution automobile catalysts (reduction of NO, to nitrogen). The catalyst is composed of a porous ceramic material impregnated with about 0.2% platinum metals. Leaching the ground material with a 5% NaCN solution from 1 hour at 160 °C dissolves about 90% of the precious metals. The platinum metals are recovered from solution by decomposing the cyanide complexes in an autoclave at 250 •C for 1 hour (US Bureau of Mines, Report 9384, 1991).

COPPER, NICKEL, AND COBALT

Leaching of copper, nickel, and cobalt is similar in many respects; it is based on their selective dissolution from low-grade ores by aqueous ammonia in presence of air (or oxygen) to form the ammine complexes $[M(NH_3)_n]^{2+}$, where M is copper, nickel, or cobalt and n is a variable number that depends mainly on the free ammonia concentration in the solution. Ammonium hydroxide is selected in preference to acids, e.g., H_2SO_4, which is less expensive for two reasons:

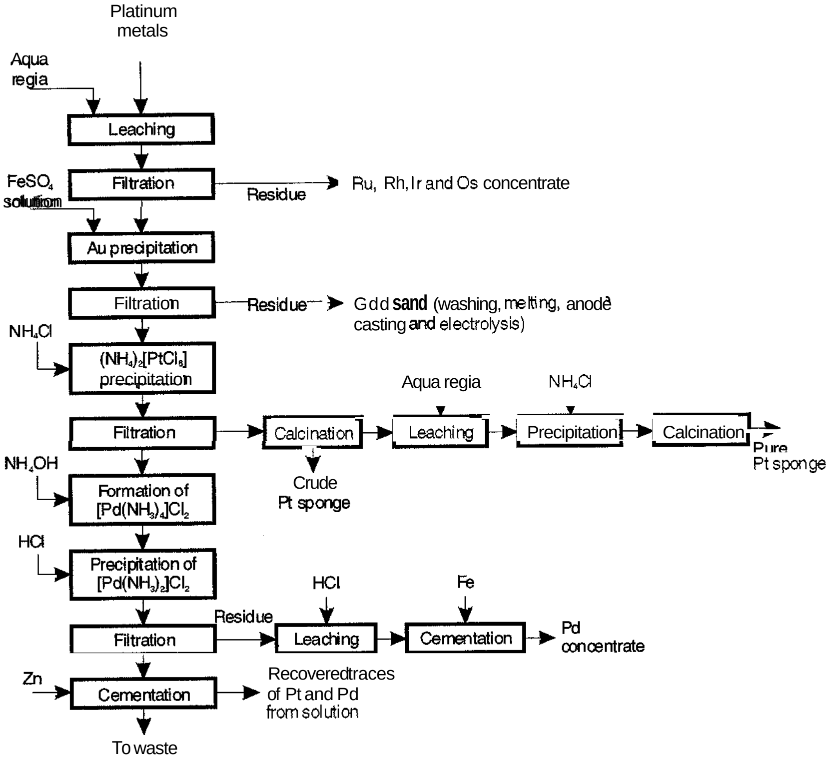


Figure 9.16: Processing platinum metals concentrate.

- Presence of excessive acid-consuming gangue such as limestone or dolomite in the ore.
- Presence of an iron oxide matrix which partially dissolves in acid and makes the separation of the metal values difficult.

The dissociation of ammonium hydroxide is small:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

and NH_3 can be considered as the active complexing agent. Like cyanidation process, the dissolution reaction can be represented by the equations:

$$\text{Oxidation: } M \rightarrow M^{2+} + 2e^-$$

$$\text{Complex formation: } M^{2+} + nNH_3 \rightarrow [M(NH_3)_n]^{2+}$$

Reduction: $^1/_2O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

and the overall reaction is:

$$M + nNH_3 + {}^1/_2O_2 + H_2O \rightarrow [M(NH_3)_n]^{2+} + 2OH^-$$

The rate of dissolution of the metal depends on the oxygen partial pressure when the ammonia concentration is low, and is a function of the ammonia concentration when the oxygen partial pressure is high (Figure 9.17). Ammonium ion alone does not dissolve these metals, but when added to ammonium hydroxide solution, it increases the rate of dissolution as a result of inhibiting the ionization of ammonia (Figure 9.18). For this reason a mixture of ammonium hydroxide and ammonium carbonate is usually used. Ammonium carbonate is selected because it decomposes readily when the solution is boiled to recover the ammonia, and also because the carbonate ion is present any way in the solution as a result of contact with air. The process is also known as the *Caron Process* after its inventor.

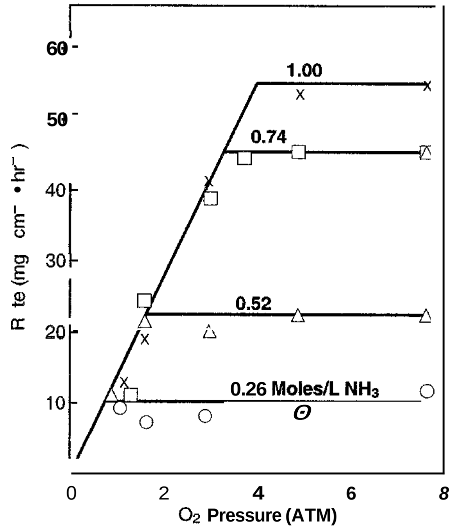


Figure 9.17: Effect of NH_3 and oxygen pressure on the rate of dissolution of copper (Halpern, 1953).

Leaching is carried out under atmospheric pressure, but the tanks are closed to prevent the loss of ammonia. After filtering the gangue minerals, the solution is boiled to distill off excess ammonia and to decompose the ammine complex to precipitate a hydroxide or a basic carbonate:

$$[M(NH_3)_n]^{2+} + 2OH^- \rightarrow M(OH)_2 + nNH_3$$

$$2[M(NH_3)_n]^{2+} + 2OH^- + CO_3^{2-} \rightarrow M(OH)_2 \cdot MCO_3 + 2nNH_3$$

The precipitate is filtered, washed, and calcined to yield a high-grade oxide containing 75–78% metal. The gases evolved are absorbed in water and recycled. Also, ammonia retained in the gangue residue is recovered by steam stripping. Instead of calcination, the precipitated basic carbonate is sometimes dissolved in ammonium sulfate solution and the pure metal is precipitated by hydrogen under pressure.

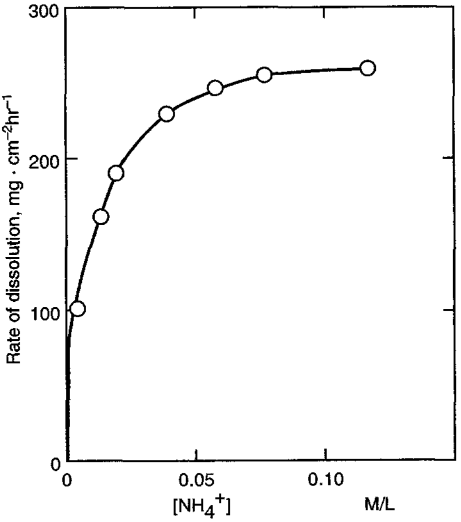


Figure 9.18: Effect of ammonium ion on the rate of dissolution of copper (Fisher and Halpern, 1956).

Applications

Metallic copper, nickel, and cobalt suitable for leaching by ammonia are obtained from the following sources:

- *Native copper.* In Lake Superior district, native copper was found in abundance. At one time, the ore was smelted and the tailings from this process were treated by ammonia leaching (Figure 9.19). The tailings contained 0.4% metallic copper.

- *Reduction of oxide or silicate ores:*
  - Low-grade copper oxide ores that are not economically amenable to acid leaching are first reduced to metallic copper then leached with ammonia. This was the case in South Africa where the Bwana M'Kubwa Company reduced the oxide ore with CO and leached the resultant metallic copper with ammonia. An oxide ore deposit in Australia is treated in a similar way.
  - Laterite nickel ores at Nicaro in Cuba, at Marinduque in the Philippines, and at Greenvale in Australia containing much acid-soluble gangue (Table 9.4) are first reduced then leached with ammonia. Leach solution analyses 12 g/L Ni, 0.17 Co, 65 NH_3, 35 CO_2, and trace amounts of iron.
  - Manganese nodules (see p. 259) found on ocean floor containing about 1% Cu and 1% Ni. It was suggested to recover copper and nickel from this source by reducing the nodules then leaching selectively by ammonia.

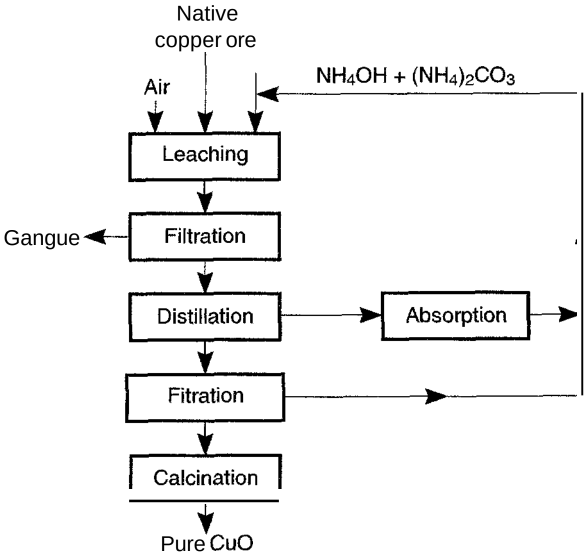


Figure 9.19: Ammonia leaching of native copper ore.

Table *9.4:* Typical analysis of laterites containing serpentine (dry basis).

	%
Ni	1.4
Co	0.1
Fe	38
MgO	8
SiO_2	14

Table 9.5: INCO pyrrhotite concentrate containing nickel and treated by the ammonia leaching process.

	%
Fe	57
S	37
Ni	0.7–0.9
Cu	0.04–0.07
SiO_2	1–3

- *Oxidation of iron sulfides followed by selective reduction.* For example, at the International Nickel Company in Sudbury, pyrrhotite concentrate having the analysis given in Table 9.5 is oxidized in a fluidized bed reactor at 800–900 °C. The hot calcine is then introduced into a rotary kiln in which a reducing atmosphere is maintained. Nickel, cobalt, and copper oxides are reduced to metals while iron oxide is reduced to Fe_3O_4; the product is leached with ammonia solution. Copper in solution is removed by precipitation with sodium sulfide and nickel is then recovered from the solution as basic nickel carbonate by boiling. The residue containing mainly Fe_3O_4 is dried and sintered whereby it is transformed into Fe_2O_3, and is shipped as high-grade iron ore (Figure 9.20). The process was shut down for economic reasons.

SELENIUM

Selenium is a by-product of electrolytic copper refining. During the oxidation of the copper anodic slimes with concentrated H_2SO_4, some of the selenium is volatilized and is collected in dust precipitators as crude selenium, analyzing 92–99% Se and 0.1–8% Te. Selenium is purified by leaching with sodium sulfite; it is dissolved as sodium selenosulfate, while tellurium is left behind:

$$\mathrm{Se} + \mathrm{SO}_3^{2-} \rightarrow \mathrm{SeSO}_3^{2-}$$

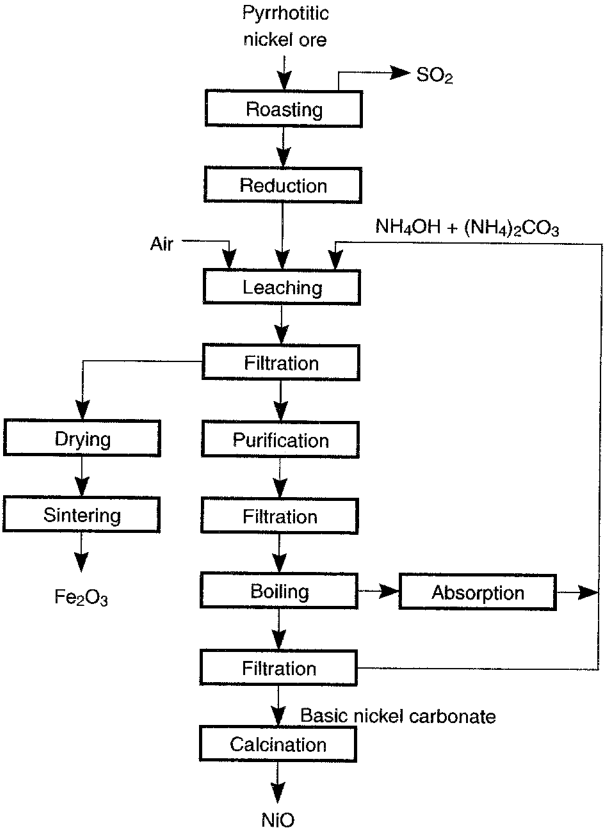
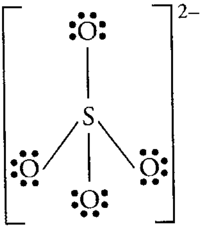
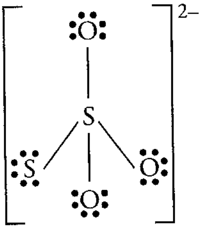


Figure 9.20: Recovery of nickel from pyrrhotitic ore by roasting, reduction, and ammonia leaching.

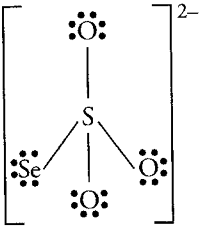
This reaction is similar to the dissolution of elemental sulfur in sodium sulfite to form sodium thiosulfate. The electronic configuration of selenosulfate ion is compared below with thiosulfate and sulfate ions:



Sulfate



Thiosulfate



Selenosulfate

Pure selenium is precipitated from the solution by acidification with sulfuric acid (see p. 628).

SUMMARY

Table 9.6 gives a summary of processes for leaching of metals.

Table **9.6:** Leaching of metals.

Metal	Origin	Leaching agents	Remarks
Gold and silver	Native	Cyanide ($NaCN + O_2$)	pH 10.5
		Thiourea ($(NH_2)_2CS + Fe^{3+}$)	Acid medium
		Aqueous Cl_2	Acid medium
	Bullion (refining)	HNO_3 or H_2SO_4	Suitable for low-gold bullion (25% Au); alloys containing between 25 and 92% Au must be melted and alloyed with Ag to decrease Au content to below 25% Au.
		$HNO_3 + 3HCl$ (aqua regia)	High-gold bullion (> 92% Au). Gold is solubilized, silver transformed to AgCl.
Platinum metals	Native	$HNO_3 + 3HCl$ (aqua regia)	Only Pr and Pd are solubilized as chlorides.
Copper	Native	$NH_3 + O_2$	Low-grade ore containing acid-consuming gangue.
	From oxides by reduction	$NH_3 + O_2$	Low-grade ore not amenable to acid leaching.
Nickel and cobalt	From oxides by reduction	$NH_3 + O_2$	Laterites (1.3% Ni) containing acid-consuming gangue (Nicaro, Cuba).
	From sulfides by oxidation then reduction	$NH_3 + O_2$	Massive pyrrhotite (0.8% Ni).
Copper, nickel, and cobalt	From MnO_2 nodules by reduction	$NH_3 + O_2$	Manganese nodules (1% Cu, 1% Ni, 0.2% Co).
Selenium	Dust from anodic slimes of copper refining	Na_2SO_3	Sodium selenosulfate similar to the dissolution of sulfur in Na_2SO_3 to form thiosulfate.

Chapter Ten

Oxides and Hydroxides

Bauxite 241
  The Bayer Process 243
Copper Oxide Ores 248
  Sulfuric acid process 253
  Ammonium hydroxide process 253
Laterites 254
Manganese Ores 257
  Sulfuric acid process 258
  Hydrochloric acid process 259
  Ammonium hydroxide process 260
Uranium ores 260
  Acid leaching 263
  Alkali carbonate process 265
  Leach residues.. 266
Zinc Oxide Ores and Calcines 268
  The ferrite problem and its solution 269
  Purification of solution 272
  Sodium hydroxide process 272
Summary 272

Major oxide and hydroxide ores are bauxite (aluminum ore). laterites (nickel–cobalt ores). copper. manganese. and uranium ores. A minor amount of zinc occurs as oxide. carbonate. and basic carbonate. but the bulk occurs as sulfide. However. a great part of zinc sulfide is first oxidized to oxide which is then treated by wet methods.

BAUXITE

Bauxite'. named after the village *Les Beaux* near Marseille in southern France where it was first discovered. is not a mineral. but

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1. Bauxite was originally spelled *beauxite*. For the production of alumina from sources other than bauxite. see Chapter 16.

designates various kinds of aluminum ores consisting mainly of aluminum hydroxide. Three aluminum hydroxide minerals occur in bauxite: gibbsite, bohmite, and diaspore. They differ considerably in their physical properties, as shown in Table 10.1. A bauxite deposit consists mainly of either one of these types, although cases are known when mixed hydroxides are present in one ore. Bauxites vary in color from cream to dark brown when the iron content is high. Table 10.2 shows the composition of a typical bauxite. The main occurrences of bauxites are in Jamaica, Suriname, Ghana, Sierra Leone, Australia, Russia, and Hungary.

Table 10.1: Aluminum minerals in bauxite.

	Gibbsite (Hydrargillite)	Bohmite	Diaspore
Formula	γ-$Al(OH)_3$	γ-$AlOOH$	α-$AlOOH$
$Al_2O_3:H_2O$	1:3	1:1	1:1
Crystal system	monoclinic	orthorhombic	orthorhombic
Hardness (Moh)	2.5–3.5	3.5–4	6.5–7
Specific gravity	2.42	3.01	3.44
Refractive index	1.568	1.649	1.702
Temperature of rapid dehydration	150 °C	350 °C	450 °C
Product of dehydration	χ-Al_2O_3	γ-Al_2O_3	α-Al_2O_3
Solubility in 100 g/L Na_2O solution at 125°C; g/L Al_2O_3	128	54	insoluble

Table 10.2: Composition of typical bauxites.

	%		%
Al_2O_3	40–60	Ga_2O_3	0.01
SiO_2	1–6	K_2O	0.01
Fe_2O_3	2–25	P_2O_5	0.02–0.4
TiO_2	1–5	V_2O_5	0.01–0.1
CaO + MgO	0.2–0.6	Ln_2O_3[a]	0.01
Loss on ignition	10–30	F	0.01–0.05

a. Ln = Lanthanide.

The treatment of bauxite to produce pure $Al(OH)_3$ from which pure alumina is obtained by the Bayer Process using sodium hydroxide solution is the oldest and the largest pressure leaching operation in terms of the tonnage of raw material treated (Figure 10.1). Aluminum minerals in bauxite are soluble in dilute H_2SO_4 but this acid is not used on large scale for the following reasons:

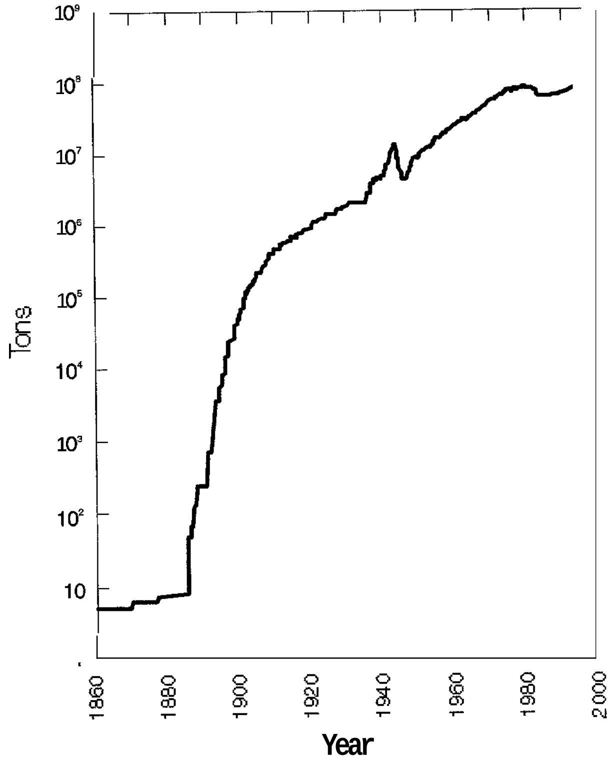

Figure 10.1: Tonnage of bauxite treated annually.

- Iron minerals and to some extent titanium minerals are also soluble; this will lead to an excessive reagent consumption and solution purification problem later.
- $Al(OH)_3$ precipitated from acid solutions is gelatinous and difficult to filter and wash.

Acid leaching is used only on a small scale to produce aluminum sulfate needed for water treatment.

The Bayer Process

The **use** of sodium hydroxide to leach bauxite was invented in 1892 by Karl Josef Bayer as a process for obtaining pure aluminum hydroxide which can be calcined to pure Al_2O_3 suitable for processing to metal. About 90 million tons of bauxite are treated annually by this process. About 2 tons bauxite yield 1 ton Al_2O_3 from which 0.5 ton aluminum is produced. Also 2 tons bauxite produce I ton waste minerals called *red mud*. Crushed bauxite is usually washed to remove fine particles of clay, dried in a rotary kiln then ground to 60–100 mesh; the drying process is essential to facilitate grinding. Drying temperature should be less than the temperature of dehydratation of aluminum hydroxides otherwise the solubility will be impaired. Figure 10.2 shows a flowsheet of the process and Figure 10.3 shows an operating plant. The reactions in leaching are the following:

$$Al(OH)_3 + OH- \rightarrow [AlO(OH)_2]^- + H_2O$$

$$AlOOH + OH- \rightarrow [AlO(OH)_2]^-$$

Leaching is usually carried out in mild steel autoclaves, with direct steam injection for heating and agitation. Operating conditions depend on the type of minerals in the bauxite. Bauxites containing gibbsite are leached at a lower temperature, with lower NaOH concentration, and for a shorter time than those containing bohmite and diaspore as shown in Table 10.3. The more concentrated the NaOH, the faster the rate; however, highly concentrated solutions will require excessive dilution in the later stage of precipitation, which presents difficulties in handling and filtration. Therefore, there must be an optimum concentration which compromises between digestion time and subsequent operations. Leaching time could be shortened to 3–4 minutes if the process is conducted in tube autoclaves at 330 "C and 25 000 kPa; also, the settling properties of the mud are improved.

Table 10.3: Typical leaching conditions of bauxite with NaOH.

Ore	Temp., °C	Pressure, kPa	NaOH, g/L	Time, h
Gibbsite	140	400	140	1
Bohmite	180	800	350–600	2-4
Diaspore	180	800	350–600	2–4

Sometimes NaOH is formed in situ in the autoclaves by adding sodium carbonate and calcium hdyroxide:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

To a leach solution containing 200–250 g/L Na_2CO_3, enough lime is added such that the solution contains about 140 g/L NaOH. Leaching is carried out at 140 "C for about one hour. This method applies only to gibbsite, because in the case of bohmite or diaspore a sodium hydroxide concentration above that which can be obtained directly from Na_2CO_3 and lime is required. So it is necessary to prepare NaOH separately and concentrate it by evaporation for use in leaching.

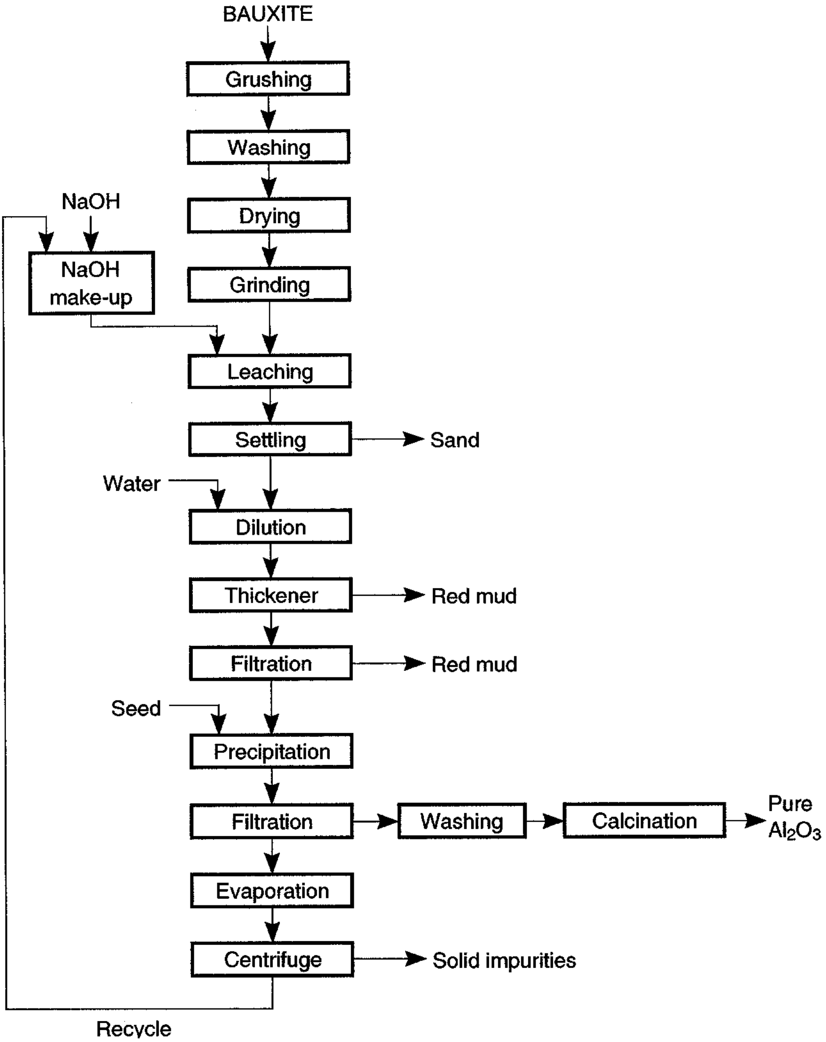

Figure 10.2: Flowsheet of the Bayer Process for the production of Al_2O_3 from bauxite.

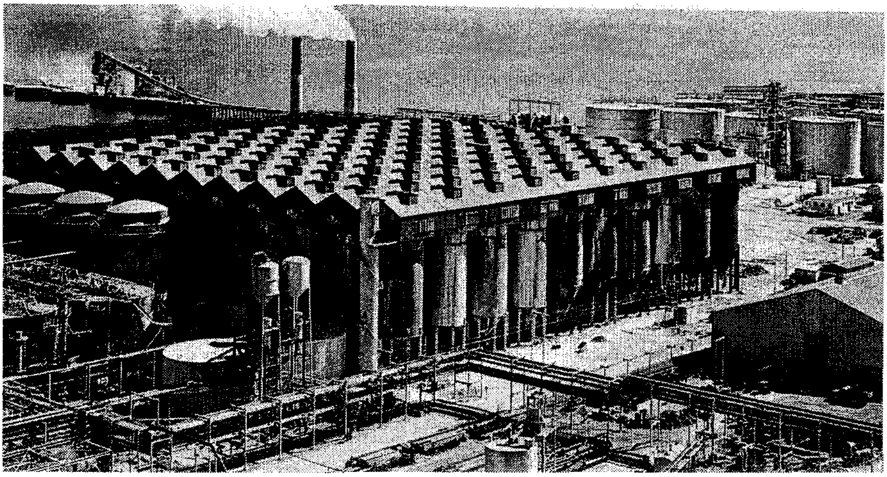

Figure 10.3: Bauxite treatment plant by the Bayer Process in Kwinana near Perth in Australia produces 1 250 000 tons/year alumina (ALCOA).

Table 10.4: Distribution of impurities during the processing of bauxite.

	Bauxite %	Red mud (dried at 105°C) %	Calcined Al_2O_3 %
Al_2O_3	57.8	14.0	99.55
SiO_2	3.5	7.6	0.05
Fe_2O_3	24.3	57.6	0.04
TiO_2	2.5	5.7	—
Na_2O		7.4	0.18
Loss on ignition	12.5	7.7	0.18

The behavior of impurities

Depending on their chemical properties, impurities in the ore may be found either in solution, or in the insoluble residue. Impurities that go into solution are either redeposited during a later operation, or remain in the mother liquor during crystallization of aluminum hydroxide. However, due to recycling, they will accumulate in solution and would contaminate the product. Certain tolerable levels are therefore maintained by bleeding the solution at regular intervals. Table 10.4 shows the distribution of impurities during the processing of bauxite, and Table 10.5 shows the composition of the leach solution. Essentially, the Bayer Process eliminates the three major impurities in bauxite Fe_2O_3, SiO_2, and TiO_2. Calcium and magnesium are mainly present as dolomite and are not dissolved. Apatite is partially soluble and is usually eliminated during leaching by adding $Ca(OH)_2$.

Table 10.5: Composition of typical aluminate solution.

g/100 g free Na_2O			
Al_2O_3	32.80[a]	Cl^-	1.00
CaO	0.12	CO_2	3.74
Fe_2O_3	0.05	F^-	0.03
Ga_2O_3	0.22	MgO	0.17
Na_2O	100.00	P_2O_5	0.90
SiO_2	0.60	SO_3	0.07
TiO_2	Trace	V_2O_5	0.45

a. In the precipitation step, about $^2/_3$ of the aluminum in solution is precipitated.

Organic matter. Most bauxites contain about 0.1% organic matter. During digestion, some of this material is dissolved, causing the liquors to darken, while the remaining part is degraded and oxidized to oxalates. Some of the organic matter is therefore responsible for NaOH losses. Their presence may also cause liquors to froth, or it may interfere with the subsequent process of hydroxide precipitation, or it may color the hydroxide. It may be largely eliminated during digestion by adding an oxidizing agent, e.g., MnO_2. In some cases sodium oxalate is crystallized and removed. It should be noted, however, that the organic matter in the liquor may come from the flocculants added to assist the mud to settle.

Iron. Iron occurs in bauxite mainly as hematite, Fe_2O_3, and is not attacked by the caustic leaching. Thus the residue remaining after leaching has a high percentage of iron oxides, and therefore has a red color. That is why this residue is usually referred to as red mud. However, some ores contain ferrous iron in form of siderite, $FeCO_3$. This is attacked by NaOH, forming colloidal ferrous hydroxide:

$$FeCO_3 + 2OH^- \rightarrow Fe(OH)_2 + CO_3^{2-}$$

which is difficult to settle. It would therefore be advantageous to oxidize ferrous minerals to ferric during leaching.

Silicon. Silicon occurs as quartz, SiO_2, or as clays, e.g., kaolinite, $Al_2(OH)_4(Si_2O_5)$. Quartz is insoluble in NaOH under the conditions of leaching but the silicates are soluble. During digestion, silica that goes into solution combines with alumina and sodium hydroxide forming insoluble hydrated aluminosilicates such as $2Na_2O \cdot 2Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$, which are carried away in the red mud, thus causing losses. About 1 kg of NaOH is lost for each kilogram of soluble silica in bauxite. Although most of the soluble silica in bauxite is precipitated during digestion by forming sodium aluminosilicate, small amounts may still be found in solution, especially when concentrated NaOH solution is used. To precipitate the silica completely, addition of CaO is recommended, since insoluble calcium silicate can be formed. Lime addition during digestion has a further advantage: any Na_2CO_3 present in the solution due to absorption of CO_2 from the atmosphere, and which has no dissolving action on bauxite, will be converted to NaOH.

Gallium. Gallium occurs in most bauxites, and is highest in French bauxites (0.0–0.05% Ga_2O_3). It dissolves completely during extraction. Recycling of NaOH in the process results in gallium enrichment up to 0.5 g/L. Such liquors are therefore an important source of gallium, from which it can be recovered, e.g., by solvent extraction or electrolysis using a mercury cathode. If, however, gallium is not recovered and is left to build up in the leach liquor, it will reach a certain concentration beyond which it will be partially deposited, together with aluminum hydroxide during precipitation, thus causing contamination.

Vanadium. Vanadium in bauxite is partly soluble during digestion. In some ores it is precipitated during evaporating the leach solution as complex salts such as $2Na_3VO_4 \cdot NaF \cdot 19H_2O$. This is especially the case for ores containing fluorine since fluorides are dissolved during leaching. Sometimes these precipitate to form a hard scale in the evaporators which interferes with heat transfer. In other ores vanadium builds up in the recycle NaOH to a concentration of about 0.5 g/L V_2O_5 and is recovered.

COPPER OXIDE ORES

The main copper ores are sulfides, oxides, or a mixture of sulfides and oxides. The last type is the world's most extensive copper ore bodies; they are disseminated, i.e., they are composed of minute grains of copper minerals in large bodies of rock. They contain on the average 2% Cu and are also called *porphyry ores* from the Greek πορφυρος meaning purple; originally the word referred to hard Egyptian rock having red and white felspar crystals embedded in a fine-grained dark red mass. Later it referred to any igneous rock of similar texture (not necessarily red). Porphyry copper ores are usually green. The sulfide–oxide ore is usually separated by flotation into two fractions: a high-grade sulfide concentrate and a low-grade oxide fraction (Figure 10.4). While the sulfide concentrate is usually treated by pyrometallurgical methods, the oxide fraction is usually treated by hydrometallurgical methods; copper sulfides are insoluble in acid. The main copper oxide minerals are given in Table 10.6.

Table **10.6:** Copper oxide minerals.

Cuprite	Cu_2O	Red
Tenorite	CuO	Black
Malachite	$CuCO_3 \cdot Cu(OH)_2$	Green
Azurite	$2CuCO_3 \cdot Cu(OH)_2$	Blue
Chalcanthite	$CuSO_4 \cdot 5H_2O$	Blue
Pisanite	$(Cu, Fe)SO_4 \cdot nH_2O$	Pale blue
Antherite	$CuSO_4 \cdot 2Cu(OH)_2$	Green
Brochantite	$CuSO_4 \cdot 3Cu(OH)_2$	Green
Linarite	$CuSO_4 \cdot Pb(OH)_2$	Green
Atacamite	$CuCl_2 \cdot 3Cu(OH)_2$	Green
Libethenite	$Cu_3(PO_4)_2 \cdot Cu(OH)_2$	Olive green
Olivenite	$Cu_2(AsO_4)(OH)$	Green
Liroconite	$Cu_2Al(AsO_4)(OH)_4 \cdot 4H_2O$	Light blue
Chalcosiderite	$Cu(Fe, Al)_6(PO_4)_4(OH)_8 \cdot 4H_2O$	Green
Turquoise	$CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$	Blue green
Torbenite	$Cu(UO_2)_2(PO_4)_4 \cdot nH_2O$	Green
Caledonite	$Cu_2Pb_5(SO_4)_3(CO_3)(OH)_6$	Light blue
Chrysocolla	$Cu_8(Si_4O_{10})(OH)_{12} \cdot 8H_2O$	Pale blue
Dioptase	$CuSiO_3 \cdot H_2O$	Pale blue

in some special cases particles of copper sulfide minerals are coated with an oxide layer thus preventing their separation by flotation. In these cases, if the ore is sandy, i.e., granular, then it is leached, filtered, and copper is recovered from the solution and the residue is floated to recover the sulfides that have been cleaned by the leaching step (Figure 10.5). if the ore is slimy, i.e., composed of very fine particles that are difficult to settle, then the ore is treated by what is known as *LPF* **Process**, i.e., leaching–precipitation–flotation (Figure 10.6). In one variety of this process, sponge iron is used to precipitate metallic copper, in another variety, H_2S is used to precipitate CuS. Precipitation in this method is directly conducted in the slurry thus avoiding filtration. Metallic copper or CuS formed by either reaction is then floated and recovered.

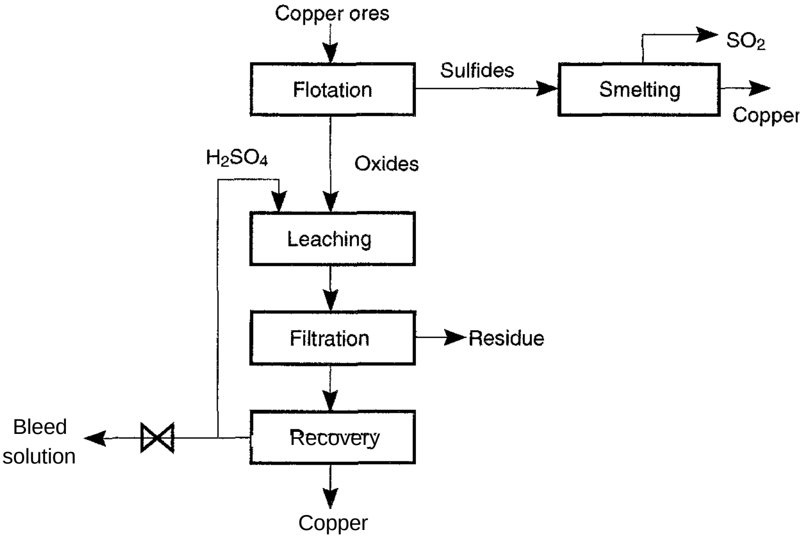

Figure 10.4: Flowsheet for the treatment of porphyry copper ores.

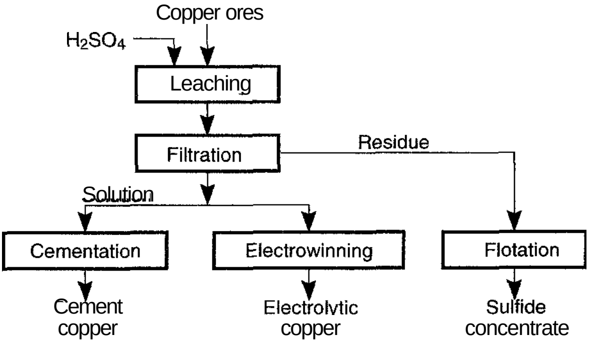

Figure 10.5: Processing of sandy oxidized copper ores.

Porphyry copper ores are characterized by the fact that the sulfide fraction contains traces of molybdenite which is usually separated as a flotation concentrate containing up to 90% MoS_2. This concentrate is also characterized by its high rhenium content (about 700 ppm Re) and is a major source of this metal (Figure 10.7). Further, the oxide fraction may be also a source of uranium. Although the amount of uranium may be negligibly small in the ore, yet because of the large tonnage of ore treated and the continuous recycling of solutions, uranium becomes enriched in solution and can be recovered by ion exchange technology, as for example at Kennecott's operation at the Bingham Canyon in Utah, and in Twin Buttes, Arizona.

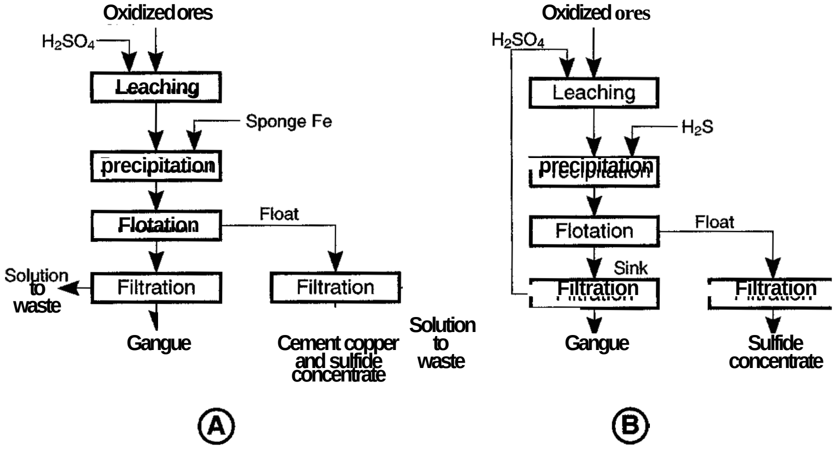

Figure 10.6: Processing slimy oxidized copper ores by L-P-F Process (Leaching — Precipitation — Flotation): **(A)** Using sponge iron. (B) Using hydrogen sulfide.

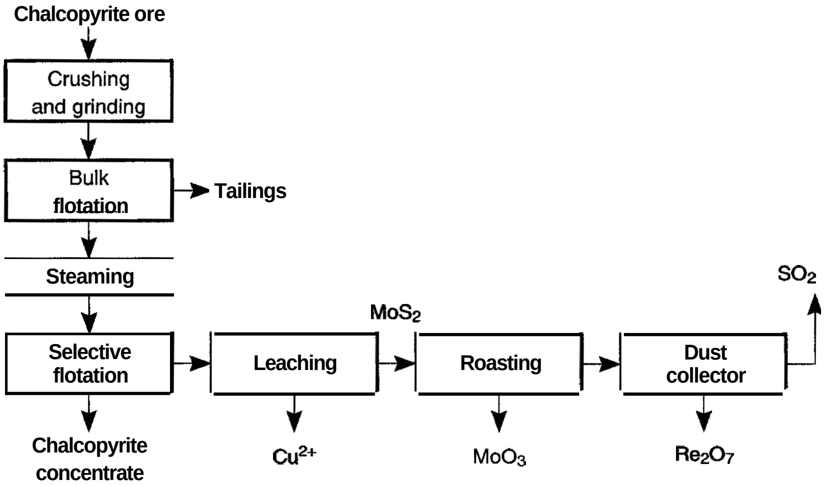

Figure 10.7: Recovery of molybdenum and rhenium from the sulfide fraction of porphyry copper ores.

There are two cobalt-containing minerals; tricuite, $2Co_2O_3 \cdot CuO \cdot 6H_2O$, and mindigite, $2Co_2O_3 \cdot CuO \cdot 3H_2O$, which are characteristic of copper ores in Shaba (Katanga), in Zaire. The ore is an important source of copper as well as cobalt. An analysis of a high-grade Shaba ore is shown in Table 10.7. The ore, which is predominately malachite, is processed by leaching as well as by reduction in a blast furnace. In the leaching process, cobalt is recovered from the spent electrolyte after the electrolytic precipitation of copper (Figure 10.8).

A variety of reagents have been suggested for leaching copper oxide ores, e.g., sulfurous acid, ammonium sulfite, sodium cyanide, and sodium hydroxide; however, the most commonly used reagent is sulfuric acid and to a minor extent ammonium hydroxide.

Table 10.7: High-grade copper–cobalt ores at Shaba, Zaire.

	%
Cu	9.3
Fe	3.2
Co	0.4
CaO	1.3
MgO	5.1
Al_2O_3	7.4
SiO_2	64.2

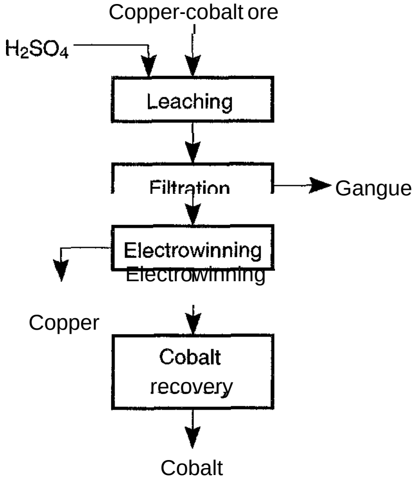

Figure 10.8: Processing of copper–cobalt ore.

Sulfuric acid process

Sulfuric acid is the usual leaching agent for oxidized copper ores; copper is recovered from the leach solution by cementation with iron or by solvent extraction followed by electrolysis, or directly by electrolysis. In the latter case, the spent electrolyte is recycled in the leaching circuit. With the exception of cuprite, all copper oxide minerals dissolve to give $CuSO_4$. Copper in cuprite is in the cuprous state; it dissolves according to:

$$Cu_2O + 2H^+ \rightarrow Cu^{2+} + Cu + H_2O$$

i.e., half the copper in the mineral dissolves and the other half precipitates as metallic copper, a typical disproportionation reaction of Cu^+ ion (see page 539). In presence of oxidizing agents (air or ferric ion), cuprite dissolves completely:

$$Cu_2O + 4H^+ + {}^1/_2O_2 \rightarrow 2Cu^{2+} + 2H_2O$$

Leaching equipment for copper oxide ores depends on the grade and physical nature of the ores as well as on economic factors (Table 10.8).

Table 10.8: Typical copper oxide leaching operations.

Method	Examples
Leaching in place	Arizona
Dump leaching	Utah, Montana
Percolation tanks	Chuquicamata, Chile
Pachuca tanks	Shaba, Zaire
Agitated tanks	Twin Buttes (Arizona)

Ammonium hydroxide process

Ammonia is used when the gangue is acid-consuming. Dissolution takes place according to:

$$CuO + 2NH_4^+ + 3NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + H_2O$$

$$2CuCO_3 \cdot Cu(OH)_2 + 12NH_3 \rightarrow 3[Cu(NH_3)_4]^{2+} + 2CO_3^{2-} + 2OH^-$$

After filtering off the gangue, the solution is boiled so that the above reactions are reversed. Ammonia is then absorbed from the gas phase and the basic carbonate recovered by filtration, which is then calcined to CuO (Figure 10.9). The process was in operation at Kennecott, Alaska, in the period 1916 to 1931; operation discontinued because the mine exhausted. Similar operation is presently in Australia.

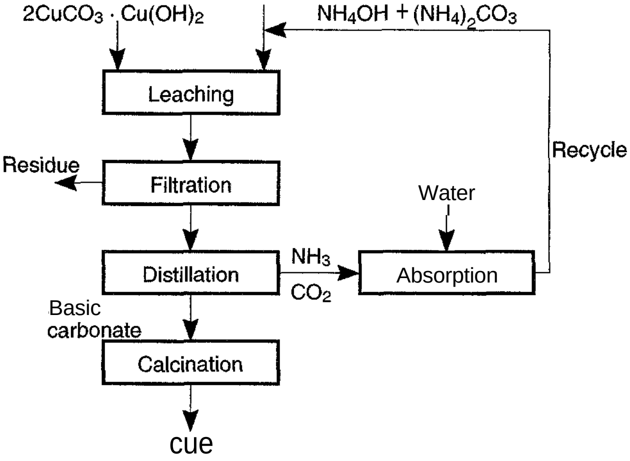

Figure 10.9: Ammonia leaching of copper oxide ores.

LATERITES

While the laterites containing serpentine are reduced then leached with ammonium hydroxide to selectively solubilize metallic nickel (p. 236), those containing limonite are leached directly with sulfuric acid at high temperature and pressure. The reason is that the first deposits contain appreciable amounts of acid-consuming gangue while the second do not. Although ferric oxide which composes the bulk of laterite is soluble in sulfuric acid, yet at high temperature ferric ions hydrolyze precipitating iron oxide and generating the acid:

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$$

Table 10.9 shows analysis of Moa laterite. The ore is leached with H_2SO_4 at 250 °C and *4000* kPa in vertical autoclaves with acid-resisting bricks (p. 148). Figure 10.10 shows a view of the Moa leaching plant, while Figure 10.11 shows a similar operation in Australia but using horizontal titanium-lined autoclaves 5 m diameter and 35 m long.

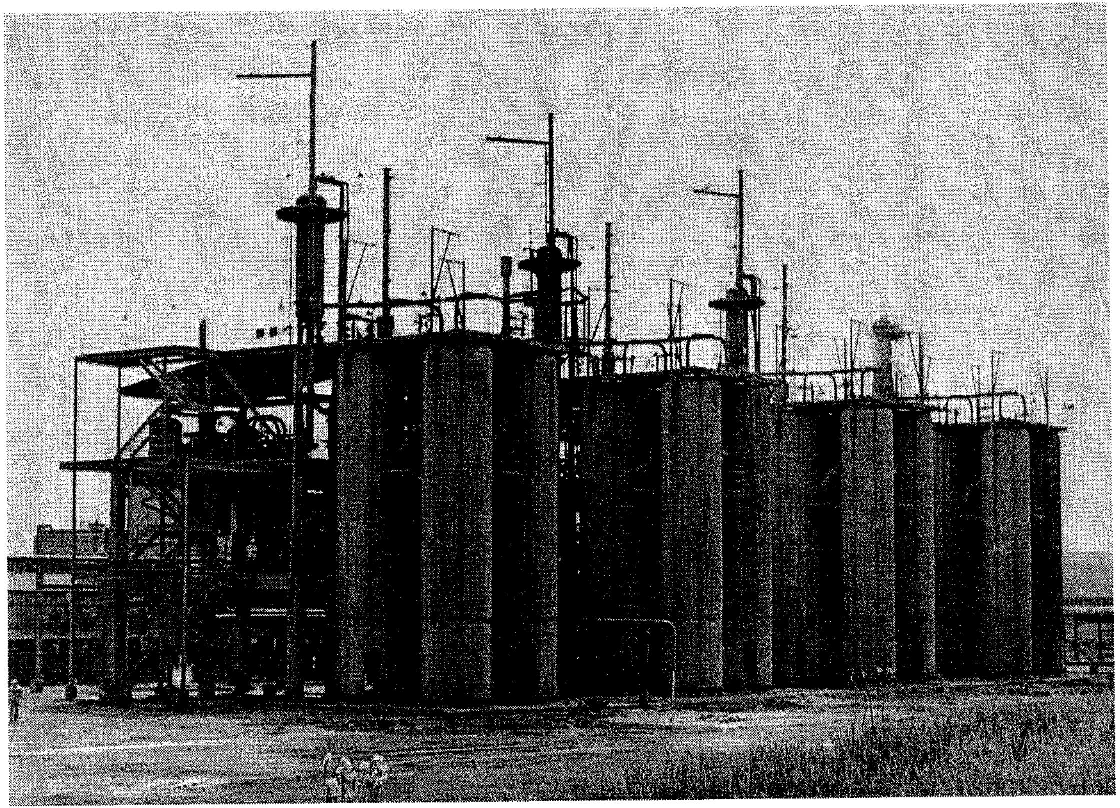

Figure 10.10: View of the acid leaching plant Pedro Sotto Alba at Moa, Cuba (Unión de Empresas del Niquel, Havana). Four units in parallel, each unit has four vertical autoclaves. A fifth unit was added in 1998.

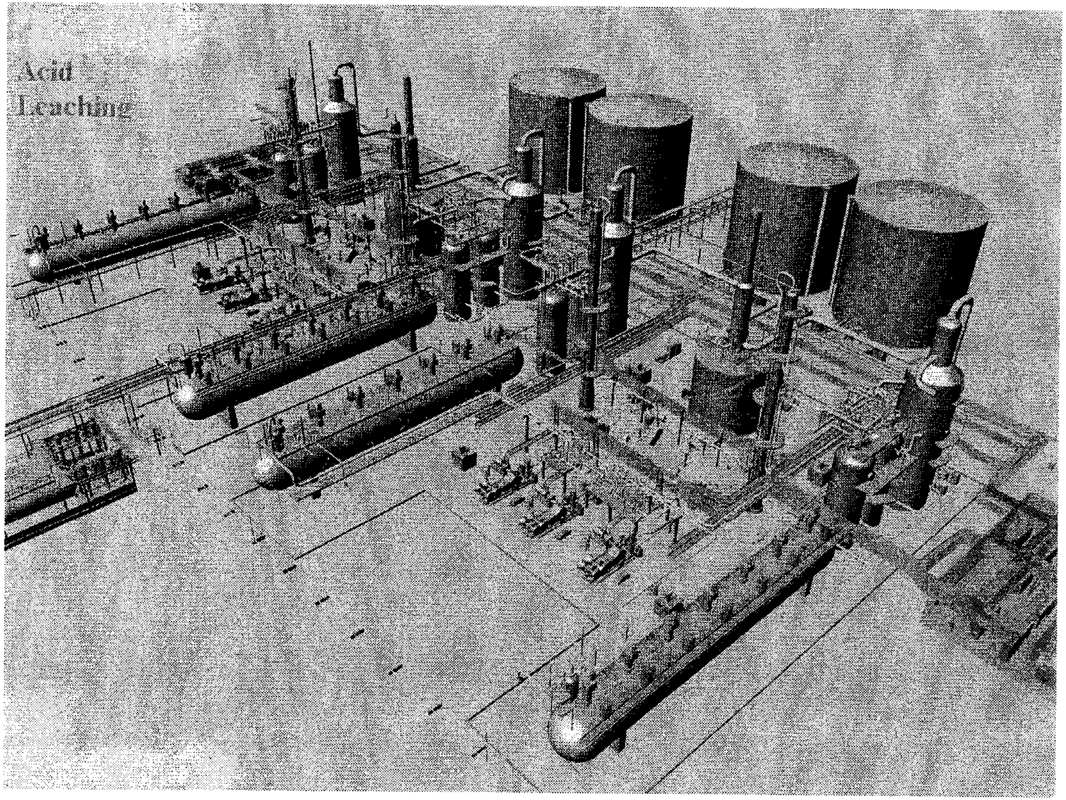

Figure 10.11: Acid leaching of laterites in four horizontal titanium-lined autoclaves (courtesy Anaconda Ni Murrin Murrin, Western Australia).

Table 10.9: Typical analysis of laterite at Moa, Cuba (dry basis).

	%		%
Fe	47.5	CrO_3	2.9
Ni	1.35	SiO_2	3.7
Co	0.15	MgO	1.7
Cu	0.02	Al_2O_3	8.5
Zn	0.04	H_2O (combined)	12.5
Mn	0.8		

Table 10.10: Typical analysis of manganese raw materials.

	High-grade ore	Low-grade ore	Nodules
Mn	48–52	10–40	30
Fe	3–12	35–45	15
SiO_2	3–9	9–20	30
Al_2O_3	0.5–5	1–4	30
Cu	0	0	1
Ni	0	0	I
Co	0	0	0.2
H_2O	1–6	2–10	10

MANGANESE ORES

Pyrolusite, MnO_2, is the most important manganese mineral. Manganese ores are used for making ferromanganese, pure MnO_2 for batteries, or to a minor extent metallic manganese. In the production of the last two materials, hydrometallurgical methods are used. Manganese nodules found at the bottom of the ocean are not only an important source of manganese but also of copper, nickel, and cobalt (Table 10.10). They are composed mainly of MnO_2 and iron hydroxide; nickel, cobalt, and copper do not form minerals.

The fact that the nodules when collected contain appreciable amounts of water suggests that their treatment by pyrometallurgical methods would not be practical because of the cost of drying. The high porosity ($\approx$ 200 m^2/g) suggests that that hydrometallurgical methods could be more suitable. While the processing of manganese ores is always for the recovery of its manganese values, that for nodules may be carried out only for the recovery of copper, nickel, and cobalt, i.e., by selective leaching. The nodules may, therefore, be treated in practically the same way as copper oxide ores or nickel laterites, i.e., leaching agents are selected to dissolve copper, nickel, and cobalt but not MnO_2 and Fe_2O_3. Any leaching agent that solubilizes MnO_2 will also solubilize copper, nickel, and cobalt. Figures 10.12 and 10.13 give a summary of leaching processes for manganese ores and nodules.

Sulfuric acid process

Manganese dioxide is insoluble in dilute H_2SO_4, but when reduced to MnO, it readily dissolves to give a solution of $MnSO_4$:

$$MnO + 2H^+ \rightarrow Mn^{2+} + H_2O$$

Since manganese is recovered from this solution by electrolysis, the spent electrolyte can be used for leaching. Manganese dioxide can be solubilized, however, in dilute H_2SO_4 in presence of a reducing agent (see page 539) such as ferrous sulfate, sulfur dioxide, coal, or oxalic acid which react by oxidation–reduction steps as follows:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$SO_2 + 2H_2O \rightarrow H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

$$(COO)_2^{2-} \rightarrow 2CO_2 + 2e^-$$

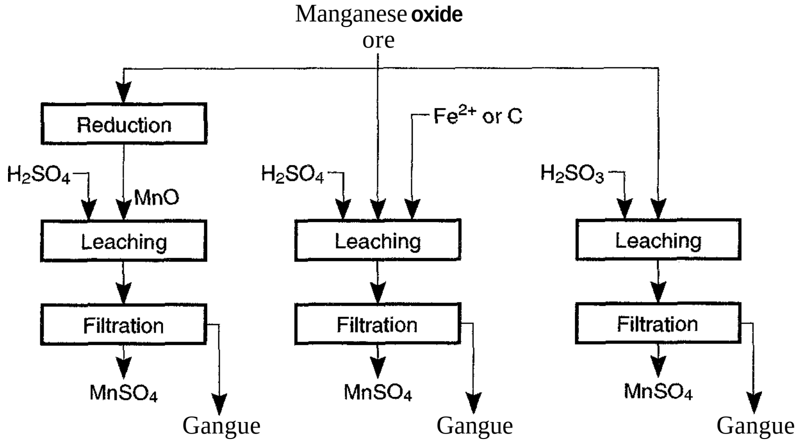

Figure 10.12: General scheme for the treatment of manganese ores.

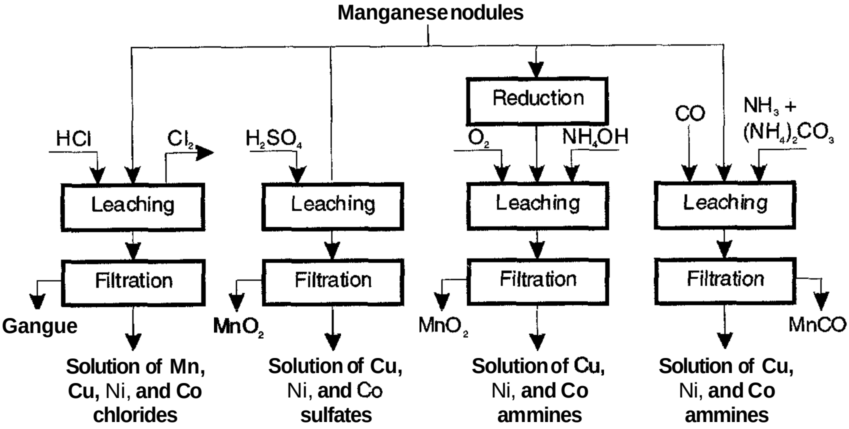

Figure 10.13: Proposed hydrometallurgical methods for the treatment of manganese nodules.

while MnO_2 reacts according to:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

Because of the insolubility of MnO_2 in dilute H_2SO_4, this reagent has been suggested for treating manganese nodules to selectively extract copper, nickel, and cobalt. Dilute H_2SO_4 at atmospheric temperature and pressure is capable of extracting most of the copper and nickel, a major part of cobalt, and minor amounts of iron. However, the process is slow and few days are needed with intensive agitation.

Hydrochloric acid process

Manganese dioxide dissolves in hydrochloric acid liberating chlorine:

$$2Cl^- \rightarrow Cl_2 + 2e-$$

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

The large proportion of acid used per mole MnO_2 necessitates its regeneration from the chlorine as well as from the aqueous solutions. Although this technology may be established for the treatment of manganese nodules yet it becomes costly because of the large number of circuits involved. Copper, nickel, cobalt, and iron oxides dissolve readily in hydrochloric acid, forming metal chlorides.

Ammonium hydroxide process

Manganese dioxide and manganese monoxide are insoluble in ammonium hydroxide. Two processes were therefore developed to recover copper, nickel, and cobalt selectively from manganese nodules based on this fact:

- *Reduction followed by leaching.* The nodules are first heated in a reducing atmosphere to transform copper, nickel, and cobalt oxides to the metallic state which can then be leached by ammonium hydroxide.
- *Leaching in a reducing atmosphere (Kennecott Process).* In ammoniacal ammonium carbonate solution and carbon monoxide, manganese dioxide matrix is decomposed to form an insoluble manganese carbonate while copper, nickel, and cobalt go into solution as ammine complexes; iron oxide remains unattacked. The reaction takes place at room temperature but because of the exothermic nature of the process, the temperature rises to 50 °C:

Oxidation: $CO + 2H_2O + 4NH_3 \rightarrow CO_3^{2-} + 4NH_4^+ + 2e-$

Reduction: $MnO_2 + 2NH_4^+ + 2e- \rightarrow Mn^{2+} + 2NH_3 + 2OH^-$

Precipitation: $CO_3^{2-} + Mn^{2+} \rightarrow MnCO_3$

Overall reaction:

$$MnO_2 + CO + 2H_2O + 2NH_3 \rightarrow MnCO_3 + 2NH_4^+ + 2OH^-$$

which is equivalent to:

$$MnO_2 + CO_{(aq)} \rightarrow MnCO_3$$

URANIUM ORES

Uranium occurs in nature mainly in the form of an oxide. Although it forms numerous oxides (Table 10.11), only two are the most important: UO_2 and U_3O_8 because they constitute the bulk of uranium ores. Uranium trioxide, UO_3, is soluble without the need of an oxidizing agent. Uranium in this oxide is in the hexavalent state; it does not however occur in nature in the free state, but in association with vanadium and potassium in the mineral carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5$. Carnotite is readily soluble in acids in the absence of oxidizing agents. Leaching of carnotite ores, however, is usually done after a preliminary salt roasting to convert vanadium minerals into a water-soluble sodium vanadate which can be recovered ahead of the acid leaching (Figure 10.14).

Table 10.11: Uranium oxides.

Oxide	Valency	Natural form	Solubility in dilute H_2SO_4 in absence of oxygen
UO_2	4	uraninite	insoluble
U_2O_5	4	does not occur in nature	partially soluble
U_3O_8	4, 6	pitchblende	partially soluble
UO_3	6	occurs only in combination with vanadium oxide as the mineral carnotite	soluble

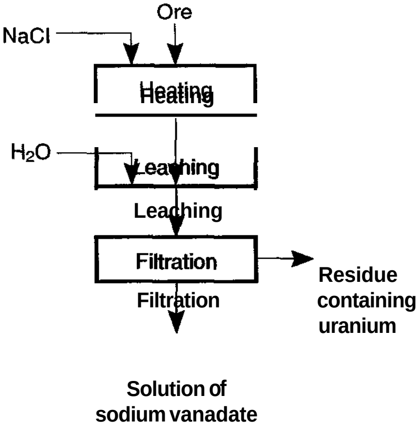

Figure 10.14: Treatment of carnotite ore.

Uraninite, UO_2, is insoluble in dilute H_2SO_4, and uranium in this oxide occurs in the tetravalent state. Pitchblend, U_3O_8, is partially soluble in dilute H_2SO_4; uranium in this oxide occurs in both the hexavalent and tetravalent states and may be represented as $UO_2 \cdot 2UO_3$. This accounts for the fact when dissolved in dilute H_2SO_4 in absence of air, mixtures of uranium(IV) and uranium(VI) are obtained:

$$U_3O_8 + 4H^+ \rightarrow UO_2 + 2UO_2^{2+} + 2H_2O$$

The reaction, however, seems to be more complex because the composition UO_2 is never reached; in practice a maximum dissolution of about 58% is reached as shown in Figure 10.15 and not 66.67% as expected according to the above equation. It seems that the intermediate oxide U_2O_5 is formed and the product is a mixture of UO_2 and U_2O_5:

$$U_3O_8 + 2H^+ \rightarrow U_2O_5 + UO_2^{2+} + H_2O$$

$$U_2O_5 + 2H^+ \rightarrow UO_2 + UO_2^{2+} + H_2O$$

The formula $UO_2 \cdot 2UO_3$ should not be taken as indicating the presence of two types of uranium in U_3O_8. X-ray analysis shows that all uranium atoms in U_3O_8 occupy equivalent positions; there is probably a resonance between two (or more) valence states, e.g., U^{4+} and U^{6+}.

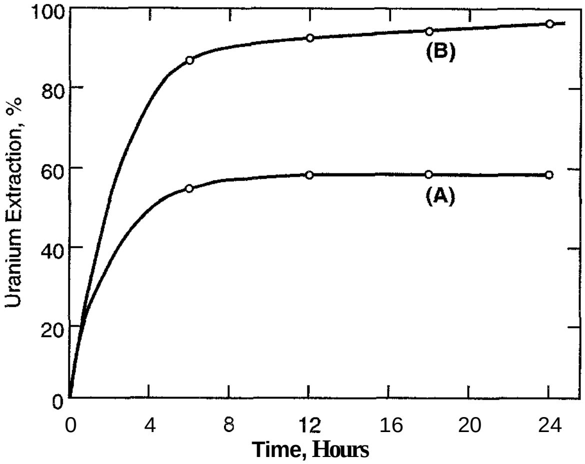

Figure 10.15: Solubility of a pitchblende ore sample containing 0.22% U_3O_8 in dilute H_2SO_4. (A) In absence, and (B) in presence of oxidizing agents. Plotted from data in a Canadian report (Anonymous, 1955).

As mined, pitchblende contains about 1% U_3O_8, but it can be easily concentrated by gravity methods to 50% U_3O_8. The main occurrences are in Joachimsthal (Czechoslovakia), Shinkolobwe (Zaire), Elliot Lake (Ontario), and Athabasca Lake (N.W. Canada). Thucholite is a uranium mineral containing thorium, carbon, hydrogen, and oxygen that occurs mainly in South African gold ores. These ores average 0.02–0.1% U_3O_8 and are processed first for the recovery of gold. Davidite is another uranium mineral containing iron, cerium, titanium, vanadium, chromium, and zirconium that occurs mainly at Broken Hill, Australia. It is a refractory mineral difficult to dissolve. At Palabora in South Africa, uranium is associated with copper sulfides; it is recovered from the flotation tailings by gravity methods as a concentrate containing 2.5–5% U_3O_8 mainly as the mineral urano-thorianite. Uranium recovery as a by-product of copper oxide leaching operations has already been referred to on page 250. Leaching agents commonly used are the following.

In Australia, a uranium deposit containing 0.06% U_3O_8 and 2.1% Cu as sulfide is under exploitation at Olympic Dam. A copper sulfide concentrate is obtained by flotation leaving a residue containing the bulk of uranium and 0.3% Cu. Both copper and uranium are leached from the residue by acid in presence of Fe^{3+} ion. On the other hand Northern Saskatchewan in Canada became the world center for uranium industry: large deposits are under exploitation at Key Lake (1.5% U_3O_8), Cigar Lake (13.6% U_3O_8), and McArther River (18.7% U_3O_8).

Acid leaching

- *Sulfuric acid.* Sulfuric acid, either dilute for easily soluble uranium minerals, or concentrated for the refractory minerals, is the most commonly used acid. Leaching may be represented by the following equations:

$$UO_2 \rightarrow UO_2^{2+} + 2e^-$$

$${}^1/{}_2O_2 + 2H^+ + 2e- \rightarrow H_2O$$

Overall reaction:

$$UO_2 + 2H^+ + {}^1/{}_2O_2 \rightarrow UO_2^{2+} + H_2O$$

Negatively charged sulfate complexes are formed, e.g., $[UO_2(SO_4)_3]^{4-}$. Oxygen or other oxidizing agents such as MnO_2, $NaClO_3$, or $NaNO_3$ are commonly used. Uranium is recovered from solution by ion exchange or solvent extraction. Figure 10.16 shows a typical uranium ore treatment plant.

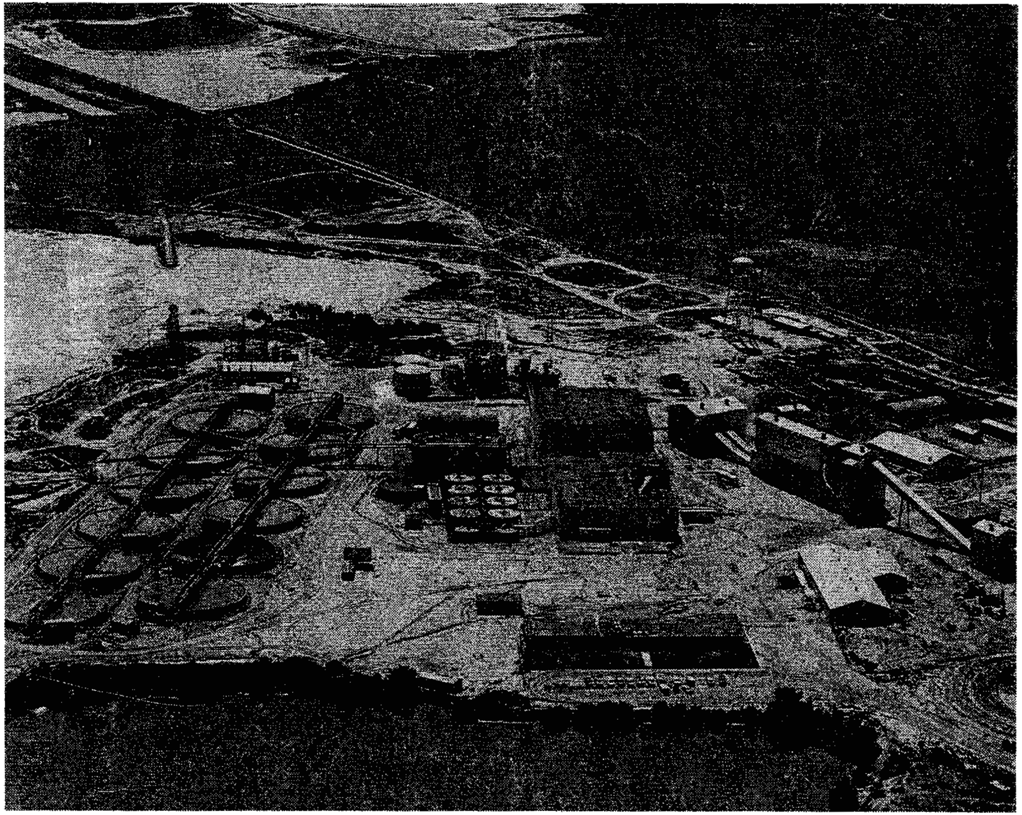

Figure 10.16: Uranium ore treatment **plant** in New Mexico.

- *Nitric acid.* At Palabora, South Africa, the uranium concentrate is leached by concentrated nitric acid at 75 °C:

$$UO_2 \rightarrow UO_2^{2+} + 2e^-$$

$$2H^+ + NO_3^- + e^- \rightarrow NO_2 + H_2O$$

Overall reaction:

$$UO_2 + 4H^+ + 2NO_3^- \rightarrow UO_2^{2+} + 2NO_2 + 2H_2O$$

or $$UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O$$

Alkali **carbonate process**

The reactions that take place in this case are:

$$UO_2 \rightarrow UO_2^{2+} + 2e^-$$

$$UO_2^{2+} + 3CO_3^{2-} \rightarrow [UO_2(CO_3)_3]^{4-}$$

$${}^1/_2O_2 + H_2O + 2e- \rightarrow 2OH^-$$

Overall reaction:

$$UO_2 + 3CO_3^{2-} \text{ t } H_2O + {}^1/_2O_2 \rightarrow [UO_2(CO_3)_3]^{4-} + OH-$$

Since OH– ion is formed during leaching and there is a possibility that insoluble uranates may be formed, sodium bicarbonate is usually added to the solutions to prevent such side reactions:

$$HCO_3^- + OH- \rightarrow CO_3^{2-} + H_2O$$

Figure 10.17 shows a typical flowsheet for this process. Ammonium carbonate leaching under pressure has the advantage of having less attack on silicate minerals and on alumina and uranium can be precipitated by stripping with steam to decompose the uranium complex; the evolved NH_3 and CO_2 are absorbed and recycled. It is used together with hydrogen peroxide for in situ leaching of underground uranium ores, e.g., in Texas.

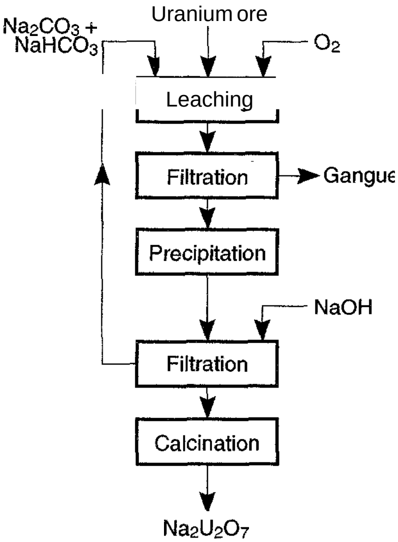

Figure 10.17: Leaching of uranium ores with sodium carbonate.

Leach residues

Residues from uranium extraction plants using either H_2SO_4 or Na_2CO_3 contain all the radium originally present in the ore. These residues are at present stock piled because radium is not in demand. Radium decays into the radioactive gas radon. The diffusion of this gas in the environment, the scattering of radioactive dust particles by wind, and erosion of the piles of residues by water, represent a serious pollution problem. A typical disposal pond contains 0.6 mg radium per ton of solids. Abandoned plant sites are particularly hazardous because tailings dams may either erode or rupture and release tailings to streams, Therefore, controlled storage of uranium mill residues must be maintained after the life of the plant to safeguard the environment from radioactive pollution. Considering the 1622-year half life of radium 226, storage must be controlled for many thousands of years to enable abatement of the radiation hazard by natural decay of radium and its products. For this reason, leaching uranium ores with HNO_3 or HCl followed by precipitation and separation of (Ra, Ba)SO_4 by adding $BaCl_2$ is being considered as a mean to solve this problem although these acids are more expensive than the commonly used H_2SO_4.

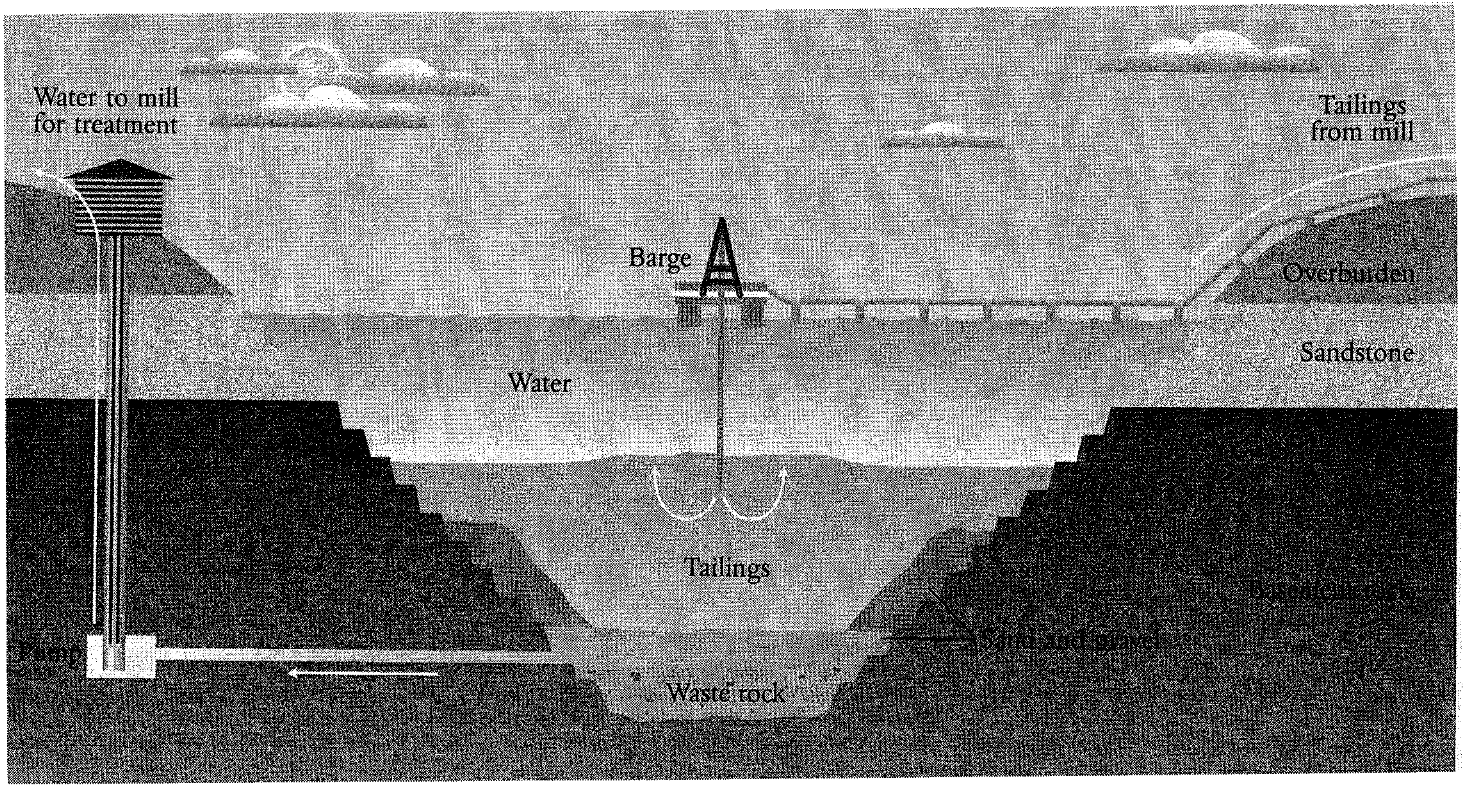

Figure 10.18: Tailings and residues from uranium treatment plant being stockpiled under water in an unused open pit mine (courtesy Cameco Corporation).

A more practical solution, however, is to fill the open pit mine with water and deposit the tailings and residues at the bottom, thus the water above will act as a protective layer against radiation (Figure 10.18).

ZINC OXIDE ORES AND CALCINES

Zinc sulfide is the major zinc mineral. However, minor amounts of zinc occur as the minerals zincite, ZnO, hydrozincite, $ZnCO_3 \cdot 2Zn(OH)_2$, and smithsonite, $ZnCO_3$[1]. These oxide minerals are readily soluble in dilute H_2SO_4. The bulk of zinc-containing raw material treated by leaching is, however, zinc oxide produced by the oxidation of zinc sulfide. At one time all zinc sulfide concentrates were treated by pyrometallurgical route, i.e., oxidation to zinc oxide then reduction by carbon to metal. This route is not an easy route because the temperature of reduction is higher than the boiling point of the metal and therefore metal vapors have to be collected and condensed quickly to avoid their oxidation. Acid leaching of zinc oxide followed by electrolysis offered a solution to the pyrometallurgical route. Since the development of this process in 1919, zinc production by thermal reduction has been in a steady decline.

Table 10.12: Zinc oxide obtained by roasting a zinc sulfide concentrate.

	%
Zn	61.5
Pb	3.2
Cu	1.0
Mn	0.2
FeO	3.6
CaO	0.2
Ag	0.06
S	1.7
Insoluble residue	8.4
Soluble Zn	97.5

A typical analysis of zinc oxide produced by the oxidation of a zinc sulfide concentrate is given in Table 10.12. Such material is also an important source of cadmium, indium, and germanium from which they are usually recovered. Undesirable impurities include arsenic,

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[1] For the treatment of zinc silicate minerals see *Leaching of Silicates* (page 374).

antimony, and ferrites. The latter are complex oxides of zinc and iron, $ZnFe_2O_4$, formed during the oxidation step as a result of the presence of iron sulfide minerals in the concentrate by a solid state reaction between ZnO and Fe_2O_3.

The ferrite problem and its solution

The problem with ferrite is its insolubility in dilute H_2SO_4, the acid commonly used for leaching the calcines which is actually the recycle electrolyte containing 25% H_2SO_4. As a result, the early leaching process suffered from a low zinc recovery (85–93%); residues from such process contained as high as 20% Zn. Ferrites are soluble in hot concentrated H_2SO_4; but if these conditions are used, two problems will be introduced:

- The impurity level especially iron will increase and extensive purification will be required before electrowinning.
- The high acidity must be neutralized so that electrowinning would be feasible.

Since this solution was costly, residues were treated by one of the following routes (Figure 10.19):

- Stock-piled until a better solution is found.
- Treated with coal in a rotary kiln (Waelz Process) to volatilize zinc and recover it in form of zinc oxide.
- Treated in a lead blast furnace to recover their zinc content in form of a slag, which can be treated further by the “fuming process” to recover it in form of a zinc oxide fume, i.e., a fine powder rich in ZnO. This material is eventually returned to the leaching step for the recovery of its zinc values,

In the early 1970s the ferrite problem was solved when it was discovered that iron in zinc sulfate solution obtained by the hot acid leaching of residues could be precipitated in a crystalline form easy to filter in form of jarosite, goethite, or hematite and not as the gelatinous $Fe(OH)_3$ which is difficult to filter (Table 10.13); these are names of naturally occurring minerals similar in composition to the precipitates formed. As a result, the following typical flowsheet for a modern zinc oxide leaching circuit was introduced (Figure 10.20):

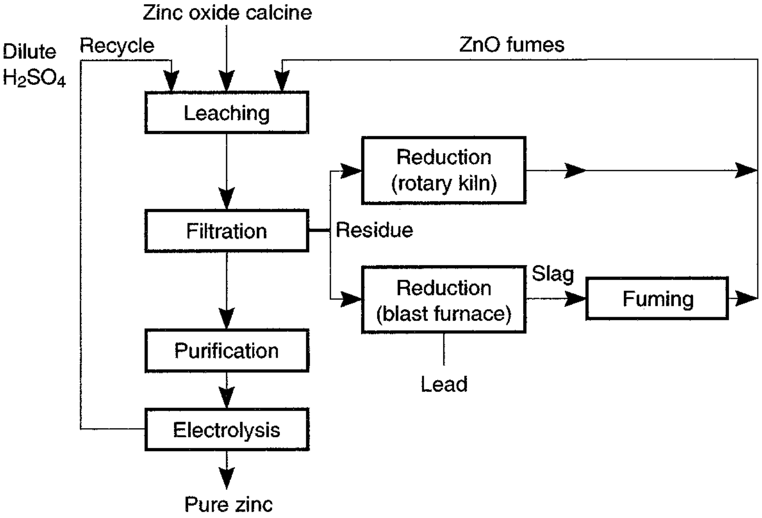


Figure 10.19: Recovery of zinc from zinc oxide calcines by leaching and treatment of the leach residue by thermal methods.

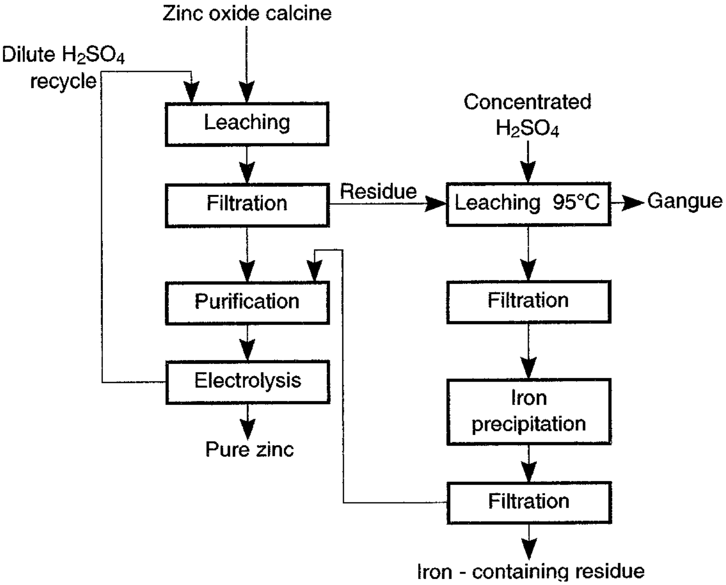


Figure 10.20: Recovery of zinc from leach residue by concentrated acid leaching.

Table 10.13: Processes for iron elimination from zinc sulfate solution.

	Jarosite $M[Fe_3(SO_4)_2(OH)_6]$	Goethite FeOOH	Hematite Fe_2O_3
Origin	Norway, Australia, Spain	Belgium	Japan
Formation	Adding Na, K, or NH_4 salt to solution at pH 1.5 and at 95 "C	Reduction of Fe^{3+} ion to Fe^{2+} by ZnS then oxidation by air at pH 2 and 95 "C	Precipitation at 200 °C by oxygen under pressure
Color	Yellow	Red	Red
Weight, tons/ton of concentrate	*0.40*	0.25	0.18
Composition, %			
Fe	25–28	40–45	58–60
Zn	4–6	5–8	0.5–1
S	10–12	2.5–5	3

- *Jarosite process.* In this process NH_4OH or NaOH are added at 95 "C and at pH 1.5 to precipitate ammonium or sodium jarosite, respectively. The chemistry of jarosites (hydroxy iron sulfates) is discussed later (pages 608–608). The jarosite process suffers from the following problems:
  - Any silver present in the raw material enters the jarosite and must be liberated by digestion with calcium hydroxide at 85–90" before cyanidation if its recovery is desired:

    $$AgFe_3(SO_4)_2(OH)_6 + 2Ca(OH)_2 + 4H_2O \rightarrow AgOH + 3Fe(OH)_3 + 2CaSO_4 \cdot 2H_2O$$
  - The jarosite residue is voluminous and causes stock piling problems. It was suggested to melt it, but the cost is high.
- *The goethite process.* In this process ferric ion is reduced to ferrous by adding zinc sulfide concentrate. Air is then injected in the hot solution at pH 2–2.5 to oxidize and precipitate crystalline ferric oxide hydroxide, FeOOH, known as goethite.
- *The hematite process.* In this process ferric ion is reduced by SO_2 to the ferrous state, then the solution is heated at 200 "C in autoclaves in presence of oxygen to precipitate ferric oxide, Fe_2O_3, known as hematite at pH 2. Copper in solution must be precipitated (by H_2S) prior to heating to avoid its co-precipitation with hematite.

Purification of solution

After removing the bulk of iron, the main impurities remaining are copper, cadmium, cobalt, nickel, thallium, arsenic, and antimony.

- Copper and cadmium are removed by precipitation with zinc powder.
- Cobalt is usually removed by precipitation with β-naphthol.

Sodium hydroxide process

Zinc oxide is soluble also in NaOH (Figure 10.21). The solution when electrolyzed yield zinc in powder form for particular uses. This process is used to a minor extent for treating fly ash produced in steel-making by the electric furnace.

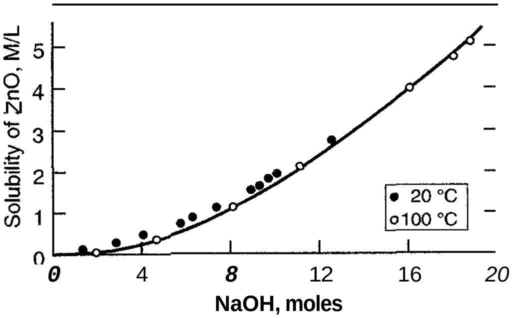


Figure 10.21: Solubility of ZnO in NaOH (Scholder and Hendrich, 1939).

SUMMARY

Table 10.14 gives a summary of leaching processes for oxides and hydroxide ores.

Table 10.14: Leaching of oxides and hydroxides.

Origin	Oxide or hydroxide	Leaching agent	Remarks
Bauxite	$Al(OH)_3$ $AlOOH$	NaOH	Bayer Process: 180–200 °C (under pressure), residue contains Fe_2O_3, TiO_2, and SiO_2 (red mud).
Copper oxide ores[a]	$Cu(OH)_2 \cdot CuCO_3$ $Cu(OH)_2 \cdot 2CuCO_3$ $Cu_8(Si_4O_{10})_2(OH)_{12} \cdot nH_2O$	H_2SO_4 or NH_4OH	Generally dilute H_2SO_4 is used; in exceptional cases NH_4OH when ore contains excessive acid-consuming gangue.
Laterite	NiO in Fe_2O_3 matrix	H_2SO_4	Moa, Cuba, 250 °C, *4000* kPa; under these conditions Fe_2O_3 dissolves then reprecipitates.
Pyrolusite or manganese nodules	MnO_2	H_2SO_4	Only Cu, Ni, Co solubilized
		H_2SO_3	$MnO_2 + H_2SO_3 \rightarrow MnSO_4 + H_2O$
		HCl	$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
		$FeSO_4$	$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$
	MnO by reduction	H_2SO_4	$MnO + 2H^+ \rightarrow Mn^{2+} + H_2O$
		NH_4OH	Only Cu, Ni, Co solubilized
Sphalerite (ZnS)	ZnO by ZnS by oxidation	H_2SO_4	$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$ Solution contains: Cl^{2+}, Cu^{2+}, Ge^{4+} Residue: $PbSO_4$, $ZnFe_2O_4$, and traces of Ge, In, TI.
		NaOH	$ZnO + NaOH + H_2O \rightarrow NaZn(OH)_3$ Minor operation
Uranium ores	UO_2, U_3O_8	H_2SO_4	$UO_2 + 2H^+ + {}^1/_2O_2 \rightarrow UO_2^{2+} + H_2O$
		Na_2CO_3	$UO_2 + 3CO_3^{2-} + {}^1/_2O_2 + H_2O \rightarrow [UO_2(CO_3)_3]^{4-} + 2OH^-$

a. Malachite, azurite, and chrysocolla, respectively.

Chapter Eleven

Complex Oxides

Ilmenite and Titanium Slag. 276
  Leaching of ilmenite 277
  Production **of** synthetic rutile. 278
  Leaching **of** titanium **slag** 280
Chromite 280
Columbite, Tantalite, and Pyrochlore. 281
Wolframite and Scheelite 283
  Acid digestion. 283
  Alkaline digestion 284
Summary 284

A complex oxide is composed of two or more metal oxides in form of a compound. One of these oxides is considered valuable while the others are usually not. The valuable oxides are those of titanium, niobium, tantalum, chromium, tungsten, and sometines iron while the other oxides of no value are those of manganese, calcium, and barium. Table 11.1 shows a list of the most important complex oxide minerals. Complex oxides are either completely dissolved or partially leached for the recovery of metal values (Table 11.2). Partial leaching can be considered as a chemical benefication method (page 15). Complex oxide minerals like ilmenite, pyrochlore, wolframite, and scheelite can be transformed into relatively pure oxides in a single step by treatment with hydrochloric acid at high temperature and pressure in an autoclave. Dissolution followed by hydrolysis results in the precipitation of the valuable metal oxide as described below.

Table 11.1: Complex oxide minerals.

Mineral	Formula	
Chromite	$FeCr_2O_4$	$FeO \cdot Cr_2O_3$
Ilmenite	$FeTiO_3$	$FeO \cdot TiO_2$
Columbite	$(Fe, Mn)Nb_2O_6$	$(Fe, Mn)O \cdot Nb_2O_5$
Tantalite	$(Fe, Mn)Ta_2O_6$	$(Fe, Mn)O \cdot Ta_2O_5$
Pyrochlore	$(Ca, Ba)Nb_2O_6 \cdot NaF$	$(Ca, Ba)O \cdot Nb_2O_5 \cdot NaF$
Scheelite	$CaWO_4$	$CaO . WO_3$
Powellite	$Ca(Mo, W)O_4$	$CaO \cdot (Mo, W)O_3$
Wolframite	$(Fe, Mn)WO_4$	$(Fe, Mn)O . WO_3$

Table 11.2: Treatment of complex oxides.

Method		Raw material	Reagent	Process
Complete dissolution		Ilmenite Titanium slag Chromite	Concentrated H_2SO_4	Baking
		Columbite Tantalite Pyrochlore	Concentrated HF (excess)	Digestion in closed vessel with reflux condenser
Partial leaching	Acid leaching to dissolve away the basic oxide	Ilmenite Pyrochlore Wolframite Scheelite	Concentrated HCl	Pressure leaching
	Basic leaching to dissolve away the acid oxide	Wolframite Scheelite	NaOH Na_2CO_3	Pressure leaching

ILMENITE AND TITANIUM SLAG

While rutile is easy to process to titanium metal or TiO_2 pigment by the chlorination method, ilmenite is more complicated because of its high iron content. But, since the world reserves of titanium are 90% in the form of ilmenite and 10% in the form of rutile, the treatment of ilmenite is evidently an important question. Ilmenite is readily soluble in sulfuric acid[1], but because of the pollution problems associated with the disposal of $FeSO_4$, iron in the ore is usually separated first. This is achieved in two ways:

---

[1] Rutile is insoluble in concentrated H_2SO_4.

Table 11.3: Analysis of titanium raw materials.

	Rutile %	Ilmenite %	Titanium slag %	Synthetic rutile %
TiO_2	80–95	43–59	72.1	90–95
Ti_2O_3	0	0	10–20	0
FeO		9–38	8.9	
Fe_2O_3		5–25	0.0	
Fe		0.0	0.2	
SiO_2		0.4–4.0	5.8	
Al_2O_3		1.3–3.3	6.5	
MgO + CaO		0.1–4	7.3	
V		0.4–2.0	0.4	

- *Pyrometallurgical method.* Partial reduction with anthracite in an electric furnace to get cast iron and a slag rich in titanium. Titanium slag in mainly iron magnesium titanate, (Fe, Mg)Ti_4O_{10}, and a small amount of silicates; typical analysis is given in Table 11.3.

- *Hydrometallurgical method.* Leaching of iron oxide and obtaining a residue rich in titanium (90–95% TiO_2) known as "synthetic rutile".

The slag and synthetic rutile can then be processed to TiO_2 pigment or titanium metal.

Leaching of ilmenite

In the manufacture of TiO_2 pigment from ilmenite the ore may be completely transformed with concentrated H_2SO_4 at 110–120 °C into ferrous and titanyl sulfates:

$$FeTiO_3 + 4H^+ \rightarrow Fe^{2+} + TiO^{2+} + 2H_2O$$

The solid mass is then dissolved in water; scrap iron is added to reduce any ferric ion. After filtration, the solution containing 120–130 g/L TiO_2 and 250–300 g/L $FeSO_4$ is then concentrated under vacuum at 10 °C to crystallize $FeSO_4 \cdot 7H_2O$ which is then centrifuged. Titanium oxide is then precipitated from solution by dilution and seeding resulting in the formation of dilute H_2SO_4 for disposal (Figure 11.1). This route, however, is uneconomical because of disposal problems.

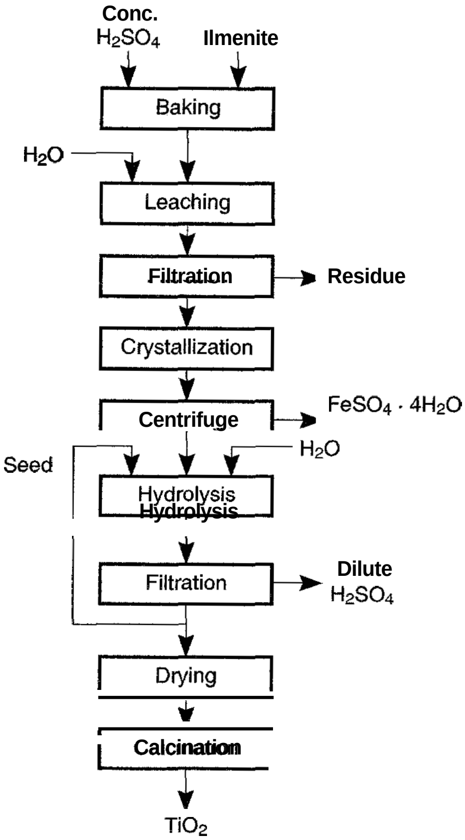


Figure 11.1: Leaching of ilmenite for the production of pure TiO_2.

Production of synthetic rutile

Ilmenite can be decomposed by 20% HCI at 120 °C and 200 kPa; iron is solubilized leaving a material containing about 93% TiO_2:

$$FeTiO_3 + 2H^+ \rightarrow TiO_{2(impure)} + Fe^{2+} + H_2O$$

A negligible amount of titanium is lost in solution. Leaching can be conducted at lower temperature, i.e., no autoclaves would be required, if a preliminary oxidation–reduction step is conducted to modify the crystalline structure of the mineral and render it more amenable to leaching. Thus, the ore is first heated in an oxidizing atmosphere to convert as much as possible of FeO into Fe_2O_3. This is followed by heating in a reducing atmosphere to convert Fe_2O_3 into iron which can be leached with HCl. Reduction is necessary to obtain a ferrous chloride solution which is less corroding as compared to ferric chloride. Hydrochloric acid is regenerated from $FeSO_4$ by oxyhydrolysis (see Chapter 3). Synthetic rutile is insoluble in H_2SO_4 and is used to manufacture TiO_2 pigment by the chlorination route. Figure 11.2 shows a general scheme for the production of synthetic rutile, while Figure 11.3 shows a hydrochloric acid regeneration plant.

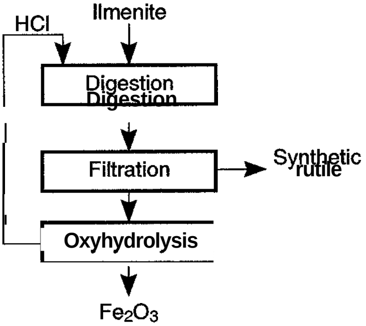


Figure 11.2: Production of synthetic rutile from ilmenite.

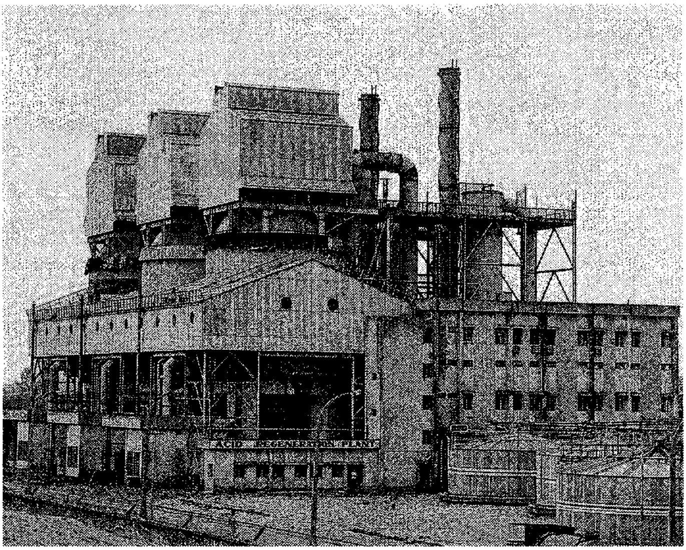


Figure 11.3: Hydrochloric acid regeneration plant in synthetic rutile production in India (courtesy Indian Rare Earths Limited).

Leaching of titanium slag

The slag is treated in the same way as ilmenite with the exception that no separation of ferrous sulfate is necessary because the bulk of iron is separated by reduction in an earlier step (Figure 11.4).

CHROMITE

Chromite (Table 11.4) is usually reduced in electric furnace to make ferrochromium. For the production of high-purity chromium, chromite is dissolved in acid then the aqueous solution of pure chromium alum is electrolyzed. According to this method finely ground (– 325 mesh) ore is digested at 130–160 °C with the spent electrolyte, to which concentrated H_2SO_4 is added to adjust its acidity to 40%. Under these conditions complete dissolution of the ore takes place:

$$FeCr_2O_4 + 8H^+ \rightarrow Fe^{2+} + 2Cr^{3+} + 4H_2O$$

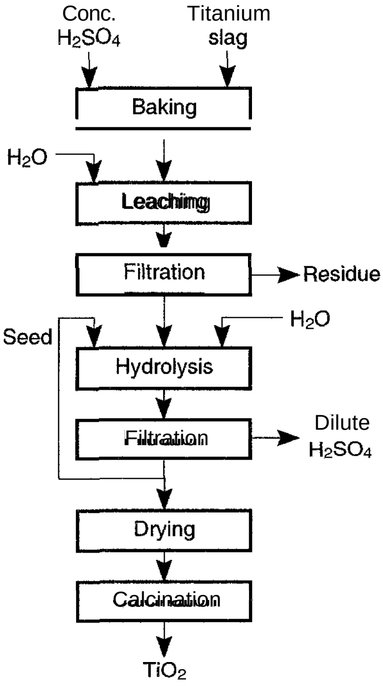


Figure 11.4: Leaching of titanium slag for the production of pure TiO_2.

Table 1 1.4: Typical analysis of chromite.

	%
Cr_2O_3	40–55
FeO	10–25
Fe_2O_3	1–4
MgO	11–16
CaO	1–2
MnO	0.2
Al_2O_3	10–15
SiO_2	1–4

The leach solution is filtered while hot, and diluted with recycled ammonium sulfate-bearing solution to a concentration of about 40 g/L Cr. The solution is heated to 80 "C to stabilize the chromium sulfate into the green modification which does not form alum. On cooling to 3 °C under vacuum, iron and aluminum are separated as ammonium alums. Crude chromium ammonium alum $(NH_4)_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ is then crystallized out by carefully heating to 35 "C and then cooling to 15 "C. **A** flowsheet is shown in Figure 11.5.

Table 11.5: Typical analyses of niobium and tantalum concentrates.

	Tantalite	Columbite	Pyrochlore [Yo]	
	%	%	Quebec	Brazil
Nb_2O_5	2.5	67.2	68.7	60
Ta_2O_5	80.6	5.7	0.2	—
FeO	10.9	18.4	0.4	4
MnO	3.8	2.2	—	—
CaO	—	—	14.8	10.2
BaO	—	—	—	16
MgO	0.2	—	0.5	
SnO_2	1.5	2.3	—	
TiO_2	0.7	2.3	0.6	
WO_3	0.1	—	—	
Rare earths	—	—	2.0	
F	—	—	3.9	
$Na_2O + K_2O$	—	—	7.3	

COLUMBITE, TANTALITE,AND PYROCHLORE

Columbite, tantalite, and pyrochlore (Table 11.5) are mainly used to prepare ferroniobium and ferrotantalum by pyrometallurgical methods. To prepare metallic niobium and tantalum a pure oxide is usually prepared first by treating the concentrates by hydrometallurgical methods. Tin slags, especially those from Malaysia and Thailand, were at one time an important source of niobium, tantalum, as well as tungsten.

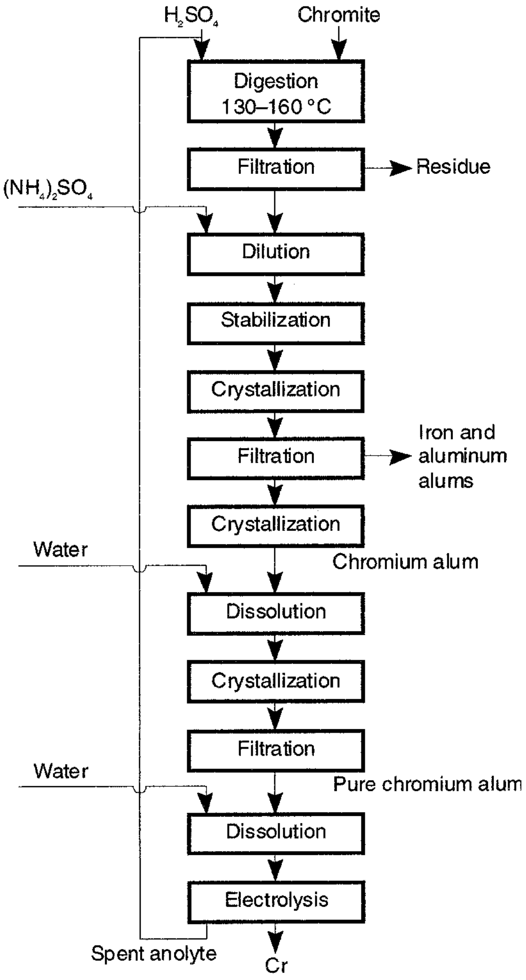


Figure 11.5: Leaching of chromite for the production of metallic chromium.

Most minerals containing tantalum and niobium are solubilized by hot concentrated hydrofluoric acid. Leaching of these minerals by

HF is based on the fact that soluble complex fluorides are formed in excess HF. For example, for columbite:

$$FeO\cdot Nb_2O_5 + 16HF \rightarrow 2H_2NbF_7 + FeF_2 + 6H_2O$$

$$MnO\cdot Nb_2O_5 + 16HF \rightarrow 2H_2NbF_7 + MnF_2 + 6H_2O$$

Similar equations can be written for tantalite. Digestion is carried out in steel tanks with reflux condenser to prevent the loss of HF. When the reaction is complete, the slurry is allowed to settle overnight, and the decanted solution is then processed for the recovery of niobium and tantalum while the unreacted residue is digested further with HF. Tantalum is usually precipitated from the solution by K_2CO_3 at room temperature as the double fluoride K_2TaF_7, while niobium is precipitated later from the filtrate by NH_4OH as crude $Nb_2O_5\cdot nH_2O$.

Pyrochlore can be decomposed by baking with concentrated H_2SO_4 then leaching with dilute H_2SO_4; niobium goes into solution, while calcium remains as insoluble $CaSO_4$. Pyrochlore containing 55–65% Nb_2O_5 can also be beneficiated to a product containing 90–97% Nb_2O_5 by reaction with 36% HCl at 150°C and about 1000 kPa for 7 hours in a pressure reactor.

WOLFRAMITE AND SCHEELITE

Wolframite and scheelite are the most important sources of tungsten. Table 11.6 shows a typical analysis of concentrates containing these minerals. Both material can be decomposed by either acids or alkaline solutions.

Table 11.6: Average analysis of tungsten concentrates.

	Wolframite	Scheelite
WO_3	75–65	70–78
FeO	5–15	0.4–2.0
MnO	5–20	0.2
CaO	0.1–0.2	17–19

Acid digestion

This is usually conducted with concentrated HCl in excess:

$$FeWO_4 + 2H^+ \rightarrow Fe^{2+} + WO_3 + H_2O$$

$$CaWO_4 + 2H^+ \rightarrow Ca^{2+} + WO_3 \cdot H_2O$$

Sulfuric acid cannot be used because of the formation of insoluble calcium sulfate. The digested mass is washed with water to remove iron and manganese chlorides, the residue is then dissolved in hot NH_4OH. Ammonium wolframate is crystallized from the solution by evaporation.

Alkaline digestion

Leaching of wolframite with concentrated NaOH at high temperature in an autoclave yields a solution of sodium wolframate, while iron and manganese are precipitated as hydroxides:

$$FeWO_4 + 2OH^- \rightarrow WO_4^{2-} + Fe(OH)_2$$

Scheelite is decomposed by sodium carbonate solution at 225 °C:

$$CaWO_4 + CO_3^{2-} \rightarrow WO_4^{2-} + CaCO_3$$

The formation of $CaCO_3$ films on the mineral particles retards the reaction. This factor can be eliminated, however, by using rotating autoclaves containing steel balls. The solution of sodium wolframate is purified by precipitation with acid:

$$WO_4^{2-} + 2H^+ \rightarrow WO_3 \cdot H_2O$$

SUMMARY

Table 11.7 gives a summary of leaching processes for complex oxides.

Table **11.7:** Summary of leaching processes for complex oxides.

Origin	Complex oxide	Leaching agent	Remarks
Ilmenite	$FeTiO_3$	H_2SO_4 conc.	Not widely used for TiO_2 pigment production because of pollution due to $FeSO_4$ and dilute H_2SO_4.
		HCl conc.	Production of synthetic rutile as a feed material for $TiCl_4$ manufacture. Regeneration of HCl by oxyhydrolysis of $FeCl_2$.
	Iron–magnesium titanate (Titanium slag)	H_2SO_4 conc.	Widely used for TiO_2 pigment production but suffers from dilute H_2SO_4 disposal.
Chromite	$FeCr_2O_4$	H_2SO_4	Complete dissolution, crystallization of alums, production of metallic chromium by electrolysis.
Columbite Tantalite	$(Fe, Mn)Nb_2O_6$ $(Fe, Mn)Ta_2O_6$	HF conc.	Complete dissolution due to formation of soluble complex fluorides: H_2NbF_7 and H_2TaF_7.
Pyrochlore	$(Ca, Ba)Nb_2O_6 \cdot NaF$		
Wolframite	$(Fe, Mn)WO_4$	HCl conc.	Partial leaching: production of $WO_3 \cdot H_2O$ as residue.
		NaOH	Partial leaching: formation of sodium tungstate solution and $Fe(OH)_2$ as residue.
Scheelite	$CaWO_4$	HCI conc.	Partial leaching: production of $WO_3 .H_2O$ as residue.
		Na_2CO_3	Partial leaching: formation of sodium tungstate solution and $CaCO_3$ as residue.

Chapter Twelve

Sulfides and Disulfides

Introduction 287
General Principles 290
Elemental Sulfur 292
  Physical properties **292**
  Chemical properties **293**
  Determination **296**
  Recovery from leach residue **296**
Leaching in Absence of Oxidizing Agents 298
  Reactions **298**
  Applications **299**
Leaching in Presence of Oxidizing Agents 301
  Mechanism **301**
  Oxygen and water **302**
  Oxygen and ammonia **303**
  Oxygen and a base **306**
  Oxygen and acid **306**
  Ferric salts **311**
  Concentrated H_2SO_4 .... **312**
  Nitric acid **316**
  Chlorine and hypochlorite **316**
Disulfides 317
  Pyrite **317**
  Arsenopyrite **321**
  Covellite **322**
Summary 323

INTRODUCTION

Pyrite and arsenopyrite are different from other sulfide minerals since they contain the disulfide ion. S_2^{2-}; arsenopyrite contains. in addition. the diarsenide ion. As_2^{2-}, In pyrite. FeS_2, the iron atoms are in a face-centered cubic arrangement with pairs of the sulfur atoms located on the cube diagonals (Figure 12.1). In arsenopyrite. FeAsS.

the iron atoms are also in a face-centered cubic arrangement like in pyrite but half of the diagonal positions are occupied by pairs of the sulfur atoms and the other half by pairs of arsenic atoms. Marcasite is another crystalline form of pyrite in which the iron atoms occupy a body-centered cubic lattice with pairs of sulfur atoms on the diagonals. Covellite, CuS, or more exactly $\mathrm{Cu_4^ICu_2^{II}(S_2)_2S_2}$ (Figure 12.2), has two thirds of the sulfur atoms as disulfide ions. The presence of disulfide ions is manifested on heating the minerals in absence of air: pyrite loses an atom of sulfur, while arsenopyrite loses an atom of arsenic:

$$\mathrm{FeS_2 \rightarrow FeS + S}$$

$$\mathrm{FeAsS \rightarrow FeS + As}$$

A similar behavior is also observed on heating covellite:

$$\mathrm{Cu_4^ICu_2^{II}(S_2)_2S_2 \rightarrow 3Cu_2^IS + 3S}$$

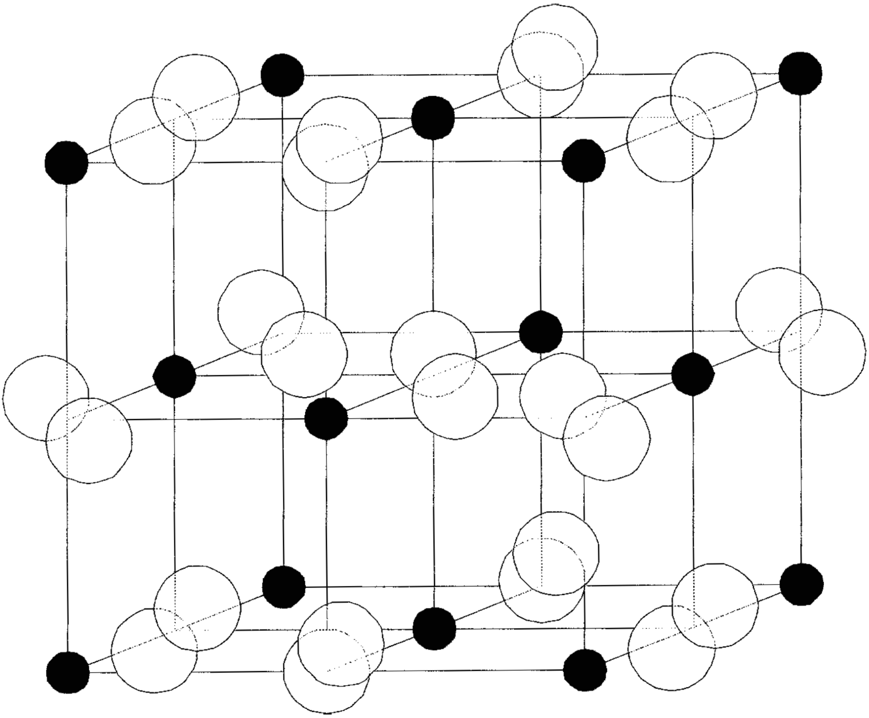


Figure **12.1:** Atomic arrangement of pyrite.

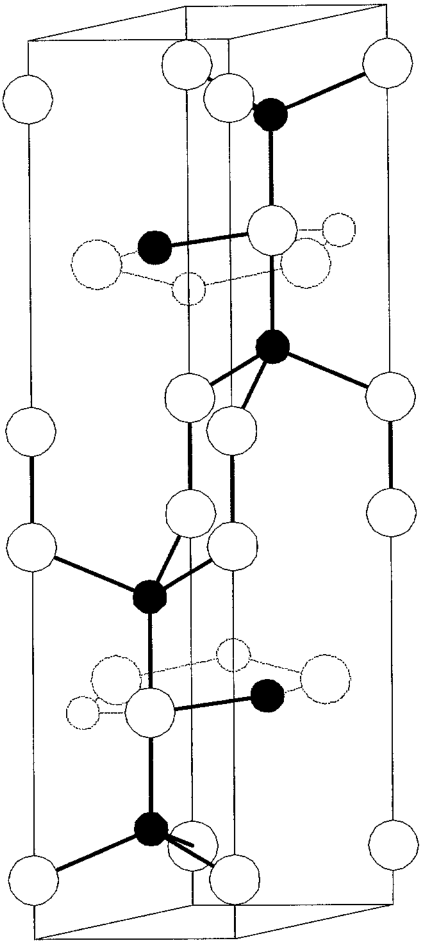


Figure 12.2: Covellite, $Cu^{I}_{4}Cu^{II}_{2}(S_2)_2S_2$.

Disulfides dissociate in water forming the metal cation and the disulfide anion. For example, pyrite dissociates as follows:

$$FeS_{2(s)} \rightleftharpoons Fe^{2+}_{(aq)} + S^{2-}_{2(aq)}$$

while covellite and arsenopyrite dissociate as follows:

$$Cu^{I}_{4}Cu^{II}_{2}(S_2)_2S_{2(s)} \rightleftharpoons 4Cu^{+}_{(aq)} + 2Cu^{2+}_{(aq)} + 2S^{2-}_{2(aq)} + 2S^{2-}_{(aq)}$$

$$2FeAsS_{(s)} \rightleftharpoons 2Fe^{2+}_{(aq)} + As^{2-}_{2(aq)} + S^{2-}_{2(aq)}$$

Disulfide ion is similar to peroxide ion which undergoes auto-oxidation as follows:

$$O_2^{2-} \rightarrow O_2 + 2e^-$$

$$O_2^{2-} + 2e^- \rightarrow 2O^{2-}$$

Overall reaction:

$$20;- \rightarrow O_2 + 2O^{2-}$$

or $$2H_2O_2 \rightarrow O_2 + 2H_2O$$

Hence, for disulfide ion, the auto-oxidation leads to elemental sulfur and sulfide ion:

$$S_2^{2-} \rightarrow 2S + 2e^-$$

$$S_2^{2-} + 2e^- \rightarrow 2S^{2-}$$

Overall reaction:

$$S_2^{2-} \rightarrow S + S^{2-}$$

This behavior should be taken into consideration when discussing the leaching of these minerals, as will be shown later.

GENERAL PRINCIPLES

Sulfide minerals are insoluble in water even at high temperature. They can be solubilized, however, by a variety of methods:

- *Under reducing conditions (absence of oxidizing agents).* Some sulfides dissolve in acid medium forming H_2S, others dissolve in basic medium forming sulfide ion.
- *Under oxidizing conditions.* Elemental sulfur usually forms but because of its instability in neutral or basic media it oxidizes to sulfates. In acid medium, however, there is a narrow region where elemental sulfur can form.

These data are summarized in the stability diagram shown in Figure 12.3, which is valid in the temperature region 25 to 150 "C. Above 150 "C, however, the narrow stability region of elemental sulfur disappears and no sulfur can form.

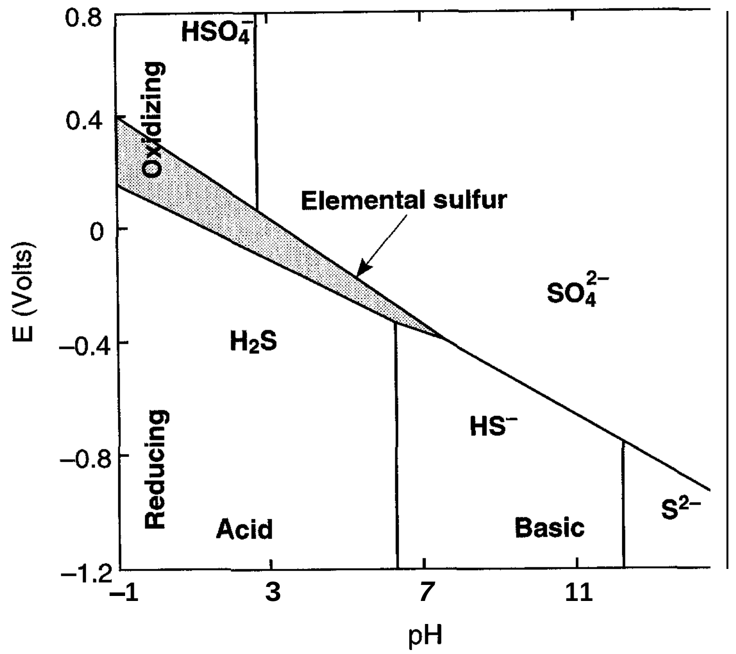


Figure 12.3: Potential–pH diagram for sulfur at 100 °C.

The behavior of some sulfides during leaching may seem anomalous. For example, Cu_2S and Ni_3S_2 form the intermediate products CuS and NiS, respectively:

$$Cu_2S + 2H^+ + {}^1/_2O_2 \rightarrow CuS + Cu^{2+} + H_2O$$

$$Ni_3S_2 + 2H^+ + {}^1/_2O_2 \rightarrow 2NiS + Ni^{2+} + H_2O$$

Or in absence of oxidizing agents, Ni_3S_2 dissolves in HCl to form H_2S and H_2:

$$Ni_3S_2 + 6H^+ \rightarrow 3Ni^{2+} + 2H_2S + H_2$$

These sulfides behave as if they were solid solutions of a metal and a sulfide. Thus Cu_2S behaves like Cu + CuS, and Ni_3S_2 behaves like Ni + 2NiS.

Although elemental sulfur is unstable in basic media or in presence of strong oxidizing agents, yet it can be isolated during leaching sulfides in such medium if during leaching an immiscible organic solvent capable of dissolving sulfur were present. Thus, it is possible to isolate appreciable amounts of elemental sulfur during leaching sulfides in ammoniacal solutions and in chlorine water in presence of tetrachloroethene, $Cl_2C{=}CCl_2$ (boiling point 121 "C, density 1.625), also known as perchloroethylene, although in absence of the organic solvent only a trace of elemental sulfur is formed. The organic solvent extracts the sulfur during leaching and thus protects it from further oxidation.

When solid elemental sulfur is liberated during leaching it is usually porous and does not form an obstacle. However, when it melts it usually forms a viscous layer around the mineral particles and retards the rate of leaching. This can be solved by adding a surface active agent such as Lignosol during leaching which helps the sulfur globules to coalease thus they do not cover the mineral particles. Finely crushed coal, when added in small amounts (about 4 kg/ton concentrate), was found to prevent the agglomeration phenomenon.

In the elemental form, sulfur can be readily stock-piled, shipped long distances, or transformed into H_2SO_4 or SO_2 when needed. It is thus evident that leaching methods resulting in elemental sulfur formation are more attractive than the others. Since elemental sulfur may be a product of leaching, its physical and chemical properties will be briefly reviewed.

ELEMENTAL SULFUR

Physical properties

Elemental sulfur is a yellow crystalline solid made of octagonal rings. The sulfur atoms in these rings are connected together by covalent bonds, while the rings are attached to each other by van der Waals' forces. The solid undergoes slow transformation at 95.4 °C from rhombic to monoclinic. The transformation is reversible, and both forms are soluble in carbon disulfide. Once in the monoclinic form, elemental sulfur melts at 119.5 "C to form a yellow fluid liquid (λ sulfur). If, on the other hand, sulfur is heated rapidly such that it will have no time to undergo the slow phase transformation, it will melt at 112.8 °C to form the λ form. In this form the octagonal ring structure is still conserved. However, on further heating it slowly breaks down: The resulting short chains connect together to form long chains, until at 160 "C the transformation is complete and a viscous dark red brown liquid (μ sulfur) is obtained (Figure 12.4). The high viscosity of this form of sulfur is due to the entanglement of the chains and thus the difficulty to flow (Figure 12.5). If quenched, a rubber-like solid is obtained which is insoluble in carbon disulfide. For this reason filtration of liquid sulfur is always done at the temperature where viscosity is minimum, i.e., between 130 and 150 "C.

On further heating above 160 "C, the long chains start to break down to smaller units and thus the viscosity decreases until at 250 "C a fluid dark red brown liquid is obtained (π sulfur) composed mainly of S_8 and S_4 chains. At 444.6 "C liquid sulfur boils and the species S_8 and S_4 are also present in the vapor state. These break down with increased temperature: At 900 "C the S_2 units are only present and at 1800 "C monoatomic sulfur is formed. All transformations are reversible (Table 12.1).

Chemical properties

Elemental sulfur is stable in acid medium but oxidizes slowly in water at high temperature (above I 50 "C) and oxygen pressure to form sulfuric acid:

$$S + {}^{3}/_{2}O_2 + H_2O \rightarrow H_2SO_4$$

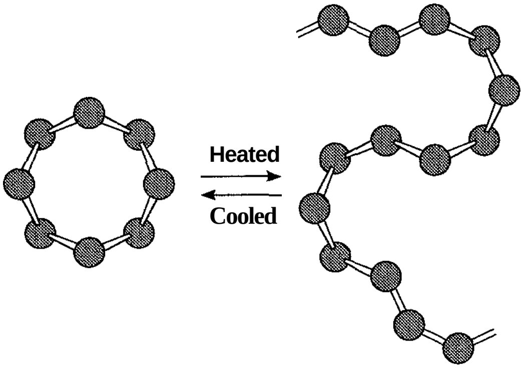


Figure 12.4: Transformation of sulfur from the λ form (fluid) to the μ form (viscous) by heating to below 160 °C.

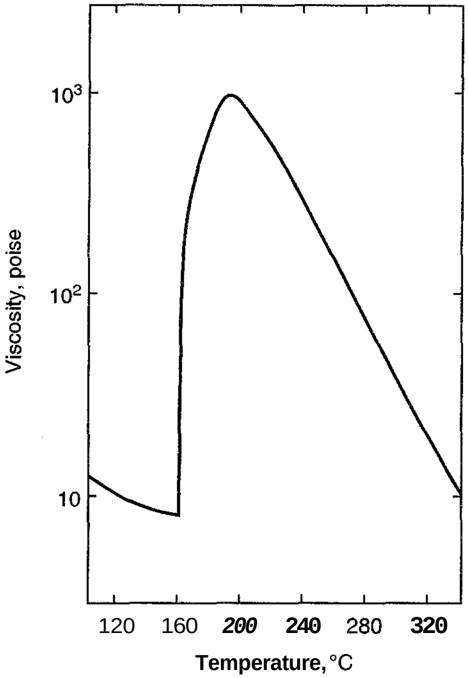


Figure 12.5: Effect of temperature on the viscosity of elemental sulfur.

In basic medium, oxidation takes place in stages whereby, thiosulfate and other sulfur compounds are formed (Table 12.2):

$$2S + O_2 + 2OH^- \rightarrow S_2O_3^{2-} + H_2O$$

These finally oxidize to sulfate as follows:

$$S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O$$

Other oxidizing agents such as HNO_3 and aqueous chlorine solutions react readily with elemental sulfur even at room temperature transforming it into sulfate:

$$S + 2HNO_3 \rightarrow H_2SO_4 + 2NO$$

$$S + 3Cl_2 + 4H_2O \rightarrow H_2SO_4 + 6HCl$$

Concentrated H_2SO_4 above 200 °C also attacks elemental sulhr:

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

A summary of the reactions of elemental sulfur is given in Table 12.3.

Table 12.1: Physical properties of elemental sulfur.

112.8 ″C **(rapid** heating)

	95.4 °C		119.5 °C		160 °C		250 °C		444.6 °C		900 °C		1800 °C	
								$S_8 + S_4$	⇌	$S_8 + S_4$	⇌	S_2	⇌	
α		β		λ		μ		π						
Solid		Solid		Very fluid liquid		Very viscous liquid		Fluid liquid		Gas		Gas		Gas
Rhombic		Monoclinic		Octagonal rings		Long chains (polymer)		Chains						
Yellow		Yellow		Yellow		Dark red brown		Dark red brown						
Soluble in CS_2		Soluble in CS_2												

Table 12.2: Oxidation products of sulfides in neutral or alkaline medium.

$S_2O_3^{2-}$	Thiosulfate
$S_nO_6^{2-}$	Polythionate
$S_2O_6^{2-}$	Dithionate
$S_2O_4^{2-}$	Dithionite (or hyposulfite)
SO_2^{2-}	Sulfoxylate

Table 12.3: Reactions of elemental sulfur.

Medium	Temperature, °C	Reaction
Dilute H_2SO_4 and oxygen	< 150	Stable
Water and oxygen	> 150	$S + {}^3/_2O_2 + H_2O \rightarrow H_2SO_4$
Basic	100	$2S + O_2 + 2OH^- \rightarrow S_2O_3^{2-} + H_2O$ $S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O$
Nitric acid	Ambient	$S + 2HNO_3 \rightarrow H_2SO_4 + 2NO$
Aqueous chlorine	Ambient	$S + 3Cl_2 + 4H_2O \rightarrow H_2SO_4 + 6HCl$
Concentrated H_2SO_4	> 150	$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$

Determination

Elemental sulfur is usually determined in hydrometallurgical residues by extraction with carbon disulfide using Soxhlet extractor (Figure 12.6). A weighed sample of the residue is put in a glass thimble with a porous bottom. The thimble is put in the siphon part of the apparatus; the condenser and flask containing solvent are then assembled. The flask is heated gradually until the solvent is at the boiling point. The vapors ascend through the side arm of the extractor then condense and drip into the thimble. The rate of extraction can be varied by adjusting the heat. When the extractor is filled to the top of the side arm, the solvent now containing dissolved sulfur from the sample, siphons over into the flask. Thus, the apparatus permits to make a series of extractions with fresh solvent, draining the solvent automatically. When extraction is complete and all the solvent has been siphoned into the flask, heating is stopped, the unit allowed to cool, then disconnected, the thimble dried, and the loss in weight determined; this represents the elemental sulfur extracted.

Recovery from leach residue

Numerous methods have been proposed to recover elemental sulfur from leach residues, for example, flotation, hot filtration at about 150 "C (minimum viscosity), extraction by organic solvents, and evaporation. When leaching is conducted under pressure at a temperature below the melting point of sulfur, then at the end of leaching the temperature may be raised for few minutes to 150 "C to melt the sulfur and the contents of the autoclave are collected in two ways:

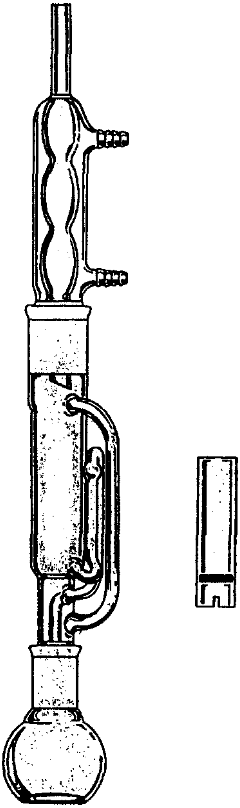


Figure 12.6: Soxhlet extractor. Thimble, to the right, to be inserted in the middle part.

- Discharged in a closed settling tank. Liquid sulfur separates at the bottom and is discharged from time to time while the aqueous slurry is directed to the heat recovery system (flash tank).
- The contents of the autoclave is sent directly to the flash tank. There the slurry cools down and elemental sulfur forms spherical pellets 0.1 to 1 cm in diameter which can be separated by sieving; the residue passes through the sieve, while the sulfur pellets are retained.

In both cases the slurry is then filtered in the usual way to separate the gangue minerals. It was found that any unreacted sulfides adhere to the sulfur. Purification of sulfur is usually conducted by hot filtration.

Figure 12.7 shows a general scheme for the recovery of elemental sulfur.

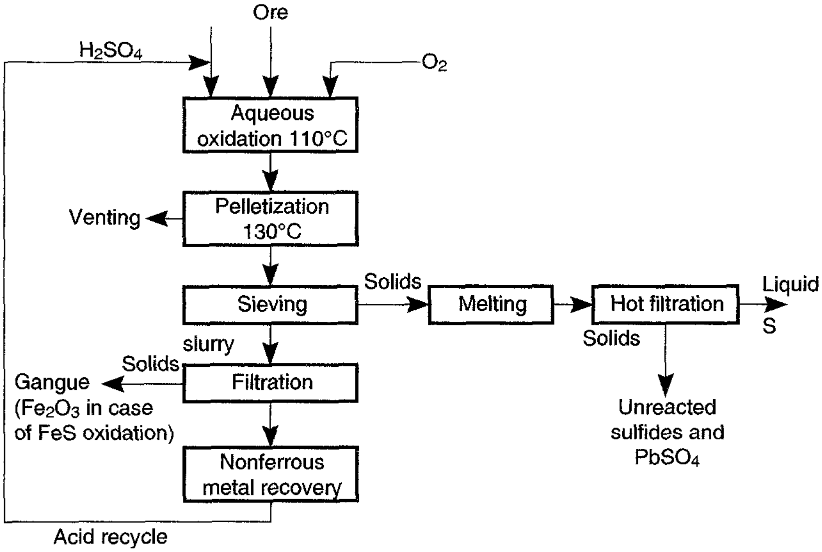


Figure 12.7: A scheme for the recovery of elemental sulfur when leaching sulfide ores.

LEACHING IN ABSENCE OF OXIDIZING AGENTS

Few sulfides are amenable to this method of treatment; these are the acid-soluble, the alkali-soluble, and the complex-forming sulfides.

Reactions

The principal reaction is the dissociation of the solid sulfide in the aqueous phase:

$$MS \rightarrow M^{2+} + S^{2-}$$

followed by reaction with the leaching agent as follows:

Acid-soluble sulfides. This is the case of NiS, CoS, ZnS, and FeS. When an acid is used for leaching, then hydrogen sulfide is formed:

$$S^{2-} + 2H^+ \rightarrow H_2S$$

Hydrogen sulfide liberated can be readily converted to elemental sulfur by controlled oxidation at 400 °C on Al_2O_3 catalyst (Claus Process):

$$H_2S + {}^1/_2O_2 \rightarrow S + H_2O$$

If sulfurous acid is used for leaching, elemental sulfur will form directly in the reactor (see page 84):

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

Alkali-soluble sulfides. This is the case of PbS and ZnS. When a base is used then the metal ion forms a stable anion with the base:

$$M^{2+} + 4OH^- \rightarrow MO_2^{2-} + 2H_2O$$

Complex-forming sulfides. This is the case of As_2O_3, Sb_2S_3, SnS, SnS_2, Bi_2S_3, and HgS. When sodium sulfide is used then complex formation takes place:

$$MS + S^{2-} \rightarrow MS_2^{2-}$$

Applications

Few industrial processes are used applying this technology:

Hydrochloric acid process. The Falconbridge Company developed a commercial process for the treatment of a mixture of Cu_2S–Ni_3S_2 obtained by smelting a copper–nickel sulfide concentrate: Ni_3S_2 is solubilized in concentrated HCl while Cu_2S is not. The leaching reaction is:

$$Ni_3S_2 + 6HCl \rightarrow 3NiCl_2 + 2H_2S + H_2$$

Cu_2S is separated by filtration for copper recovery, while $NiCl_2$ solution is first purified from dissolved H_2S by air oxidation and removal of the sulfur formed, then crystallized as $NiCl_2 \cdot 2H_2O$. Since it is technically difficult to reduce $NiCl_2$ by hydrogen to nickel, the chloride is first calcined to NiO then reduced:

$$NiCl_2 \cdot 2H_2O \rightarrow NiO + 2HCl$$

$$NiO + H_2 \rightarrow Ni + H_2O$$

Sodium sulfide process. The presence of arsenic and antimony in copper sulfide concentrates is undesirable because these metals complicate the smelting and refining of copper. As a result there is interest to remove them before smelting. One route is leaching the concentrate by an alkaline sodium sulfide solution. A copper sulfide concentrate containing 4% As and 7% Sb is treated in British Columbia by Equity Silver Company by this method. The finely divided concentrate is leached for 16 hours at 110 °C to solubilize arsenic and antimony sulfides:

$$As_2S_3 + 3S^{2-} \rightarrow 2AsS_3^{3-}$$

$$Sb_2S_3 + 3S^{2-} \rightarrow 2SbS_3^{3-}$$

After filtration, the copper concentrate is shipped to smelters. The leach solution contains 30 g/L As and 53 g/L Sb. It can be treated in two ways:

- Electrolyzed in a diaphragm cell to get antimony and regenerate the leach solution:

  $$SbS_3^{2-} + 4e^- \rightarrow Sb + 3S^{2-}$$

- Treated with oxygen in autoclaves at 150 °C and 550 kPa to decompose the antimony thiocomplex:

  $$Na_3SbS_3 + 4NaOH + H_2O + {}^{13}/_2O_2 \rightarrow NaSb(OH)_6 + 3Na_2SO_4$$

In the flash evaporator, precipitation of sodium antimonate, $NaSb(OH)_6$, takes place; it is filtered off and recovered. Arsenic remaining in solution is then precipitated by lime in another autoclave at 1600 kPa oxygen pressure to precipitate calcium arsenate:

$$2Na_3AsS_3 + 3Ca(OH)_2 + 13O_2 \rightarrow Ca_3(AsO_4)_2 + 3Na_2SO_4 + 3H_2SO_4$$

This is filtered off and packed for disposal. The remaining solution containing sodium sulfate is evaporated to crystallize $Na_2SO_4 \cdot 10H_2O$. Due to the presence of traces of arsenic in the crystals, these are redissolved and retreated with lime in autoclave to precipitate the remaining arsenic. Pure sodium sulfate is then obtained by crystallization. The plant, however, was shut down for economic reasons.

LEACHING IN PRESENCE OF OXIDIZING AGENTS

Most commonly used oxidizing agents are: Oxygen, ferric ion, nitric acid, concentrated H_2SO_4, chlorine water, and sodium hypochlorite.

Mechanism

Leaching of sulfides in presence of oxidizing agents may be chemical or electrochemical.

Chemical processes. These may lead to the formation of sulfates or elemental sulfur.

- *Sulfates.* These processes usually take place in neutral medium. They are slow at ambient conditions, but rapid at high temperature:

  $$MS \rightarrow M^{2+} + S^{2-}$$

  $$S^{2-} + 2O_2 \rightarrow SO_4^{2-}$$

- *Elemental sulfur.* This is usually the case for acid-soluble sulfides, e.g., ferrous sulfide:

  $$FeS \rightleftharpoons Fe^{2+} + S^{2-}$$

  $$S^{2-} + 2H^+ \rightarrow H_2S$$

  $$H_2S + {}^1/_2O_2 \rightarrow S + H_2O$$

Electrochemical processes. These processes usually take place with acid-insoluble sulfides and lead to the initial formation of elemental sulfur which may be oxidized further depending on the leaching conditions (temperature, pH, and electrode potential of the oxidizing agent as discussed earlier): The electrochemical process may be represented by:

$$\text{Oxidation: } MS \rightarrow M^{2+} + S + 2e^-$$

$$\text{Reduction: Oxidizing agent} + ne^- \rightarrow \text{Reduced species}$$

Typical reduction reactions are the following:

In neutral medium: $^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

In acid medium: $^1/_2O_2 + 2H^+ + 2e- \rightarrow H_2O$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

Oxygen as an oxidizing agent has the advantage that it does not need to be regenerated, and does not result in a foreign ion that contaminates the product. For example, when $FeCl_3$ is used as a leaching agent, it is reduced to $FeCl_2$ during the course of reaction and has to be separated and oxidized back for recycle. The aqueous oxidation of sulfides by oxygen at ambient conditions is a slow process; it is greatly accelerated if conducted at high temperature and high oxygen pressure. Oxygen can be used in combination with water, dilute acid (usually H_2SO_4), and ammonium hydroxide. The latter case is used only for leaching copper, nickel, and cobalt since these metals are capable of forming ammine complexes in solution.

Oxygen and water

The reaction:

$$MS + 2O_{2(aq)} \rightarrow MSO_4$$

takes place at a reasonable rare only at high temperature and pressure. This method of treatment finds the following applications:

- *Dissolution of nickel, cobalt, and copper sulfides.* In these cases a temperature of 200 °C and an oxygen pressure of *4000* kPa are needed; the reaction is complete in 2–3 hours.
- *Reaction of molybdenum sulfide.* For molybdenite, hydrolysis accompanies oxidation and as a result molybdic acid is formed as a white precipitate:

$$MoS_2 \rightleftharpoons Mo^{4+} + 2S^{2-}$$

$$Mo^{4+} + 3H_2O + {}^1/_2O_2 \rightarrow H_2MoO_4 + 4H^+$$

$$S^{2-} + 20, \rightarrow SO_4^{2-}$$

Overall reaction:

$$MoS_2 + 3H_2O + {}^9/_2O_2 \rightarrow H_2MoO_4 + 2H_2SO_4$$

Rhenium associated with molybdenum in molybdenite is expected to be in solution.

- *Removal of undesirable components of a concentrate.* For example, the purification of lead concentrates. In this case zinc, copper, arsenic, and antimony sulfides are solubilized and a purified lead sulfate residue is obtained (Table 12.4) which is then treated by pyrometallurgical method (Bunker Hill Process, Kellogg, Idaho). The leach solution is purified and treated for copper and zinc recovery. The process was, however, shut down.

Table 12.4: Aqueous oxidation of Pb–Zn sulfide concentrate by air and water at 220 °C and 5500 kPa.

	Feed, Yo	Residue, Yo	Solution, g/L
Pb	50.6	51.2	Trace
Zn	8.7	1.2	*49.5*
cu	6.5	0.8	*47.8*

Oxygen and ammonia

The process is used for treating concentrates of copper, nickel, and cobalt since they form soluble ammine complexes. The process has minimum corrosion problems and any pyrite present will not be attacked. Ammonium sulfate is a by-product; it is marketed as a fertilizer. The overall reaction is:

$$MS + nNH_3 + 2O_2 \rightarrow [M(NH_3)_n]^{2+} + SO_4^{2-}$$

Oxidation of sulfides in an alkaline medium takes place in several stages and any of the intermediate compounds: Polysulfide, thiosulfate, etc., may be present in the leach solution. The leach solution is also free from iron, since hydrated ferric oxide is precipitated. It is important to control the amount of free ammonia in solution otherwise higher ammines like cobalt hexammine complex, which is insoluble, will be formed. The method has been used successfully since 1953 for the treatment of Ni–Cu–Co sulfide concentrate on large scale at the Sherritt-Gordon Plant in Fort Saskatchewan, Canada. In this process all the sulfur is oxidized and recovered as ammonium sulfate and marketed as fertilizer. Analysis of the concentrate treated is given in Table 12.5.

Table 12.5: Pressure leaching of Sherritt-Gordon sulfide concentrate.

	Flotation concentrate, %	Residue, %
Ni	10–14	*0.6–1.4*
Cu	1–2	0.2–0.3
Co	0.3–0.4	0.1–0.2
Fe	33–40	*42–52*
S	28–34	9–15
Insol.	8–14	12–16

The process involves the following steps (Figure 12.8):

- *Leaching.* The concentrate is mixed with water and ammonia and leached in autoclaves under air pressure of 700 kPa and at 70–80 "C for 20–24 hours. Reaction is exothermic and therefore extra heating of the autoclaves is not required.

- *Purification.* The leach solution contains beside nickel and cobalt ammines, excess ammonia, copper, thiosulfates, and thionates. Ammonia is removed by distillation and is recovered in scrubbers. During distillation most of the dissolved copper is precipitated as sulfide:

$$S_3O_6^{2-} + [Cu(NH_3)_4]^{2+} + 2H_2O \rightarrow 2SO_4^{2-} + CuS + 4NH_4^+$$

$$\begin{aligned} S_2O_3^{2-} + [Cu(NH_3)_4]^{2+} + H_2O \rightarrow \\ SO_4^{2-} + CuS + 2NH_4^+ + 2NH_3 \end{aligned}$$

After filtration, the residual copper (about 1 g/L) is precipitated by a controlled amount of H_2S in autoclaves at 130 "C. This second precipitate contains some NiS and is recycled to the leaching stage.

- *Oxyhydrolysis.* In this step oxidation of thionates and hydrolyzing sulfamate takes place. The presence of thiosulfates and thionates in a nickel or a cobalt solution is undesirable because it leads to contamination of the fertilizer produced later. For this reason the copper-free solution is then digested at 175–200 "C in an autoclave in the presence of compressed air at 4200 kPa for two reasons:

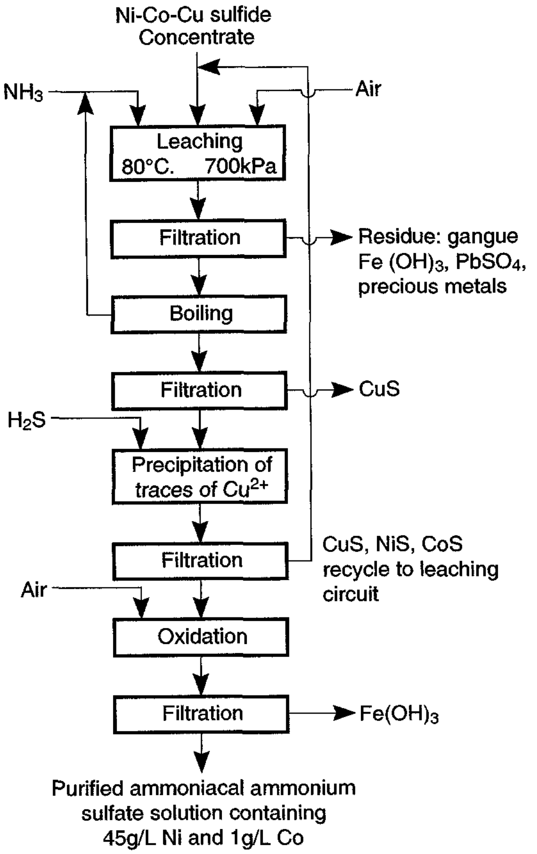


Figure 12.8: Pressure leaching of Ni–Co–Cu sulfide concentrate; the Sherritt-Gordon process.

- To oxidize thiosulfates and thionates to sulfates:

$$S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O$$

- To oxidize traces of ferrous ion to ferric, which is hydrolyzed and precipitated.

The purified solution upon clarification contains 45 g/L nickel and 1 g/L cobalt as ammines, and ammonium sulfate.

- *Recovery.* This involves the precipitation of metallic nickel by hydrogen, oxidation of Co^{2+} to Co^{3+} by air, then precipitation of metallic cobalt by hydrogen. The remaining solution is evaporated and the crystals of ammonium sulfate separated and sold as fertilizer. Precious metals, if present, remain in the residue and may be recovered by a separate leaching cycle.

Oxygen and a base

Molybdenite can be solubilized by aqueous oxidation in an alkaline medium to form molybdates:

$$MoS_2 \rightleftharpoons Mo^{4+} + 2S^{2-}$$

$$Mo^{4+} + 6OH^- + {}^1/_2O_2 \rightarrow MoO_4^{2-} + 3H_2O$$

$$S^{2-} + 2O_2 \rightarrow SO_4^{2-}$$

Overall reaction:

$$MoS_2 + 6OH^- + {}^9/_2O_2 \rightarrow MoO_4^{2-} + 2SO_4^{2-} + 3H_2O$$

Oxygen and acid

This method is usually conducted at 115–150 °C so that elemental sulfur can be recovered in good yield. However, industrial operations are also conducted at high temperature where no elemental sulfur is formed, for example, in the treatment of Ni_3S_2. The method is most suitable when the metal values in the leach solution can be recovered by electrolysis so that the acid generated during the recovery step can be recycled to the leaching step (Figure 12.9). Because of the high temperature and the acid medium involved, acid-resisting materials of construction must be used. The following examples may be cited.

Zinc sulfide. The reaction is conducted at 150 °C and 700 kPa oxygen pressure:

$$ZnS + 2H^+ + {}^1/2O_2 \rightarrow Zn^{2+} + S + H_2O$$

This process which is now used in Canada (Figure 12.10) solves two problems facing the hydrometallurgical zinc process:

- All the zinc goes into solution because no ferrites are formed.
- The process is independent of fertilizer manufacture because no sulfur dioxide is formed.

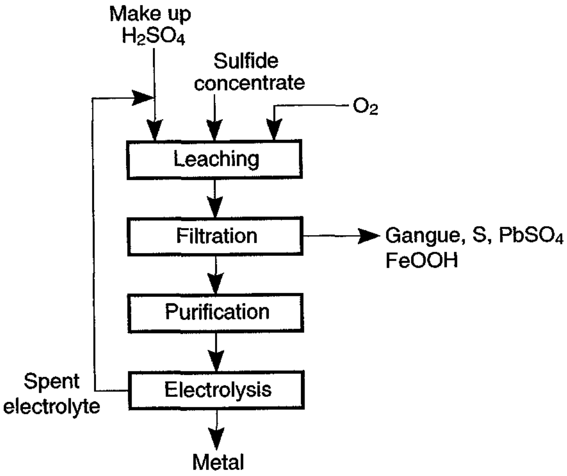


Figure 12.9: Flowsheet for the aqueous oxidation of sulfide concentrates in acid medium.

Chalcopyrite. The reaction takes place at 115–150 °C and about 2000 kPa oxygen pressure:

$$2CuFeS_2 + 4H^+ + {}^5/_2O_2 \rightarrow 2Cu^{2+} + 2FeOOH + 4S + H_2O$$

This process has the advantage that iron is separated as an insoluble residue because of the oxidation of ferrous ion to ferric and its hydrolysis:

$$2Fe^{2+} + 2H^+ + {}^1/_2O_2 \rightarrow 2Fe^{3+} + H_2O$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+$$

The process was developed by Sherritt Gordon in Canada, now known as Dynatec Process. A variation developped by Cominco Engineering, also in Canada, known as CESL process takes place in two steps. In the first step, leaching is conducted under mild acid conditions (pH about 3) and in presence of a mixture of HCl and H_2SO_4. Under such conditions copper hydroxysulfate is formed which is solubilized in a second step at atmospheric presure in dilute H_2SO_4. There is no obvious advantage, however, in this process as compared to Dynatec. In both processes, the precious metals are recovered from the residue by cyanidation after the flotation of elemental sulfur.

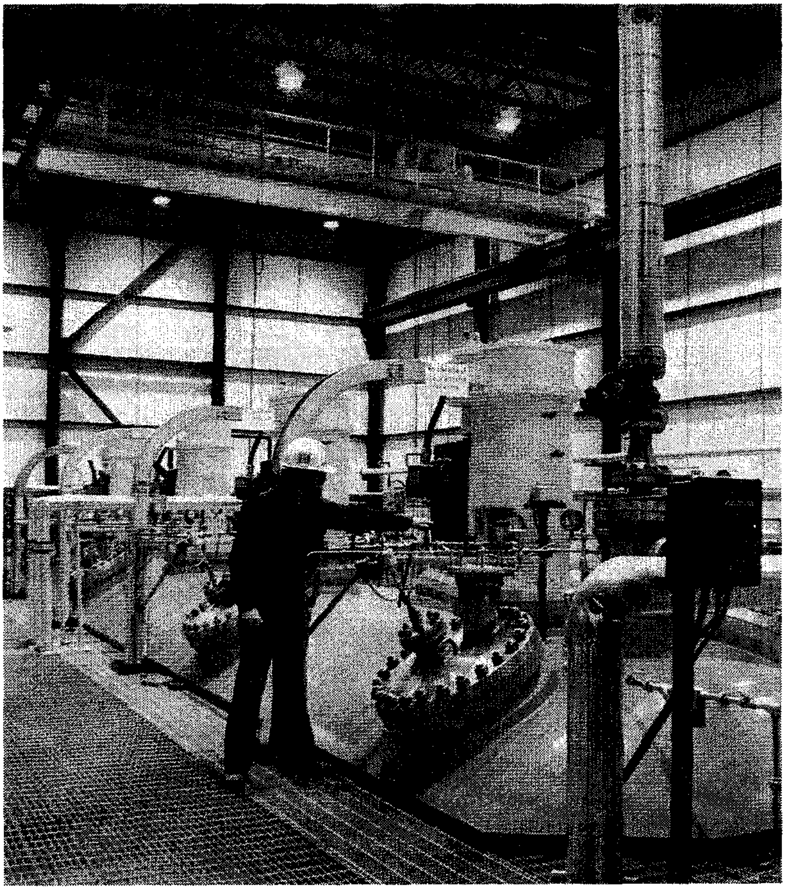


Figure **12.10:** Pressure leaching plant of zinc sulfide concentrates at Cominco, Trail, British Columbia (Sherritt-Gordon).

In an attempt to solubilize simultaneously copper and any gold present in chalcopyrite, the Halex process was developed by Intec Copper Proprietary in Australia. The leach solution contains large amounts of NaCl and NaBr in circulation between the copper electrowinning stage and a diaphragm cell in which the following reaction takes place at the anode compartment:

$$Br^- + 2Cl^- \rightarrow BrCl_2^- + 2e-$$

It is claimed that the $BrCl_2^-$ ion, called Halex, can solubilize chalcopyrite and gold:

$$2CuFeS_2 + 5BrCl_2^- \rightarrow 2Cu^{2+} + 2Fe^{3+} + 4S + 5Br^- + 10Cl^-$$

$$Au + 4Cl^- \rightarrow AuCl_4^- + 3e-$$

$$Au + 4Br^- \rightarrow AuBr_4^- + 3e-$$

Nickel sulfide. Nickel sulfide, Ni_3S_2, also known as white metal, is obtained by smelting nickel sulfide or nickel–copper sulfide concentrates to form matte from which iron sulfide is then removed by oxidation and slagging. At Impala in South Africa, in Botswana in Africa, and in Germany the white metal is treated by oxygen in acid medium:

$$Ni_3S_2 + {}^9/_2O_2 + 2H^+ \rightarrow 3Ni^{2+} + 2SO_4^{2-} + H_2O$$

$$Cu_2S + {}^5/_2O_2 + 2H^+ \rightarrow 2Cu^{2+} + SO_4^{2-} + H_2O$$

Copper in solution is then precipitated by adding fresh white metal whereby more nickel sulfide is solubilized:

$$Ni_3S_2 + 3Cu^{2+} \rightarrow 3Ni^{2+} + CuS + Cu_2S$$

Pyrrhotite. Pyrrhotite is used mainly for making sulfuric acid. However, transportation cost to sulfuric acid manufacturers may be prohibitive. It was realized a long time ago that a process for recovering elemental sulfur from iron sulfide would be attractive. Pyrrhotite is slowly solubilized in water at 110 °C and 200 kPa oxygen pressure as ferrous sulfate:

$$FeS + 2O_{2(aq)} \rightarrow FeSO_{4(aq)}$$

If, however, the reaction is conducted in presence of dilute acid (0.1 M), the formation of elemental sulfur and ferric oxide takes place:

$$2FeS + {}^3/_2O_{2(aq)} \xrightarrow{H^+} Fe_2O_3 + 2S$$

It will be also observed that the acid initially added will be present unchanged at the end of reaction. In fact the acid is consumed at the initial stage of the reaction and then regenerated later (Figure 12.11). It should be observed that the oxygen utilization in the presence of acid is less than in the first case. The reaction may be chemical or electrochemical in nature:

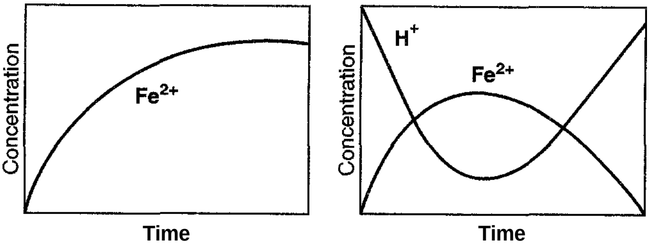


Figure 12.11: Aqueous oxidation of ferrous sulfide or pyrrhotite. Left: in absence of acid; Right: in presence of acid (From data by Downes and Bruce, 1955).

Chemical:

$$FeS \rightleftarrows Fe^{2+} + S^{2-}$$

$$S^{2-} + 2H^+ \rightarrow H_2S$$

$$H_2S + {}^1/_2O_2 \rightarrow S + H_2O$$

Electrochemical:

Cathodic reaction: $^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Anodic reaction: $FeS \rightarrow Fe^{2+} + S + 2e-$

In both cases the oxidation of Fe^{2+} ion to Fe^{3+} and its hydrolysis follow the reactions:

$$2Fe^{2+} + 2H^+ + {}^1/_2O_2 \rightarrow 2Fe^{3+} + H20$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

It can be seen that in absence of acid the Oxidation of ferrous ion to ferric is not possible. That is why FeS suspended in water will yield only a solution of $FeSO_4$ when oxidized. In presence of acid, however, the formation of Fe^{3+} becomes possible, but because of hydrolysis, Fe_2O_3 is formed and the acid is regenerated. Thus, it seems as if the acid acted as a catalyst.

Ferric salts

Leaching of sulfides in acid medium in presence of ferric chloride or ferric sulfate takes place readily with liberation of elemental sulfur. The disadvantage of this route is the formation of ferrous ion, which requires separation and reoxidation to ferric for reecycle. This method has found the following applications:

- *Leacbing of copper sulfides in dumps or in situ.* The dissolution of cuprous sulfide takes place in steps as follows:

  $$5Cu_2S + 2Fe^{3+} \rightarrow Cu_9S_5 + Cu^{2+} + 2Fe^{2+}$$

  $$Cu_9S_5 + 8Fe^{3+} \rightarrow 5CuS + 4Cu^{2+} + 8Fe^{2+}$$

  $$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S$$

- *Purification of molybdenite concentrates.* Copper sulfide impurities are removed from MoS_2 by boiling with $FeCl_3$ solutions.
- *Leaching of chalcopyrite concentrates.* Leaching of chalcopyrite with ferric ion takes place readily at the boiling point:

  $$CuFeS_2 + 3Fe^{3+} \rightarrow Cu^{+} + 4Fe^{2+} + 2S$$

  Copper is solubilized in the cuprous form, but in presence of excess Fe^{3+} the cuprous is oxidized to cupric:

  $$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S$$

  Although CuCl has a low solubility in water, yet, due to the presence of Fe^{2+} ion in the leach solution it is completely soluble. The fact that CuCl can be obtained instead of $CuCl_2$ under carefully controlled conditions is of importance in the subsequent recovery step, since Cu^{+} ion is easier to reduce than Cu^{2+} ion, e.g., by precipitation with iron:

  $$2Cu^{+} + Fe \rightarrow 2Cu + Fe^{2+}$$

  Ferrous chloride can be partly crystallized and treated further for HCl regeneration while the remainder in solution is oxidized to $FeCl_3$ for recycle. Oxidation of $FeCl_2$ is usually conducted by chlorine:

  $$FeCl_2 + {}^{1}/{}_{2}Cl_{2(aq)} \rightarrow FeCl_3$$

  A flowsheet of the proposed process is shown in Figure 12.12.

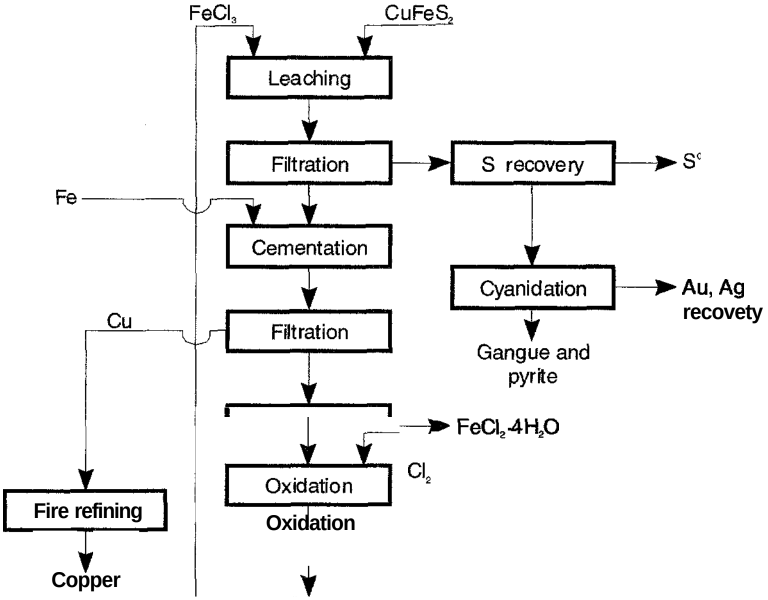


Figure 12.12: The proposed treatment of chalcopyrite by $FeCl_3$ solution.

- *Leaching of lead sulfide concentrates.* This usually takes place in presence of a concentrated solution of NaCl so that lead chloride produced is solubilized as a complex chloride:

$$PbS + 2Fe^{3+} + 4Cl^- \rightarrow PbCl_4^{2-} + 2Fe^{2+} + S$$

After hot filtration to separate the gangue minerals, the solution is cooled to crystallize pure $PbCl_2$, which is then separated and electrolyzed in the fused state to recover lead and chlorine; the latter is to be used for the generation of the leaching agent as proposed in Figure 12.13.

Concentrated H_2SO_4

Concentrated H_2SO_4 reacts with sulfides at 150–200 °C liberating elemental sulfur:

$$MS \rightarrow M^{2+} + S + 2e^-$$

$$4H^+ + SO_4^{2-} + 2e^- \rightarrow SO, \ + 2H_2O$$

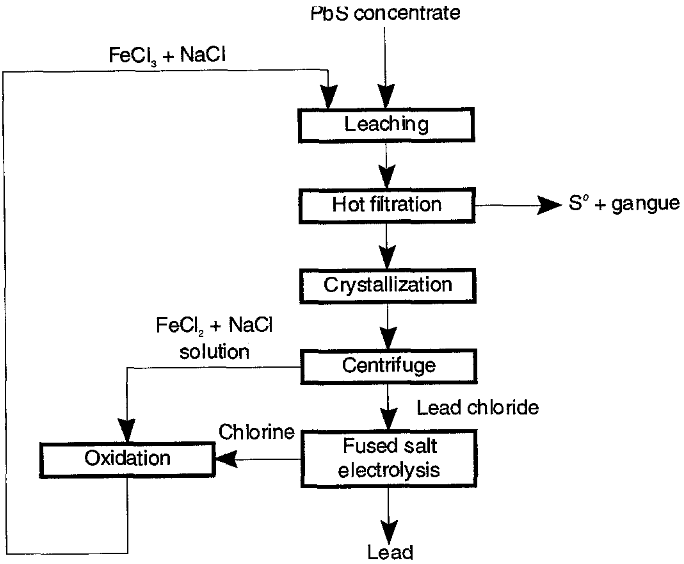


Figure 12.13: Proposed process for lead recovery by ferric chloride leaching of galena.

The temperature and the quantity of acid must be carefully controlled otherwise a part or all the sulfur will react further to form SO_2:

$$2H_2SO_4 + S \rightarrow 3SO_2 + 2H_2O$$

Sulfur dioxide formed is collected and transformed to sulfuric acid for recycle to supply one half of the acid requirement. The other half should come from the metal sulfate solution. This can be accomplished during the metal recovery step, e.g., by electrolysis where one mole H_2SO_4 is generated for each metal equivalent produced. The problem with this process is, however, that the acid generated during electrolysis has to be concentrated to the strength required for leaching: this may be uneconomical (Figure 12.14).

Due to the evolution of SO_2 and H_2O during the reaction, the liquid/solid ratio decreases gradually and as a result the reaction mixture solidifies. The reaction must be conducted, therefore, in two steps: agitation leaching followed by baking. For example:

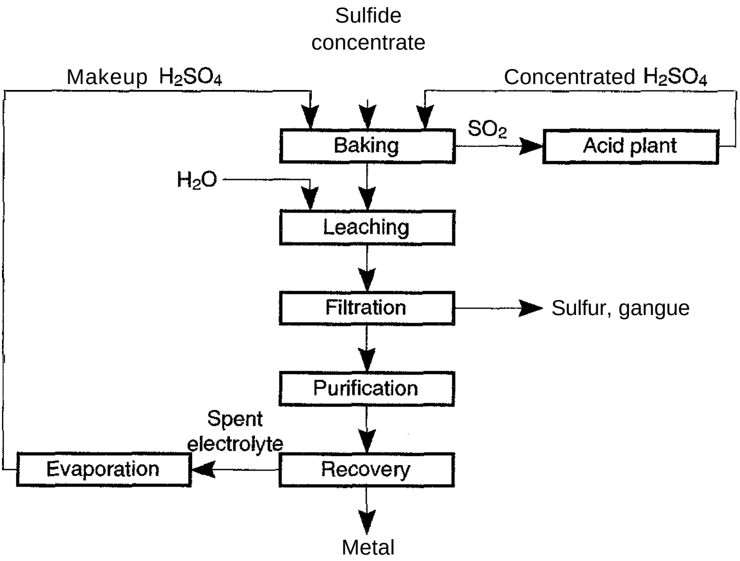


Figure 12.14: Treatment of sulfides by concentrated H_2SO_4.

Chalcopyrite. Leaching of chalcopyrite by concentrated H_2SO_4 has been studied and developed to a large scale pilot plant (The Treadwell Process):

- Below 150 "C, no reaction.
- Between 150 "C and 250 "C, there is a formation of elemental sulfur, $CuSO_4$, and $FeSO_4$. Since chalcopyrite ($Cu_2S \cdot Fe_2S_3$) contains Cu^+ and Fe^{3+} ions in the crystal structure, the formation of $CuSO_4$ and $FeSO_4$ (and not Cu_2SO_4 and $Fe_2(SO_4)_3$) must be due to an oxidation–reduction reaction that takes place in the solid state during heating:

  $$Cu^+ + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+}$$

  This can be represented by:

  $$Cu_2S \cdot Fe_2S_3 \rightarrow 2(CuS \cdot FeS)$$

  $$CuS \cdot FeS \rightarrow Cu^{2+} + Fe^{2+} + 2S + 4e-$$

  $$4H^+ + SO_4^{2-} + 2e- \rightarrow SO_2 + 2H_2O$$

  Overall reaction:

  $$CuFeS_2 + 8H^+ + 2SO_4^{2-} \rightarrow Cu^{2+} + Fe^{2+} + 2S + 2SO_2 + 4H_2O$$

- Above 250 °C, both elemental sulfur and ferrous ion are oxidized:
  - Oxidation of elemental sulfur by concentrated H_2SO_4:

$$H_2SO_4 \rightarrow SO_2 + {}^1/_2O_2 + H_2O$$

$$S + O, \rightarrow SO,$$

$$2H_2SO_4 + S \rightarrow 3SO_2 + 2H_2O$$

  - Oxidation of ferrous ion by concentrated H_2SO_4:

$$Fe^{2+} \rightarrow Fe^{3+} + e–$$

$$4H^+ + SO_4^{2-} + 2e^- + SO_2 + 2H_2O$$

$$2Fe^{2+} + 4H^+ + SO_4^{2-} \rightarrow 2Fe^{3+} + SO_2 + 2H_2O$$

Overall reaction:

$$2CuFeS_2 + 13H_2SO_4 + 10H^+ \rightarrow 2Cu^{2+} + 2Fe^{3+} + 17SO_2 + 18H_2O$$

or

$$2CuFeS_2 + 18H_2SO_4 \rightarrow 2CuSO_4 + Fe_2(SO_4)_2 + 17SO_2 + 18H_2O$$

It is obvious that the optimal reaction conditions are between 150 and 250 °C. The residue containing the anhydrous sulfates, elemental sulfur, and the gangue minerals, is leached with water to solubilize the sulfates, precipitate CuCN by HCN, crystallize $FeSO_4 \cdot nH_2O$ which is then decomposed to recover the SO_3 for recycle as H_2SO_4. The process has the advantage of forming elemental sulfur, but the disadvantage of solubilizing iron and the necessity of regenerating H_2SO_4 by decomposing the ferrous sulfate.

Zinc *sulfide.* Sulfuric acid at a concentration of 83–85% and at 170–190 °C reacts with zinc sulfide simultaneously as an oxidizing and non-oxidizing acid:

$$ZnS + 2H_2SO_4 \rightarrow ZnSO_4 + S + SO_2 + 2H_2O$$

$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S$$

As a result, with a careful control of these variables and the acid–solid ratio, SO_2 formed in the first reaction interacts with H_2S in the second to form elemental sulfur and the overall reaction becomes:

$$3ZnS + 4H_2SO_4 \rightarrow 3ZnSO_4 + 4S + 4H_2O$$

The advantage of this process is the possibility of conducting the reaction at ambient pressure, i.e., no autoclaves are necessary but the acid requirement is more than obtained later during the electrolysis of $ZnSO_4$ solution.

Nitric acid

The use of nitric acid or a mixture of nitric and sulfuric acids has been extensively studied for leaching sulfides but not utilized industrially because of the high cost (p. 78) and the necessity to capture NO and NO, gases for the regeneration of the acid. The yield of elemental sulfur is usually improved when a mixture of HNO_3 and H_2SO_4 is employed. Molybdenite does not yield elemental sulfur, and because of the hydrolysis of Mo^{4+} ions accompanying the oxidation mentioned earlier (p. 302), molybdic acid is obtained:

$$MoS_2 + 6HNO_3 \rightarrow H_2MoO_4 + 2H_2SO_4 + 6NO$$

Chlorine and hypochlorite

Aqueous chlorine solutions solubilize sulfides at ambient conditions with formation of elemental sulfur:

$$MS \rightarrow M^{2+} + S + 2e^-$$

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

At high concentrations, long contact time, or high temperature, elemental sulfur oxidizes to sulfate. Sodium hypochlorite, NaClO, attacks molybdenite in alkaline medium to form soluble molybdate. Also elemental sulfur forms at mild conditions and sulfate at more severe conditions. The process is applied industrially for at least two cases:

- *The treatment of* Ni_3S_2–Cu_2S *(white metal)*. The process is used at the Falconbridge refinery in Sudbury. Both nickel and copper are solubilized, then separation is effected by adding fresh white metal to solubilize more nickel and precipitate the copper:

$$Ni_3S_2 + 3Cu^{2+} \rightarrow 3Ni^{2+} + CuS + Cu_2S$$

When nickel chloride solutions are electrolyzed to recover metallic nickel, chlorine is generated at the anode which is collected and recycled to the leaching step.

- *The treatment of pyrite ores containing gold.* This is the case when gold cannot be recovered by cyanidation; therefore, the pyrite-containing gold is decomposed by chlorine to liberate the gold.

DISULFIDES

Pyrite and arsenopyrite have received great attention recently because in some gold ores called “refractory”, they entrap gold in their crystal structure and render the metal unextractable by cyanide solution unless the mineral structure is destroyed by thermal or aqueous oxidation prior to cyanidation. Pyrite is also the major sulfur-bearing impurity mineral in coal. Attempts to upgrade the coal include the aqueous oxidation of the pyrite.

Pyrite

Pyrite usually accompanies other sulfides and its behavior should be well known. Leaching pyrite at 80 °C can follow two different paths, depending on the pH of the medium: At low pH, the formation of elemental sulfur is favorable, and with increasing pH the formation of sulfate is favorable. The following equations correspond to the extreme cases of decomposition:

$$FeS_2 + 2H^+ + {}^1/_2O_2 \rightarrow Fe^{2+} + H_2O + 2S$$

$$FeS_2 + H_2O + {}^7/_2O_2 \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-}$$

It is evident that the molar ratio $[SO_4^{2-}]/[Fe^{2+}]$ can vary from 0 to 2. Under mild conditions no oxidation of Fe^{2+} takes place, thus minimizing side reactions. From Figure 12.15 it can be seen that below pH 2.5, the ratio $[SO_4^{2-}]/[Fe^{2+}]$ increases linearly from 0 to 2, i.e., at very low pH the first reaction (formation of elemental sulfur) is predominant, while at pH 2.5 the second reaction (formation of sulfate) is predominant. At pH above 3, the ratio $[SO_4^{2-}]/[Fe^{2+}]$ increases rapidly, since Fe^{2+} disappears from solution forming ferric ion, which, at high temperature, hydrolyzes to ferric oxide:

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$$

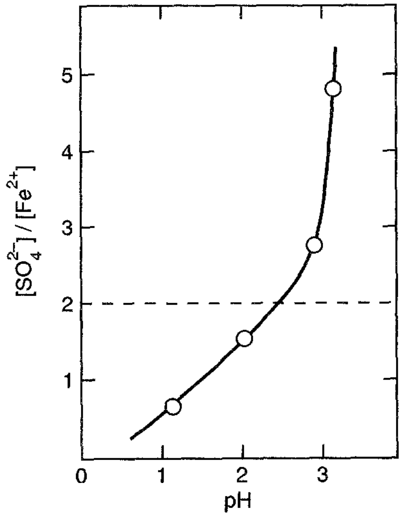


Figure 12.15: Effect of pH on leaching pyrite at 80 °C (Ichikuni, 1960).

A satisfactory explanation of this behavior is as follows. Pyrite dissociates in water forming ferrous ion and disulfide ion:

$$FeS_{2(s)} \rightleftarrows Fe^{2+}_{(aq)} + S^{2-}_{2(aq)}$$

When the disulfide ion reacts further, the equilibrium is shifted to the right, and more pyrite goes into solution. Disulfide ion may undergo auto-oxidation to elemental sulfur and sulfide ion as mentioned earlier (p. 290):

$$S_2^{2-} \rightarrow 2S + 2e^-$$

$$S_2^{2-} + 2e^- \rightarrow 2S^{2-}$$

Overall reaction:

$$S_2^{2-} \rightarrow S + S^{2-}$$

Hence, three paths may arise depending on the conditions:

- *High acidity and the absence of oxygen.* In this case, H_2S **is** formed:

$$S^{2-} + 2H^+ \rightarrow H_2S$$

or $FeS_2 + 2H^+ \rightarrow Fe^{2+} + S + H_2S$

- ***High** acidity and low oxygen concentration.* In this case, elemental sulfur is formed:

  $S^{2-} \rightarrow S + 2e^-$

  $^1/_2O_2 + 2H^+ + 2e- \rightarrow H_2O$

  Overall reaction:

  $S^{2-} + {}^1/_2O_2 + 2H^+ \rightarrow S + H_2O$

  or $FeS_2 + {}^1/_2O_2 + 2H+ \rightarrow Fe^{2+} + 2S + H_2O$

  In this case, the aqueous oxidation of pyrite may be considered to take place by an electrochemical mechanism like other sulfides in acid medium and can be represented by:

  Anodic reaction: $FeS_2 \rightarrow Fe^{2+} + 2S + 2e-$

  Cathodic reaction: $^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

- *In neutral medium and high oxygen concentration.* In this case, it seems that the auto-oxidation of the disulfide ion does not take place because in neutral medium, thiosulfates and other lower-oxidation products were identified. Thiosulfates may, therefore, form directly from the disulfide ion by the following reaction:

  $S_2^{2-} + {}^3/_2O_2 \rightarrow S_2O_3^{2-}$

  which oxidizes further to sulfate:

  $S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e^-$

  $^1/_2O_2 + H_2O + 2e- \rightarrow 2OH^-$

  $H^+ + OH- \rightarrow H_2O$

  The overall reaction in this case is:

  $S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$

  which leads to the global oxidation reaction of pyrite in neutral medium:

  $S_2^{2-} + {}^7/_2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$

  $FeS_2 + {}^7/_2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

  Two points should be noted from the above scheme:

- Pyrite takes up one eighth of its oxygen required for oxidation to sulfate from the water and the remaining from molecular oxygen. This was confirmed experimentally by using radioactive oxygen in following up the reaction.
- Under certain conditions, hydroxyl ions are formed during the oxidation. This was confirmed when pyrite was in contact with water containing agar-agar, thus minimizing the diffusion of OH^- ions (Figure 5.3, page 115). Cathodic regions form on pyrite whereby oxygen is reduced according to:

  $$^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

  while at the anodic zone the following reactions would take place:

  $$FeS_2 \rightarrow Fe^{2+} + S_2^{2-}$$

  $$S_2^{2-} + {}^3/_2O_2 \rightarrow S_2O_3^{2-}$$

  $$S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e-$$

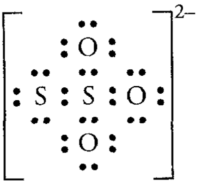
The presence of thiosulfates in waste solutions (Table 12.6) raises an environmental problem because these are usually not precipitated by standard methods like sulfates, e.g., when adding $Ca(OH)_2$. Hence they escape the mine sire and may contaminate surface waters. This topic was the subject of an extensive research project in Canada.

Table 12.6: Relative formation of thiosalts during aeration of sulfide minerals for 5 hours in a flotation cell.

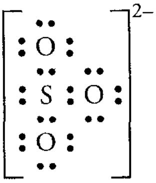
Mineral	Thiosulfate formed, mg/L
Galena	200
Chalcopyrite	300
Sphalerite	300
Pyrrhotite	1500
Pyrite	2700

Sulfites were also identified in deaerated solutions. The relation between disulfide, thiosulfate, sulfites, and sulfate ions is shown schematically below:

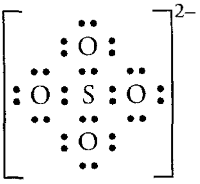
Disulfide



Thiosulfate



Sulfite



Sulfate

Aqueous oxidation at high temperature and pressure in alkaline medium yield Fe_2O_3 and sulfate ions:

$$2FeS_2 + {}^{15}/_2O_2 + 8OH^- \rightarrow Fe_2O_3 + 4SO_4^{2-} + 4H_2O$$

The advantage of such reaction is no corrosion problems but the disadvantage is the high cost of the reagent.

Arsenopyrite

Arsenopyrite may dissociate in water as follows:

$$2FeAsS_{(s)} \rightleftharpoons 2Fe^{2+}_{(aq)} + As^{2-}_{2(aq)} + S^{2-}_{2(aq)}$$

The behavior of disulfide ion is probably the same as in the case of pyrite in acid and in neutral medium, while the diarsenide ion forms arsenic acid:

$$As_2^{2-} + 3O_2 + 2H^+ + 2H_2O \rightarrow 2H_3AsO_4$$

The overall reactions are:

- In acid medium:

$$4FeAsS + 7O_2 + 8H^+ + 2H_2O \rightarrow 4H_3AsO_4 + 4Fe^{2+} + 4S$$

- In neutral medium:

$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4H_3AsO_4 + 4Fe^{2+} + 4SO_4^{2-}$$

- In alkaline medium:

$$2FeAsS + 10OH^- + 7O_2 \rightarrow$$
$$Fe_2O_3 + 2AsO_4^{3-} + 2SO_4^{2-} + 5H_2O$$

Ferrous ion formed in the above reactions oxidizes further to form ferric arsenate precipitates:

$$2Fe^{2+} + {}^{1}/{}_{2}O_2 + 2H^{+} \rightarrow 2Fe^{3+} + H_2O$$

$$Fe^{3+} + H_3AsO_4 + 2H_2O \rightarrow FeAsO_4 + 2H_2O + 3H^{+}$$

Covellite

When covellite is suspended in water, it apparently dissociates as follows:

$$Cu_4^{I}Cu_2^{II}(S_2)_2S_{2(s)} \rightleftharpoons 4Cu^{+}_{(aq)} + 2Cu^{2+}_{(aq)} + 2S^{2-}_{2(aq)} + 2S^{2-}_{(aq)}$$

When oxygen is present, oxidation of Cu^{+}, S_2^{2-}, and S^{2-} ions takes place as follows:

- Oxidation of cuprous ion:

$$Cu^{+} \rightarrow Cu^{2+} + e-$$

$${}^{1}/{}_{2}O_2 + H_2O + 2e- + 2OH^{-}$$

Overall reaction:

$$4Cu^{+} + O_2 + 2H_2O \rightarrow 4Cu^{2+} + 4OH^{-}$$

- Oxidation of disulfide ions:

$$S_2^{2-} + {}^{3}/{}_{2}O_2 \rightarrow S_2O_3^{2-}$$

$$S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^{+} + 8e^{-}$$

$${}^{1}/{}_{2}O_2 + H_2O + 2e- \rightarrow 2OH^{-}$$

Overall reaction:

$$2S_2^{2-} + 7O_2 + 2H_2O \rightarrow 4SO_4^{2-} + 4H^{+}$$

- Oxidation of sulfide ions:

$$S^{2-} + 20, \rightarrow SO_4^{2-}$$

Hence, the overall oxidation of covellite in water can be obtained from the above equations which yield the simple equation:

$$cus + 2O_{2(aq)} \rightarrow Cu^{2+} + SO_4^{2-}$$

This corresponds to what is actually obtained in practice. On the other hand, in acid medium, the sulfide ion will undergo auto-oxidation with the formation of elemental sulfur as shown in the case of pyrite; and the sulfide ion also leads to the formation of elemental sulfur, hence the overall reaction:

$$CuS + {}^{1}/{}_{2}O_2 + 2H^+ \rightarrow Cu^{2+} + S + H_2O$$

SUMMARY

Figure 12.16 and Table 12.7 give a summary of processes used for leaching sulfides. It should be pointed out that these processes has not only found applications in the treatment of sulfide ores and concentrates of copper, lead, zinc, nickel, and cobalt but also for treating the so-called refractory ores, i.e., pyrite containing dissiminated gold that cannot be treated directly by cyanidation. As a result, the sulfide must first be decomposed to liberate the gold so that cyanidation may become possible.

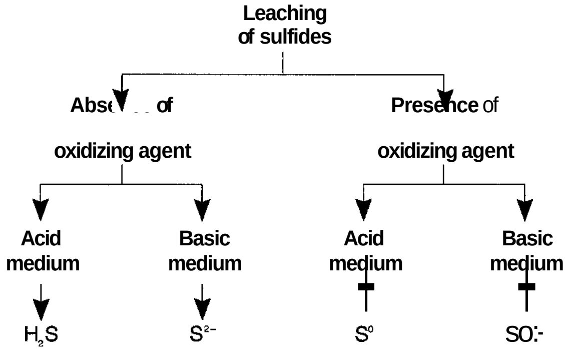


Figure 12.16: Summary of processes for leaching sulfides.

Another potential application is also in the partial desulfurization of coal. Coal contains about 4% sulfur which exists in two forms: Inorganic sulfur which comprises about 80% of the total sulfur (mainly pyrite, a small amount of pyrrhotite and calcium sulfate), and organic sulfur compounds which account for the rest.

The behavior of pyrite, covellite, and arsenopyrite during leaching is different from other sulfides due to the presence of the disulfide ion, S_2^{2-}. Arsenopyrite contains in addition the diarsenide ion, As_2^{2-}. The disulfide ion undergoes auto-oxidation in high acidity, leading to elemental sulfur and sulfide ion formation:

Table 12.7: Methods of leaching of sulfides.

Oxidizing agent	Medium	Reaction	Examples
Absent	Acid	$MS + 2H^+ \rightarrow M^{2+} + H_2S$	$Ni_3S_2 + 6HCl \rightarrow 3NiCl_2 + 2H_2S + H_2$
	Base	$MS + 4OH^- \rightarrow MO_2^{2-} + S^{2-} + 2H_2O$	$PbS + 4NaOH \rightarrow Na_2PbO_2 + Na_2S + 2H_2O$ $ZnS + 4NaOH \rightarrow Na_2ZnO_2 + Na_2S + 2H_2O$
	Alkali sulfide	$MS + S^{2-} \rightarrow MS_2^{2-}$	$HgS + Na_2S \rightarrow Na_2HgS_2$ $Sb_2S_3 + 3Na_2S \rightarrow 2Na_3Sb_2S_3$ $As_2S_3 + 3Na_2S \rightarrow 2Na_3As_2S_3$
	Alkali cyanide	$MS + 3CN^- \rightarrow M(CN)_3^- + S^{2-}$	$Cu_2S + 6NaCN \rightarrow 2Na_2[Cu(CN)_3] + Na_2S$
Present	Water	$MS + 2O_2 \rightarrow M^{2+} + SO_4^{2-}$	$ZnS + 2O_2 \rightarrow ZnSO_4$
	Acid	$MS + 2H^+ + {}^1/_2O_2 \rightarrow M^{2+} + S + H_2O$	$ZnS + H_2SO_4 + {}^1/_2O_2 \rightarrow ZnSO_4 + S + H_2O$
	Base	$MS + 4OH^- + 20, \rightarrow MO_2^{2-} + SO_4^{2-} + 2H_2O$	$MoS_2 + 6NaOH + {}^9/_2O_2 \rightarrow Na_2MoO_4 + Na_2SO_4 + 3H_2O$
	Ammonia	$MS + nNH_3 + 20, \rightarrow [M(NH_3)_n]^{2+} + SO_4^{2-}$	$NiS + nNH_3 + 2O_2 \rightarrow [Ni(NH_3)_n]^{2+} + SO_4^{2-}$

$$S_2^{2-} \rightarrow 2S + 2e^-$$

$$S_2^{2-} + 2e^- \rightarrow 2S^{2-}$$

Overall reaction:

$$S_2^{2-} \rightarrow S + S^{2-}$$

The sulfide ion may oxidize further by oxygen to elemental sulfur if high acidity is maintained:

$$S^{2-} \rightarrow S + 2e^-$$

$$^1/_2O_2 + 2H^+ + 2e- \rightarrow H_2O$$

In neutral medium, the disulfide ion does not undergo auto-oxidation but oxidizes to thiosulfate, then to sulfate:

$$S_2^{2-} + {}^3/_2O_2 \rightarrow S_2O_3^{2-}$$

$$S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e^-$$

$$^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

$$H^+ + OH- \rightarrow H_2O$$

This leads to the two overall reactions observed experimentally:

- In acid medium:

$$FeS_2 + {}^1/_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2S + H_2O$$

- In neutral medium:

$$FeS_2 + {}^1/_2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

Covellite and arsenopyrite behave similarly.

Chapter Thirteen

Selenides and Tellurides

Introduction **327**
Acid Process. **328**
  Pressure leaching **329**
  Multi-stage leaching **331**
Alkaline Process **332**

INTRODUCTION

Selenium and tellurium are relatively rare metalloids; their relative abundance is $5 \times 10^{-6}\%$ and $2 \times 10^{-7}\%$ respectively, i.e., about the same order of magnitude as silver and gold. However, they do not occur in the native state but mostly in association with non-ferrous metal sulfides, especially those of copper and nickel. During pyrometallurgical processing of concentrates of these metals, appreciable amounts of selenium and tellurium are volatilized. The remainder deposits during the electrolytic refining as slimes at the bottom of the cell. For example, fire-refined copper contains 0.01–0.02 Yo Se and up to 0.004% Te, as selenides and tellurides of gold, silver, and copper. The following compounds have been identified in the slimes: (Ag, Au)Te_2, Ag_2Se, Ag_2Te, CuAgSe, Cu_2Se, ans Cu_2Te. The slimes are a grayish black powder, minus 200 mesh. From 2 to 20 kg of slimes are produced per ton of copper cathode: they are usually collected every 14 to 21 days of electrolysis. A typical analysis of slimes at a refinery in Canada is given in Table 13.1.

The treatment of slimes has undergone numerous changes in recent years to the extent that the once commonly used hydrometallurgical process has now been replaced in some plants by a pyrometallurgical route in which the selenides and tellurides are intensively oxidized over a long period of time in a top-blown rotary converter to get directly an alloy of gold and silver, called doré metal. Selenium and tellurium are collected in the gas scrubbing system.

Table 13.1: Typical analysis of anodic slimes at the Canadian Copper Refiners, Montreal East.

	%		%
Cu	30	As	0.25
Ag	21	Sb	1
Au	1	Bi	0.3
Se	15	Sn	0.5
Te	5.5	Si	1
Pb	10	Balance[a]	14.45

[a] Mainly sulfur and oxygen (as $PbSO_4$, $CuSO_4$), SiO_2, and traces of Fe, Ni, Al, Ca, and Mg.

The hydrometallurgical route for treating the slimes comprises two methods: the acid and alkaline processes. In the acid process elemental selenium and tellurium and their oxides are formed, while in the alkaline process both metals go into solution. Gold selenides and tellurides, however, are not decomposed in both processes and these are melted under oxidizing conditions to slag selenium and tellurium and to recover gold, silver, and the platinum metals as a bullion.

ACID PROCESS

This is the oldest method of treating slimes. The slimes are charged in digesters of 360–400 kg capacity, heated to 260 °C with 78% H_2SO_4, for 8–12 hours. During digestion the following reactions take place:

$$Cu_2Se + 4H_2SO_4 \rightarrow 2CuSO_4 + Se + 4H_2O + 2SO_2$$

$$Cu_2Te + 4H_2SO_4 \rightarrow 2CuSO_4 + Te + 4H_2O + 2SO_2$$

$$Ag_2Se + 2H_2SO_4 \rightarrow Ag_2SO_4 + Se + 2H_2O + SO_2$$

$$Ag_2Te + 2H_2SO_4 \rightarrow Ag_2SO_4 + Te + 2H_2O + SO_2$$

Gold selenides and tellurides are not decomposed by this treatment. The reaction mass is then dumped into open pans heated to 700 °C in order to complete the above reactions and to volatilize selenium and tellurium. A small amount of selenium and tellurium is oxidized to gaseous dioxides:

$$Cu_2Se + 6H_2SO_4 \rightarrow 2CuSO_4 + SeO_2 + 4SO_2 + 6H_2O$$

$$Cu_2Te + 6H_2SO_4 \rightarrow 2CuSO_4 + TeO_2 + 4SO_2 + 6H_2O$$

These are washed into scrubbers to recover selenium and tellurium, while the residual sulfates are leached with water to recover copper and silver. The residue is then treated by pyrometallurgical operations to recover residual selenium, tellurium, copper, and the gold–silver alloy (doré bullion), which contains the platinum metals. The problem with the baking step is the formation of SO_2 as shown in the above equations. A simplified flowsheet is given in Figure 13.1.

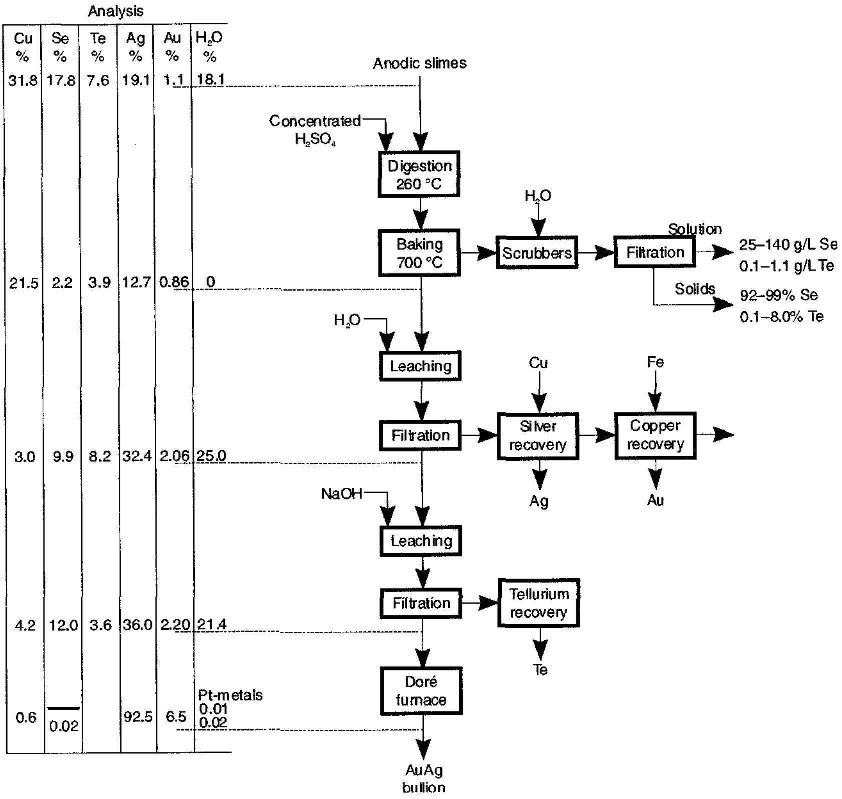


Figure 13.1: Processing anodic slimes from copper electrolytic refining.

Pressure leaching

This is an improvement to the acid-baking process. Instead of using concentrated acid which produces SO_2 as shown above, dilute H_2SO_4 (30%) and oxygen under pressure are used. The process is conducted in stainless steel autoclaves at 125 °C and 300 kPa and the reactions taking place are the following:

$$Cu_2Se + 4H^+ + O_2 \rightarrow 2Cu^{2+} + Se + 2H_2O$$

$$Cu_2Te + 2H^+ + {}^5/_2O_2 \rightarrow 2Cu^{2+} + TeO_4^{2-} + H_2O$$

$$Cu + 2H^+ + {}^1/_2O_2 \rightarrow Cu^{2+} + H_2O$$

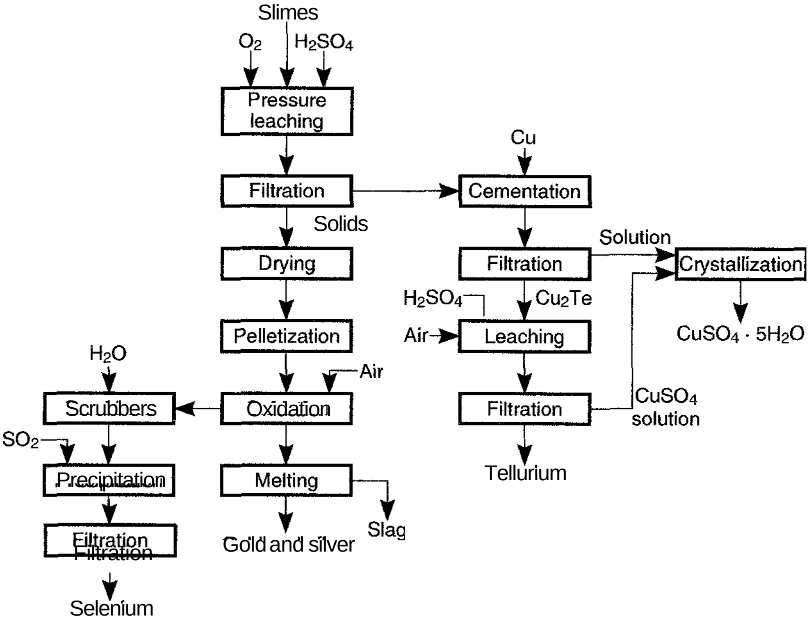


Figure 13.2: Pressure leaching of anodic slimes at Canadian Copper Refiners, Montréal East, Canada.

This process has also the advantage of an early separation of selenium from tellurium, since under the leaching conditions selenium is precipitated in the elemental form, while the tellurium goes into solution. A flowsheet of this process is shown in Figure 13.2.

After the solid–liquid separation step, the solution containing copper and tellurium is agitated with metallic copper in form of pellets to precipitate tellurium as Cu_2Te:

$$TeO_4^{2-} + 5Cu + 8H^+ \rightarrow Cu_2Te + 3Cu^{2+} + 4H_2O$$

Excess copper is added to neutralize the remaining acid, then the copper sulfate solution is evaporated to crystallize $CuSO_4 \cdot 5H_2O$ for the market. The residue from pressure leaching containing mainly selenium, silver selenide, gold, and lead sulfate is pelletized, then roasted at 815 °C in air. Selenium dioxide is recovered in the scrubbers, and the precious metal fraction collected from the roaster is melted in the usual way in a doré furnace.

In a recent development, the steps comprising pressure leaching and air oxidation of residue are replaced by a single high-temperature oxidation in a top-blown rotary converter to get directly doré metal. Gases evolved during this treatment are collected for selenium and tellurium recovery.

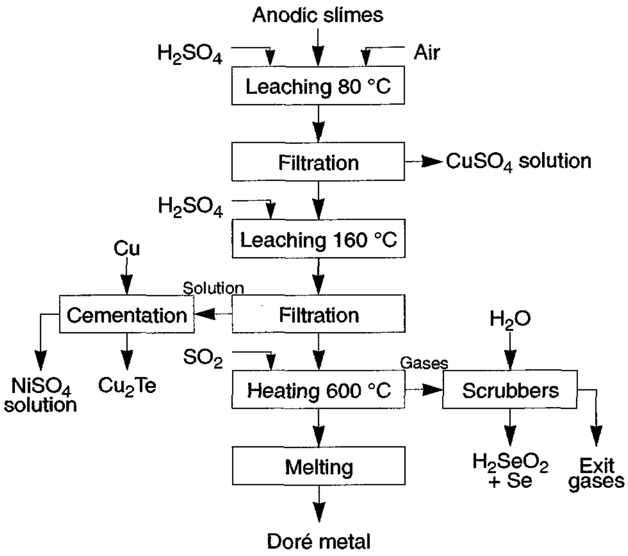


Figure 13.3: Outokumpu Process for the treatment of anodic slimes.

Multi-stage leaching

This process (Figure 13.3) was developed in Finland by Outokumpu Company. The slimes are not filtered but treated directly as a slurry in the electrolyte. The process involves the following steps:

- *Leaching of copper.* Metallic copper in the slimes is first removed selectively by air oxidation at 80 °C:

$$Cu + {}^{1}/{}_{2}O_2 + 2H^+ \rightarrow Cu^{2+} + H_2O$$

- *Leaching of nickel and tellurium.* Nickel oxide in the slimes is removed by dilute H_2SO_4 at 160 "C in pressure reactors:

  $$NiO + 2H^+ \rightarrow Ni^{2+} + H_2O$$

  In this operation most of the tellurium and any remaining copper go into solution. After filtration, tellurium is precipitated from solution by cementation with metallic copper.

- *Selenium recovery.* Selenides were found to decompose readily at 600 "C in an atmosphere of SO_2:

  $$Ag_2Se + SO_{2(g)} \rightarrow SeO_{2(g)} + Ag_2S$$

  Volatilized SeO_2 is captured in the gas scrubbing system. Due to the presence of SO_2 in solution, elemental selenium is formed which is collected by filtration and refined by distillation.

- *Formation of doré metal.* The residue from the previous step is melted with fluxes to form doré metal which is refined electrolytically.

ALKALINE PROCESS

Sodium hydroxide and oxygen under 1400 kPa pressure decompose selenides and tellurides of copper and silver at 150 "C as follows:

$$Cu_2Se + 2O_2 + 2OH^- \rightarrow 2CuO + SeO_3^{2-} + H_2O$$

$$Cu_2Te + 2O_2 + 2OH^- \rightarrow 2CuO + TeO_3^{2-} + H_2O$$

$$Ag_2Se + {}^{3}/{}_{2}O_2 + 2OH^- \rightarrow Ag_2O + SeO_3^{2-} + H_2O$$

$$Ag_2Te + {}^{3}/{}_{2}O_2 + 2OH^- \rightarrow Ag_2O + TeO_3^{2-} + H_2O$$

The selenites and tellurites are soluble in the solution. However, further oxidation converts all the tellurite to insoluble sodium tellurate:

$$Na_2TeO_3 + {}^{1}/{}_{2}O_2 \rightarrow Na_2TeO_4$$

Only a small amount of selenite is oxidized to insoluble selenate. The slurry is filtered and selenium is recovered from the sodium selenite solution, while the residue is treated further with H_2SO_4 to dissolve the tellurates. Gold and silver are recovered from the insoluble residue (Figure 13.4).

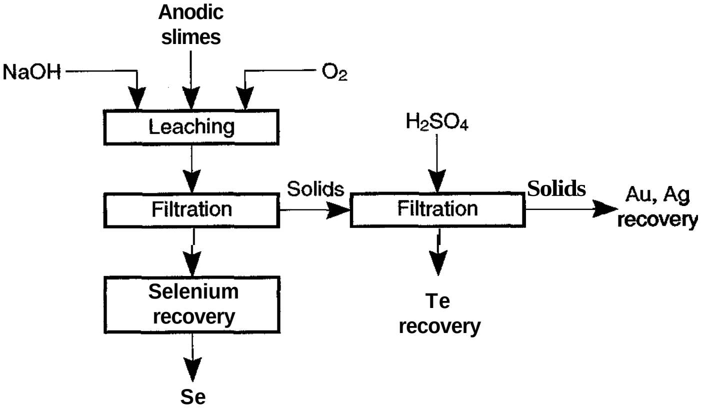


Figure 13.4: Sodium hydroxide process for treatment of anodic slimes from electrolytic copper refining.

Chapter Fourteen

Arsenides

Introduction 335
Ores and Concentrates 336
Acid leaching 337
Alkaline leaching 338
Speiss. 339

INTRODUCTION

Arsenic compounds are highly poisonous and therefore treatment of arsenic ores needs special measures to protect the workers and the environment. The most important arsenic minerals are shown in Table 14.1[1]. Arsenical ores may be treated in two ways:

- Leaching with acid or alkali in presence of an oxidizing agent.
- Melting in presence of fluxes to volatilize as much as arsenic and sulfur as possible, and the resulting product, called *speiss,* is then leached. **A** speiss is mainly a complex mixture of metal arsenides whose composition varies widely, depending on the type of ore treated. A typical speiss contains 15–35% arsenic.

Table 14.1: Arsenic minerals.

Arsenides	Niccolite	$NiAs$
	Smaltite	$CoAs_2$
	Skutterudite	$CoAs_3$
Sulfarsenides	Cobaltite	$CoAsS$
	Enargite,75	Cu_3AsS_4
	Arsenopyrite	$FeAsS$
Arsenic sulfides	Realgar	As_4S_4
	Orpiment	As_2S_3

Arsenic forms two oxides As_2O_3 and As_2O_5 which dissolve in water to form a variety of species, depending on the pH, as shown in Figures 14.1 and 14.2, respectively. Arsenious oxide is volatile while

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[1] For the treatment of arsenic sulfides see *Leaching of Sulfides* (Chapter Twelve).

arsenic oxide is not volatile. Arsine, AsH_3, is a highly poisonous gas that forms from arsenides by the action of dilute acids or even humidity from the atmosphere. Proper storage of these materials is therefore of special concern. Some arsenic compounds are used as insecticides, weed killers, and wood preservative.

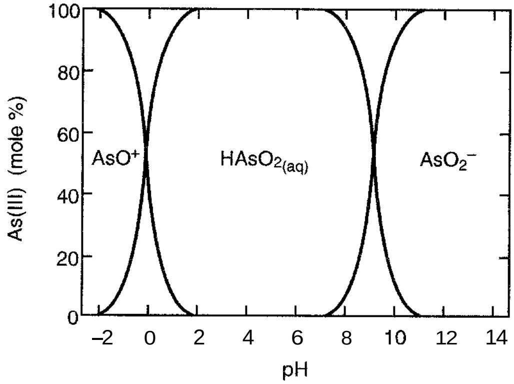

Figure 14.1: Distribution of trivalent arsenic species as a function of pH.

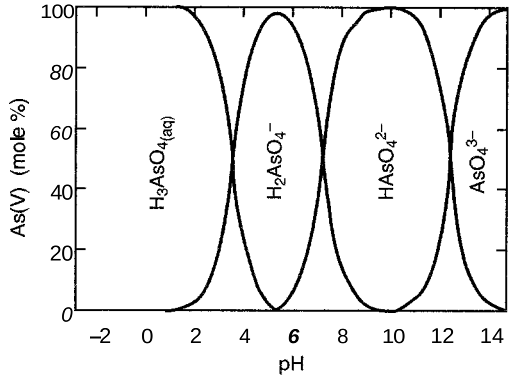

Figure 14.2: Distribution of pentavalent arsenic species as a function of pH.

ORES AND CONCENTRATES

Arsenide ores and concentrates can be leached by acids or alkalies. In the first case both the metal and arsenic go into solution while in the second case only arsenic is solubilized.

Acid leaching

This process (Figure 14.3) has the advantage of eliminating the danger of having arsenic in solution; instead, it is removed as an insoluble residue. The process has been applied for the recovery of cobalt from a sulfarsenide ore. Leaching is carried out at 200 °C, and under oxygen pressure of about 1200 kPa. Metals are converted to soluble sulfates while iron and arsenic salts are oxidized, and these combine to form insoluble iron arsenate:

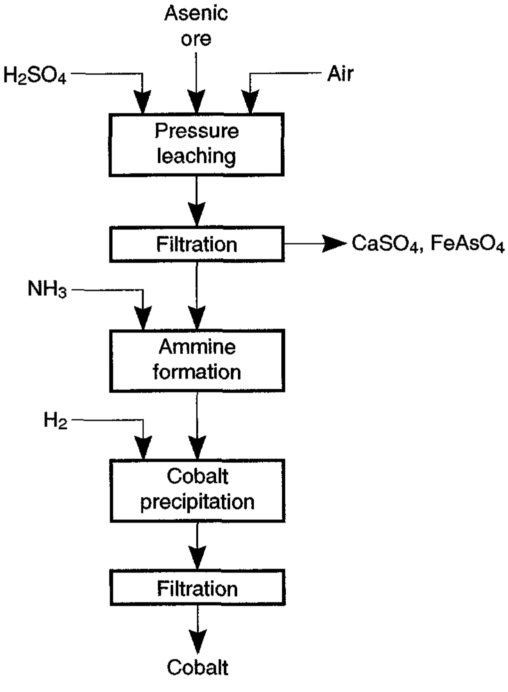

Figure 14.3: Calera Process for pressure leaching of arsenical ores.

$$CoAsS + {}^{7}/_{2}O_2 + H_2O \rightarrow Co^{3+} + SO_4^{2-} + AsO_4^{3-} + 2H^+$$

$$AsO_4^{3-} + Fe^{3+} \rightarrow FeAsO_4$$

The reaction is slow unless dilute acid is present. The slurry is filtered to recover cobalt from the solution. The process is known as the Calera process. Analysis of the concentrate processed is given in Table 14.2.

Table 14.2: Analysis of cobalt–arsenic sulfide concentrare at Calera Cobalt Refinery.

	%
As	24
Co	17.5
Cu	0.5
Fe	20
Ni	1
S	29
Gangue	5
H_2O	12

Alkaline leaching

Oxidation in presence of NaOH results in solubilizing both arsenic and sulfur to arsenate and sulfate respectively, while the metal values remain undissolved (Figure 14.4).

$$\mathrm{CoAsS} + {}^{7}/_{2}\mathrm{O_2} + 5\mathrm{OH^-} \rightarrow$$
$$\mathrm{Co(OH)_3} + \mathrm{SO_4^{2-}} + \mathrm{AsO_4^{3-}} + \mathrm{H_2O}$$

The residue can then be processed by conventional methods to yield cobalt (or nickel) free from arsenic. Treatment is carried out at 115 °C, 840 kPa oxygen pressure. Arsenic can be removed from the leach solution by precipitation with lime to give calcium arsenate, or with H_2S to give arsenic sulfide. When lime is used, sodium hydroxide is regenerated:

$$2\mathrm{AsO_4^{3-}} + 3\mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca_3(AsO_4)_2} + 6\mathrm{OH^-}$$

The process is known as the Sill Process after its inventor Harley Sill. Analysis of an ore treated by this process is given in Table 14.3.

Table 14.3: Analysis of ore processed by sodium hydroxide leaching.

	%
As	45
S	20
Fe	19
Co	12
Ni	3
Cu	1
Ag	100–150 oz/ton

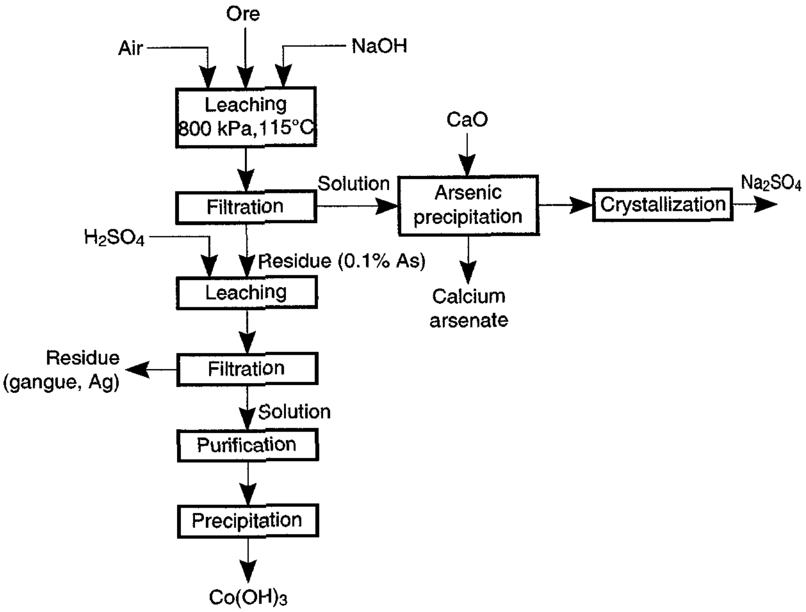

Figure 14.4: Leaching of arsenide ore with sodium hydroxide.

SPEISS

The process used for treating a silver–cobalt arsenide ore makes use of the formation of speiss. The ore is melted in a blast furnace to get silver bullion and speiss. Speiss is then leached directly as in the previous cases, or is oxidized in a roasting furnace to yield arsenate which is then leached with dilute H_2SO_4; the nonferrous metals go into solution from which they can be separated and recovered, while arsenic and iron remain in the residue. Table 14.4 gives the analysis of a speiss and its oxidation product. Roasting, however, usually creates pollution problems, since considerable amounts of sulfur and arsenic are volatilized. Leaching of speiss by ammonia under oxygen pressure has been suggested; the following equation represents the reaction:

$$2CoAs + {}^{7}/_{2}O_2 + 2nNH_3 + H_2O \rightarrow$$
$$2[Co(NH_3)_n]^{2+} + 2HAsO_4^{2-}$$

Table 14.4: Roasting arsenides (speiss) to arsenates.

	Speiss (arsenide) %	Speiss oxidation product (arsenate) %
As	31.0	10–12
Co	11.3	23.0
Ni	9.0	9.0
Cu	0.9	2.5
Fe	6.0	21.5
S	10.0	2–8.6
Ag	100–900 oz/ton	500–900 oz/ton

Chapter Fifteen

Phosphates

Introduction 341
Phosphate Rock 342
  Leaching methods 343
  Uranium recovery 347
  Recovery of the lanthanides 348
  Fluorine recovery 348
  Production of dicalcium phosphate. 349
Monazite Sand and Xenotime. 351
  Sulfuric acid method.. 354
  Sodium hydroxide method. 355

INTRODUCTION

Phosphatic raw material of interest to the metallurgist are phosphate rock, monazite sand, and xenotime (Table 15.1).Tonnage wise, phosphate rock is the most important as compared with the other material; about 120 millions tons of rock are treated annually while only 30 000 tons of monazite and xenotime. Apatite is the principal constituent of phosphate rock. The mineral received its name from the Greek word απατω = *I deceive* when it was realized that it was frequently confused with other mineral species, including beryl and tourmaline, prior to the latter part of the eighteenth century. Phosphate rock is the main raw material for the production of phosphatic fertilizers. A small amount of fluorine, an increasing amount of uranium, and some lanthanides are recovered as by-products. The phosphate deposits in Idaho and Wyoming are a minor source of vanadium. Phosphate rock in Wengfu, China, contains 7 ppm iodine in isomorphous substitution with fluorine.

Monazite, on the other hand, derives its name from μοναζειν = *to be alone*. The mineral monazite is a lanthanide phosphate containing some thorium and small amounts of uranium. It is widely distributed in the Earth's crust. It occurs in small proportions in granites.

When such rocks are weathered, grains of monazite are carried by waters, then deposited at the mouths of rivers, together with the heavier constituents of the parent rock, to form black sands known as monazite sand. The monazite in these sands is usually present in rounded grains, showing that the grains have previously been rolled to an fro in streams of water. Xenotime is another lanthanide phosphate in which the individual lanthanides occur in a different proportion from that in monazite. It occurs associated with monazite in the placer tin deposits especially in Southeast Asia.

Table 15.1: Main phosphatic raw material.

Raw material	Economic phosphate material	Formula	Products
Phosphate rock	Apatite: • Fluoroapatite • Hydroxyapatite • Carbonatoapatite	 $Ca_{10}(PO_4)_6F_2$ $Ca_{10}(PO_4)_6(OH)_2$ $Ca_{10}(PO_4)_6CO_3$	Phosphatic fertilizers, uranium, vanadium[a], lanthanides, fluorine.
Monazite sand	Monazite	$LnPO_4$	Lanthanides[b], uranium, thorium.
Alluvial cassiterite	Xenotime	$LnPO_4$	

a. Potential.
b. Abbreviated Ln.

Vivianite is an iron phosphate, $Fe_3(PO_4)_2 \cdot 8H_2O$, that occurs in small amounts in some iron ores, e.g., those of the Lorraine District in France, that render them undesirable. During the reduction of these ores, the phosphorus enters the pig iron, it is finally eliminated as calcium phosphate in the slag during steelmaking. Such slag is usually finely ground and used directly as a fertilizer.

PHOSPHATE ROCK

Phosphate rock is composed mainly of fluorapatite, hydroxyapatite, and carbonato-apatite (Table 15.2). Depending on the proportion of each component, the rock may be frankolite, kunskite, or colophanite (Table 15.2). Low-grade phosphate rock, may contain appreciable amounts of aluminum phosphate wavellite, $AlPO_4$, and/or calcium–aluminum phosphate, crandallite. Phosphate rock occurs either as a sedimentary deposit, e.g., in Florida and North Africa, or as igneous rock, e.g., in Kola peninsula, Russia. Sedimentary phosphates supply about 85% of the phosphate rock for the industry. Typical analyses of phosphate rocks are given in Table 15.3. Phosphate rock is used for the manufacture of fertilizers and elemental phosphorus. Pure phosphoric acid for other uses than fertilizers is prepared from the latter product although attempts are being made to prepare a moderate-grade phosphoric acid by leaching the rock.

Table 15.2: Main types of phosphate rock.

Type	Composition
Frankolite	Isomorphous mixture of fluoroapatite and carbonate apatite in the ratio 3 : 1.
Kunskite	Isomorphous mixture of fluoroapatite and carbonate apatite in the ratio 2 : I.
Colophanite	An ultra microcrystalline variety of frankolite.

Table 15.3: Analysis of typical phosphate rock.

	%		%
P_2O_5	29–38	Cl	0.01–0.7
CaO	*48–52*	CO_2	2–6
MgO	0.2–0.8	SO_3	*1–3*
Fe_2O_3	0.2–1	SiO_2	0.2–5
Al_2O_3	0.1–1	Organic carbon	*0–0.4*
Na_2O	1–2	Uranium	0.01–0.02
K_2O	*0.1–0.4*	Ln_2O_3	0.1–1
F	*3.3–4.3*		

Leaching methods

Phosphate rock is insoluble in water, but when treated with acids either water-soluble monocalcium phosphate, citrate-soluble dicalcium phosphate, or phosphoric acid can be obtained. The first two can be used directly as a fertilizer, while the latter is neutralized with ammonia to produce an ammonium phosphate fertilizer. The acids used for treating the rock are the following.

Sulfuric acid. Leaching with sulfuric acid is the most common method for treating phosphate rock. Depending on the amount of acid used, normal superphosphate or phosphoric acid are produced:

- When a small amount of acid is used the product is known as normal superphosphate:

$$\begin{aligned}&Ca_{10}(PO_4)_6F_2 + 2H_2SO_4 + 2H_2O \rightarrow \\ &\qquad \underset{\text{superphosphate}}{3Ca(H_2PO_4)_2 \cdot 2H_2O + 7CaSO_4 \cdot 2H_2O} + 2HF\end{aligned}$$

Normal superphosphate is a solidified mixture of monocalcium phosphate and gypsum; its P_2O_5 content is only 18–20%. Usually the product is ammoniated to increase its value as a fertilizer:

$$\begin{aligned}&Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4 \cdot 2H_2O + 2NH_3 \rightarrow \\ &\qquad 2CaHPO_4 + (NH_4)_2SO_4 + H_2O\end{aligned}$$

- When a large amount of sulfuric acid is used, phosphoric acid is produced. The reaction is largely complete in few minutes. Three processes are used (Table 15.4):
  - Hemihydrate Process. Conducted above 80 °C and produces 30% acid:

    $$\begin{aligned}&Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 5H_2O \rightarrow \\ &\qquad 6H_3PO_4 + 10CaSO_4 \cdot {}^1/_2H_2O + 2HF\end{aligned}$$

  - Dihydrate Process. Conducted below 80 °C and produces 60% acid:

    $$\begin{aligned}&Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow \\ &\qquad 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF\end{aligned}$$

    More time is needed, about 8 hours, to allow for the proper formation of crystals that can be removed easily by filtration.

  - Hemihydrate–dihydrate Process. Conducted above 80 °C to produce the hemihydrate crystals, then slurry is agitated for few hours to allow the crystallization of the dihydrate.

There are two types of wet process phosphoric acid: the “black acid” and the “green acid”. The black acid is the one usually produced and its black color is due to the organic matter originally present in the rock. If the organic matter is above certain limits it is usually eliminated by calcining in an oxidizing atmosphere. The acid derived from such treated rock is the green acid because it has a green tint. Both acids are a commercial product, and is shipped to fertilizer producers. It is usually neutralized by ammonia to form ammonium phosphates:

- Monoammonium phosphate (46% P_2O_5, 11% N):

$$H_3PO_4 + NH_4OH \xrightarrow{\text{pH}} 4\ NH_4{\cdot}H_2PO_4 + H_2O$$

- Diammonium phosphate (46% P_2O_5, 18% N):

$$H_3PO_4 + 2NH_4OH \xrightarrow{\text{pH}} 6\ (NH_4)_2{\cdot}HPO_4 + 2H_2O$$

Or, reacted with a fresh batch of phosphate rock in a rotary kiln to produce triple superphosphate (40–48% P_2O_5):

$$\begin{aligned}&Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + H_2O \rightarrow\\ &\qquad 10Ca(H_2PO_4)_2{\cdot}H_2O + 2HF\end{aligned}$$

This in turn is usually treated by ammonia to form ammoniated triple superphosphates:

$$\begin{aligned}&Ca(H_2PO_4)_2{\cdot}H_2O + NH_3 \rightarrow\\ &\qquad CaHPO_4 + NH_4{\cdot}H_2PO_4 + H_2O\end{aligned}$$

$$\begin{aligned}&Ca(H_2PO_4)_2{\cdot}H_2O + 2NH_3 \rightarrow\\ &\qquad CaHPO_4 + (NH_4)_2HPO_4 + H_2O\end{aligned}$$

Hydrochloric acid. Hydrochloric acid is used sometimes to leach phosphate rock to produce either monocalcium phosphate fertilizer:

$$Ca_{10}(PO_4)_6F_2 + 14HCl \rightarrow 3Ca(H_2PO_4)_2 + 7CaCl_2 + 2HF$$

or phosphoric acid:

$$Ca_{10}(PO_4)_6F_2 + 20HCl \rightarrow 6H_3PO_4 + 10CaCl_2 + 2HF$$

Calcium chloride is then removed as $CaCO_3$ by precipitation with $(NH_4)_2CO_3$:

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4Cl$$

Nitric acid. Nitric acid is also used to produce a fertilizer known as nitrophosphate:

$$\begin{aligned}&Ca_{10}(PO_4)_6F_2 + 14HNO_3 \rightarrow\\ &\qquad \underset{\text{nitrophosphate}}{3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2} + 2HF\end{aligned}$$

or phosphoric acid:

$$\begin{aligned}&Ca_{10}(PO_4)_6F_2 + 20HNO_3 \rightarrow\\ &\qquad 6H_3PO_4 + 10Ca(NO_3)_2 + 2HF\end{aligned}$$

Table *15.4:* Production of phosphoric acid by the H_2SO_4 route.

	Hemihydrate Process	Dihydrate Process	Hemihydrate–dihydrate Process
Crystal form	$CaSO_4 \cdot {}^1/_2H_2O$	$CaSO_4 \cdot 2H_2O$	Initially $CaSO_4 \cdot {}^1/_2H_2O$, then $CaSO_4 \cdot 2H_2O$
Crystal size (µm)	*15–30* (without modifier) *40–60* (with modifier)	*40–60*	
P_2O_5 losses in crystal *(Yo)*	*3–6*	lower	
Temperature (°C)	> *80*	< *80*	> *80*
Phosphoric acid concentration % P_2O_5 – *Yo* H_3PO_4	*45–54*	*28–30*	
Washing system	Vacuum belt filter (Lurgi)	Counter-current in thickeners (Dorr)	
Phosphoric acid yield (%)	*91*	*93*	*99*
Energy requirement	low because less water to be evaporated later	high because more water to be evaporated later	

Calcium nitrate is separated by cooling to −10°C then centrifuging the crystals of $Ca(NO_3)_2 \cdot 4H_2O$. It is usually transformed to ammonium nitrate by reaction with ammonium carbonate.

Present tendency. The first fertilizer produced in industry was normal superphosphate. Because of its low concentration in P_2O_5, its production has declined gradually in the past years and its place was taken over by triple superphosphate, and more recently by mono- and diammonium phosphates. Over 70% of the phosphate rock is used in making phosphoric acid by the wet process. Phosphoric acid produced by leaching phosphate rock is impure and cannot be used for manufacturing phosphates needed for the food or detergent industries unless it undergoes extensive purification, e.g., extraction by organic solvents.

Uranium recovery

Phosphate rock of sedimentary origin contains on the average 0.01% uranium. At a world production of phosphate rock of 130 millions tons this represents a potential source of about 13 000 tons uranium annually. Because the mining and processing of phosphate rock is already financed by the existing phosphate fertilizer industry, the cost of the uranium as a by-product should not be great.

Uranium in the sedimentary phosphate is present mainly in the tetravalent state; the remainder in the hexavalent state. Since the tetravalent uranium is insoluble in dilute acid while the hexavalent is soluble, the tetravalent uranium is usually determined in the following way. The rock is dissolved in dilute hydrochloric acid under inert atmosphere; uranium that goes into solution under these conditions is the hexavalent uranium. When the rock is dissolved under oxidizing atmosphere, all the uranium goes into solution. By difference, one can calculate the amount of uranium in the tetravalent state. It is believed that, in this form, uranium is in isomorphous substitution with Ca^{2+} ion in the apatite crystal. The ionic radius of U^{4+} is 1.05 Å while that for Ca^{2+} is 1.06 Å. Since most of the uranium is present in the crystal lattice of apatite it is therefore not possible to separate an uranium concentrate from phosphate rock by physical methods. As a result of the isomorphous substitution, there is a linear relation between uranium content in the rock and its P_2O_5 content.

Uranium in the rock can be readily identified by its radioactivity. In most cases, it was found that uranium existed in radioactive equilibrium with its decay products and the total gamma activity of a sample can be used as an indication of its uranium content.

The solvents used for extracting uranium are acidic esters of phosphoric acid. They are either used alone or in combination with other organic phosphorus compounds. Sometimes the rock is calcined before leaching to remove the organic matter. During the calcination step about 30% of the uranium becomes insoluble in sulfuric acid and will report with the gypsum residue. The presence of organic matter in the black acid causes difficulties in the separation of the organic phase because it is mostly present in a colloidal form which is coagulated by the extractant forming a crud that collects at the organic–aqueous interface. The organic matter can also be destroyed by oxidation in the aqueous phase.

The production of phosphoric acid by the wet process is at present facing the problem of disposal of gypsum; about 1.5 tons of gypsum are produced per ton of rock processed. This material contains all the radium originally present in the rock which results from the radioactive decay of uranium. As a result, phosphogypsum contains about 0.03 mg Ra/t or 30 pCi/g.

Recovery of the lanthanides

Phosphate rock of sedimentary origin contains about 0.5% lanthanide oxides while igneous phosphate, e.g., in Kola Peninsula, contains about 1% lanthanide oxides. During the manufacture of phosphoric acid about 70% is lost in the gypsum. However, if acidulation is conducted by nitric acid all will go into solution and can be recovered by organic solvents. In Finland, the lanthanides were recovered commercially by Kemira Oy from phosphate rock during 1965–1972 using organic solvents. It is believed that a similar operation is in existence in Russia.

Fluorine recovery

Phosphate rock contains 3 to 4% fluorine. During the treatment of the rock with sulfuric about 70% of this fluorine is volatilized, 20%

enters the gypsum as insoluble fluorides, and the remaining is solubilized in the phosphoric acid. The volatilized fluorine is mainly as hydrofluoric acid and silicon tetrafluoride; the latter being formed as a result of the interaction of HF with silica in the rock:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

Both gases represent a substantial source of fluorine. At present, most phosphate rock processors wash the exit gases in water to obtain a mixture of hydrofluoric and hydrofluosilicic acid; the latter as a result of reaction os SiF_4 with water:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

Fluorine in phosphoric acid is present mainly as the fluorosilicate ion. It can be recovered by precipitation with a sodium or potassium salt, e.g.:

$$SiF_6^{2-} + 2Na^+ \rightarrow Na_2SiF_6$$

Although its proportion is small as compared to the amount recovered from the volatilized gases, its removal is not only an additional source of fluorine but it also serves as a purification step of the phosphoric acid and hence an upgrading of the fertilizer. One potential utilization of these fluorine compounds is in the production of synthetic cryolite, Na_3AlF_6, needed for the aluminum industry.

Production of dicalcium phosphate

Dicalcium phosphate, $CaHPO_4$, is insoluble in water but soluble in dilute citric acid. It can be effectively produced at the mine location by in-situ, heap, or vat leaching using dilute nitric or hydrochloric acids, and can be marketed as a citrate-soluble fertilizer containing *40%* P_2O_5. The flowsheet of the proposed process is shown in Figure 15.1. Phosphate rock is leached with 10% HCl or 20% HNO_3, in situ, in dumps, or in vats to produce a solution of monocalcium phosphate, $Ca(H_2PO_4)_2$. The solution is then crystallized to get the double salts $CaClH_2PO_4 \cdot H_2O$ or $Ca(NO_3)H_2PO_4 \cdot H_2O$ depending on the acid used. The crystals are then separated from the mother liquor and decomposed at 200–250 °C to get dicalcium phosphate product:

$$CaClH_2PO_4 \cdot H_2O \rightarrow CaHPO_4 + HCl + H_2O$$

$$Ca(NO_3)H_2PO_4\cdot H_2O \rightarrow CaHPO_4 + HNO_3 + H_2O$$

In this operation, about 40% of the acid required for the leaching step is recovered for recycle. The remaining 60% can be regenerated by reaction of the mother liquor with H_2SO_4:

$$CaCl_2 + H_2SO_4 \rightarrow 2HCl + CaSO_4$$

$$Ca(NO_3)_2 + H_2SO_4 \rightarrow 2HNO_3 + CaSO_4$$

To get a radioactivity-free gypsum, radium must be separated in an earlier step. This can be readily achieved by adding SO_4^{2-} ion followed by a calculated amount of $BaCl_2$ solution and filtering off the precipitate formed. To recover uranium and the lanthanides, two solvent extraction steps should be incorporated before the crystallization step using the proper solvents. If in situ leaching used, then the cost of removing the overburden, mining, beneficiation, disposal of tailings and slimes which are encountered in the exploitation of phosphate mines are eliminated.

The following points should be noted:

- H_2SO_4 cannot be used in this technology because the formation of gypsum will prevent the percolation of the leach solution.
- Only dilute HCl and HNO_3 can be used because more concentrated acid will result in the formation of H_3PO_4 in the upper layers of the bed which when it percolates downwards it will form dicalcium phosphate and thus prevent percolation:

$$Ca_{10}(PO_4)_6F_2 + 4H_3PO_4 \rightarrow 10CaHPO_4 + 2HF$$

- Monocalcium phosphate solution can also be purified, then treated with ammonia to produce a mixture of dicalcium phosphate and ammonium phosphate:

$$Ca(H_2PO_4)_2 + NH_3 \rightarrow CaHPO_4 + NH_4H_2PO_4$$

$$Ca(H_2PO_4)_2 + 2NH_3 \rightarrow CaHPO_4 + (NH_4)_2HPO_4$$

Figure 15.2 shows the species formed when the pH of H_3PO_4 is increased gradually.

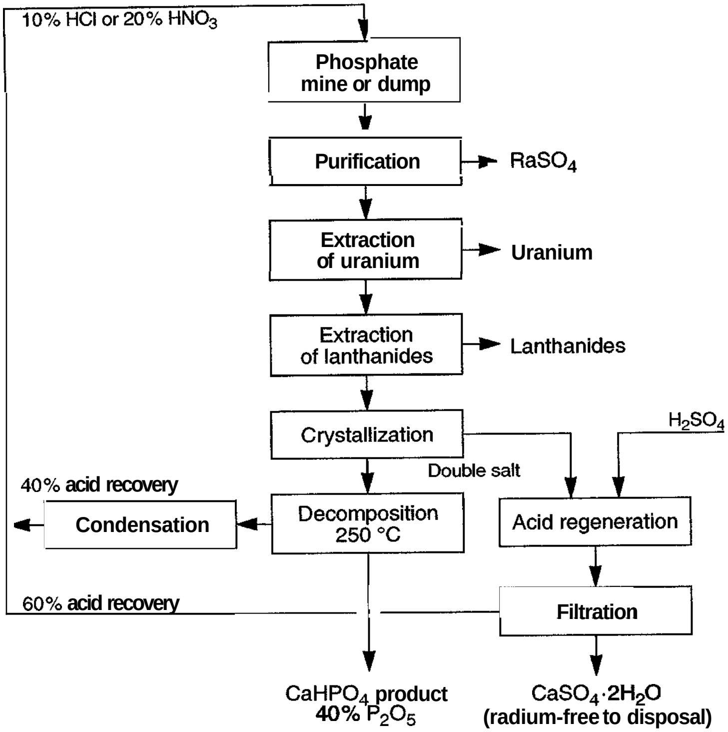

Figure 15.1: Proposed method for the production of dicalcium phosphate.

MONAZITE SAND AND XENOTIME

Monazite sands occur mainly in Brazil, India, Australia, and USA while xenotime is mainly in South East Asia associated with alluvial tin deposits. Both minerals can be easily concentrated from the sands by physical methods. For example, a monazite sand containing 1% monazite can be concentrated by gravity, magnetic, and electrostatic methods to a concentrate containing 85% monazite (Figure 15.3). Some physical properties of monazite and xenotime concentrates are given in Table 15.5. A chemical analysis of the concentrates is given in Table 15.6. The composition of the lanthanide fraction in monazite and in xenotime is given in Table 15.7, together with that of bastnasite, another important source of the lanthanides. Scandium, although in the same group with yttrium, lanthanum, and the lanthanides, is not present in any of these minerals.

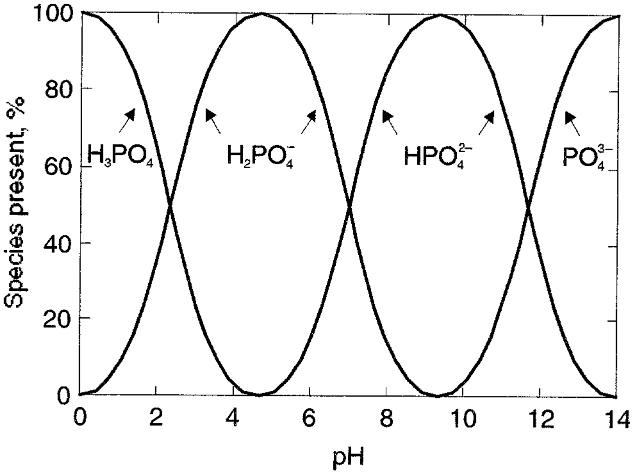

Figure 15.2: Neutralization of phosphoric acid:
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$;
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$;
$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$.

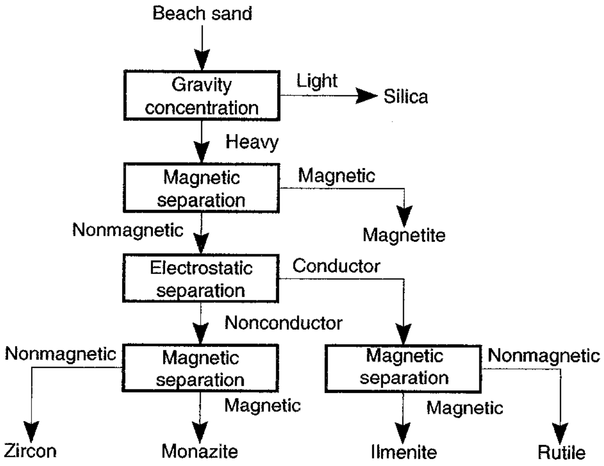

Figure 15.3: Separation of monazite and other valuable minerals from monazite sand by physical methods.

Table 15.5: Physical properties of lanthanide phosphate minerals.

	Monazite	Xenotime
Color	Yellow to red brown	Pale yellow to browish green
Specific gravity	4.9–5.5	4.45–4.59
Hardness (Mohs)	5	4.5
Crystal structure	Monoclinic	Tetragonal

Table 15.6: Chemical analysis of lanthanide phosphate concentrates.

	Monazite concentrate, %	Xenotime concentrate, %
P_2O_5	24–29	
Ln_2O_3[a]	55–65	52–63
ThO_2	5–10	1–3
U_3O_8	0.2–0.4	0.5–3.5
SiO_2	1–3	
CaO	0.2–0.8	
Fe_2O_3	1–2	
	0.1–0.8	
ZrO_2	0.7	2–3
SnO_2	—	0–9

[a] Ln = Lanthanide.

Light	La_2O_3	23.0	93	0.5	8.4	32.0	98.9
	CeO_2	46.5		5.0		49.0	
	Pr_6O_{11}	5.1		0.7		4.4	
Heavy	Sm_2O_3	2.3	7	1.9	91.6	0.5	1.37
	Eu_2O_3	0.07		0.2		0.1	
	Gd_2O_3	1.7		4.0		0.3	
	Tb_4O_7	0.16		1.0		0.01	
	Dy_2O_3	0.52		8.7		0.03	
	Ho_2O_3	0.09		2.1		0.01	
	Er_2O_3	0.13		5.4		0.01	
	Tm_2O_3	0.013		0.9		0.2	
	Yb_2O_3	0.061		6.2		0.01	
	Lu_2O_3	0.006		0.4		0.1	
	Y_2O_3	2		60.8		0.1	

[a] Bastnasite, a fluorocarbonate, $Ln_2(CO_3)_3$, LnF_3, or $LnFCO_3$, a major source of lanthanides.

Monazite and xenotime are the main source of thorium and the lanthanides; uranium is recovered as a by-product. There are two methods used for treating these concentrates: the sulfuric acid and the sodium hydroxide methods (Figure 15.4). The decision between one or the other is an economic one; for example in Brazil, the NaOH process is used because of a shortage in sulfuric acid. However, the general tendency today is to use the NaOH process.

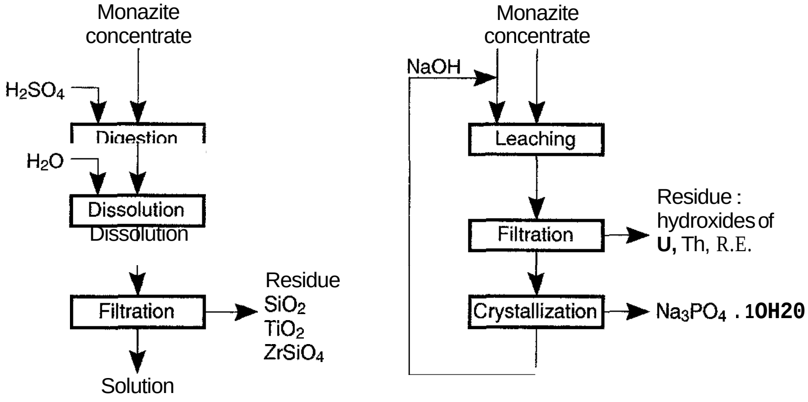

Figure 15.4: Leaching methods for monazite sand.

Sulfuric acid method

This method involves two steps:

- *Digestion.* The concentrate is digested in a closed reactor or baked in a rotary kiln with 93% H_2SO_4 at about 200 °C for 2-4 hours at an acid to concentrate ratio of 2 :1. An acid-to-concentrate ratio lower than this results in incomplete reaction, while higher ratio interferes with subsequent operations. Also, with temperatures lower than the above, the reaction will be too slow, and if higher than 300 °C, insoluble thorium pyrophosphate is liable to be formed. The reaction is exothermic and can be represented by the equation:

$$2LnPO_4 + 3H_2SO_4 \rightarrow Ln_2(SO_4)_3 + 2H_3PO_4$$

Thorium and uranium are also transformed into sulfates. Due to the high temperature used the product is a thick paste of anhydrous sulfates.

- *Dissolution of the reaction mass.* The resulting mass is allowed to cool, diluted with water to allow the insoluble material to settle, and then filtered. Typical analysis of the filtrate is shown in Table 15.8. The clear leach solution is then subjected to further treatment to separate thorium, uranium, and the lanthanides. The residue contains most of the radioactive decay products of uranium and thorium.

Table 15.8: Typical analysis of monazite leach solution, pH = 0.05.

	g/L		g/L
Th	5.3	Nd_2O_3	7.0
U	0.2	Sm_2O_3	1.3
Ce_2O_3	16.0	SO_4^{2-}	128.0
	8.5	PO_4^{3-}	26.0
Pr_2O_3	1.7		

Sodium hydroxide method

The sodium hydroxide process differs from the acid process in that water-soluble phosphates are formed while the lanthanides, thorium, and uranium form insoluble hydroxides:

$$LnPO_4 + 3NaOH \rightarrow Ln(OH)_3 \mathrm{\ t\ } Na_3PO_4$$

$$Th_3(PO_4)_4 + 12NaOH \rightarrow 3Th(OH)_4 + 4Na_3PO_4$$

$$UO_2HPO_4 + 2NaOH \rightarrow UO_2(OH)_2 + Na_2HPO_4$$

Optimum conditions of digestion are 40–50% NaOH, 160 °C, NaOH to concentrate 2 : 1, time of reaction about 3 hours. Sodium hydroxide should be free from carbonate otherwise uranium will be lost in solution, since it forms soluble carbonates. The product is a thick paste; it is slurried in water then filtered, washed, and dried. The cake obtained is composed of hydroxides of uranium, thorium, and lanthanides, containing small amounts of phosphate; it is dissolved in acid for further separation. The leach solution contains the unreacted NaOH as well as the phosphorus originally present in the concentrate. When allowed to cool to about 60 °C, trisodium phosphate hydrate ($Na_3PO_4 \cdot 10H_2O$) crystallizes out. After separation, the solution typically analyze 47.4% NaOH, 0.5% Na_3PO_4, 1.5Yo Na_2SiO_3, and can be recycled.

Chapter Sixteen

Silicates

Introduction 357
Thermal Treatment 363
Aluminum Silicates 364
  Alumina from clays 364
  Alumina from nepheline 367
  Alumina from anorthosite 368
  Aluminum fluoride from clay 368
Asbestos Tailings 368
Beryllium Ores 370
  Beryl 371
  Bertrandite 372
Other Silicates 373
  Spodumene 373
  Pollucite 373
  Siliceous and granitic rocks 373
  Zinc silicate ores 374

INTRODUCTION

Silicates are the most abundant minerals in the Earth's crust. Their basic building block is the SiO_4^{4-} tetrahedron[1]. There is a variety in the structure of silicates due to the various combinations of these tetrahedra both with each other and also with other ions (Figure 16.1 and Table 16.1). The simplest structure is the single isolated tetrahedra as in olivines. The simplest binding is the double isolated tetrahedra which results from the sharing of a corner with another neighboring SiO_4^{4-} tetrahedron to form the disilicate ion. Rings. chains. and sheets result from sharing of more corners. The chains carry a total negative charge and are bound together by positive calcium and magnesium ions placed between them. In the sheet structure. layers of $Al(OH)_3$ or

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[1] See **pages** 33 and 109.

$Mg(OH)_2$ may be built in and are bounded to the sheets by the weak van der Waals' forces and this explains the softness of such minerals such as kaolinite and mica which easily cleave into thin layers. Chrysotile, the main asbestos mineral, is composed of a silicate sheet wrapped like a scroll to form fibrils. An asbestos fiber is thousands of fibrils attached together with their axes parallel to each other.

In the framework structure, all four oxygen ions in the tetrahedron are shared resulting in a three-dimensional structure. Silica, SiO_2, is the simplest of these structures. The great hardness, the difficult cleavage, and the high boiling point are manifestations of the great energy content of this bond. Any fracture requires that many of these chemical bonds be broken. Feldspars result from the substitution of Al^{3+} ions for some of Si^{4+} ions in the silica structure. The addition of alkali ions in the holes between the tetrahedra compensates for the charge deficit which arises. Network silicates are one of the most abundant minerals; they account for over 50% of the Earth's crust. That is why they are the most common gangue minerals found associated with ore deposits.

Silicate ores of interest in hydrometallurgy can be divided into two groups: Anhydrous and hydrated silicates (Table 16.2). Hydrated silicates are formed in nature by the weathering of anhydrous silicates, e.g., kaolinite is the result of weathering of orthoclase:

$$\underset{\text{orthoclase}}{4KAlSi_3O_8} + 4H_2O + 2CO_2 \rightarrow$$

$$\underset{\text{kaolinite}}{Al_4(Si_4O_{10})(OH)_8} + 2K_2CO_3 + 8SiO_2$$

and serpentine is the result of weathering of olivine group of minerals as represented by forsterite:

$$\underset{\text{forsterite}}{4Mg_2SiO_4} + 4H_2O + 2CO_2 \rightarrow$$

$$\underset{\text{serpentine}}{Mg_6(Si_4O_{10})(OH)_8} + \underset{\text{magnesite}}{2MgCO_3}$$

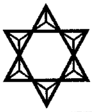
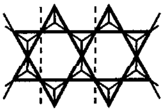
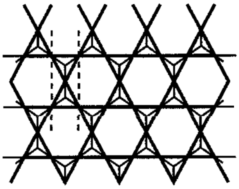
Arrangement of Si04 tetrahedra	**Number of oxygen ions of a tetrahedra participating in the link**	**Structural unit**	**Formula**	**Ratio SI : *O***
Single isolated tetrahedra	0		$[SiO_4]^{4-}$	1:4
Double isolated tetrahedra	1		$[Si_2O_7]^{6-}$	2:7
Rings (3membered)	*2*		$[Si_3O_{18}]^{6-}$	1:3
Rings (6 membered)	*2*		$[Si_6O_{18}]^{12-}$	1:3
Chains	2		$[Si_2O_6]^{4-}$	1:3
Double chains	$2\,{}^1\!/_2$		$[Si_4O_{11}]^{6-}$	4:11
Sheets	3		$[Si_2O_5]^{2-}$	2:5
Framework	4	 The top O atom is shared with a top layer	$[SiO_2]^0$	1:2

Figure 16.1: Schematic representation of silicates. Repetitive unit is shown between dotted lines.

Table **16.1:** Structure of silicates.

Class	Arrangement of SiO_4 tetrahedra	Ratio Si:O	Mineral examples		Similar species
Orthosilicates	Isolated single tetrahedra	1:4	Olivine group	$(Mg, Fe)_2SiO_4$	
			Forsrerite	Mg_2SiO_4	
			Fayalite	Fe_2SiO_4	
			Zircon	$ZrSiO_4$	Thorite $ThSiO_4$
			Andalusite	Al_2SiO_5	
			Sillimanite	Al_2SiO_5	
Pyrosilicates	Double isolated groups of tetrahedra (two SiO_4 tetrahedra sharing one of the oxygens)	2:7	Hemimorphite (calamine)	$Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$	
			Bertrandite	$Be_4(Si_2O_7)(OH)_2$	
Metasilicates	Rings	1:3	Beryl	$Be_3Al_2(Si_6O_{18})$	Dioptase
			Chrysocolla	$Cu_8(Si_4O_{10})_2(OH)_{12} \cdot nH_2O$ $Cu_6(Si_6O_{18}) \cdot 6H_2O$	
	Chains (single)	1:3	Spodumene	$LiAl(Si_2O_6)$	
			Rhodonite	$MnSiO_3$	
			Enstatite	$MgSiO_3$ or $(Mg, Fe)SiO_3$	
	Chains (double)	4:11	Tremolite	$Ca_2Mg_5(OH)_2(Si_4O_{11})_2$	

Class	Arrangement of SiO_4 tetrahedra	Ratio Si : O	Mineral examples		Similar species
Disilicates	Sheets	2 : 5	Kaolinite	$Al_4(Si_4O_{10})(OH)_8$	Montmorillonite
				$AlSi_2O_5(OH) \cdot nH_2O$, group	
				The dominant clay mineral in bentonite	
			Serpentine	$Mg_6(Si_4O_{10})(OH)_8$	Garnierite
				$(Ni, Mg)_6(Si_4O_{10})(OH)_8$	
			Talc	Crysotile asbestos	
				$Mg_3(Si_4O_{10})(OH)_2$	Soapstone
			Mica group		
			Biotite	$K(Mg, Fe)_3(Si_3AlO_{10}) \cdot (OH, F)_2$	
			Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	
Tectosilicates	Framework structure	1 : 2	Quartz	SiO_2	
			Opal	$SiO_2 \cdot nH_2O$	
			Anorthite	$Ca(Al_2Si_2O_8)$	
			Nepheline	$(Na, K)AlSiO_4$	
			Leucite	$K(AlSi_2O_6)$	Pollucite
			Orthoclase	$K(AlSi_3O_8)$	$CsAl_4Si_9O_{26} \cdot H_2O$
			Albite	$Na(AlSi_3O_8)$	
			Chabazite	$CaAl_2Si_4O_{12} \cdot 6H_2O$	
			Sodalite	$Na_4Al_3Si_3O_{12}$	

Table 16.2: Metallurgically important silicate minerals.

Type	Mineral	Preferred formula	Other formula:
Anhydrous	Beryl	$Be_3Al_2(Si_2O_{18})$	$3BeO \cdot Al_2O_3 \cdot 6SiO_2$
	Nepheline	$(Na, K)(AlSiO_4)$	$2(Na, K)_2O \cdot 2Al_2O_3 \cdot 4SiO_2$
	Spodumene	$LiAl(Si_2O_4)$	$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$
	Anorthosite	$CaAl2(Si_2O_8) + NaAl(Si_3O_8)$	
	Zircon	$ZrSiO_4$	$ZrO_2 \cdot SiO_2$
	Rhodonite	$MnSiO_3$	$MnO .SiO_2$
	Willemite	Zn_2SiO_4	$2ZnO \cdot SiO_2$
Hydrated	Kaolinite	$Al_4(Si_4O_{10})(OH)_8$	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
	Montmorillonite	$Al_4(Si_4O_{10})(OH)_4 \cdot 4H_2O$	
	Serpentine	$Mg_6(Si_4O_{10})(OH)_8$	$3MgO \cdot 2SiO_2 \cdot 2H_2O$
	Garnierite	$(Ni, Mg)_6(Si_4O_{10})(OH)_8$	
	Bertrandite[a]	$Be_4(Si_2O_7)(OH)_2 \cdot nH_2O$	$4Be(OH)_2 \cdot 2SiO_2 \cdot nH_2O$
	Chrysocolla[a]	$Cu_3(Si_4O_{10})(OH)_3 \cdot nH_2O$	$CuO \cdot SiO_2 \cdot nH_2O$
	Hemimorphite	$Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$	
	Pollucite	$CsAl_4(Si_9O_{28}) \cdot H_2O$	

a. Thermal treatment is not necessary before leaching with dilute H_2SO_4. In case of chrysocolla, however, thermal treatment is necessary if NH_4OH is used for leaching.

Silicates are attacked by alkalies but the solutions are unstable — hydrated complex silicates are precipitated; that is why alkalies are not used for leaching. Most silicates are insoluble in acids; those which dissolve usually form unstable solutions from which gelatinous silica is liable to precipitate slowly over extended period of time causing filtration problems. To solubilize valuable silicates for metal recovery a thermal treatment is usually required before leaching.

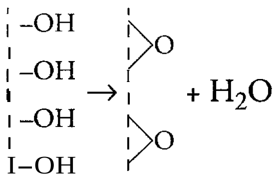
THERMAL TREATMENT

Silicates are usually subjected to a thermal treatment prior to leaching to improve their dissolution properties.

Anhydrous silicates. The anhydrous silicates may be treated in two ways:

- Melting and quenching to obtain a glassy structure that can readily be crushed, ground, and leached by acids, e.g., beryl and anorthosite.
- Heating to a temperature below the melting point to effect a phase transformation, e.g., spodumene when heated to 1,100°C is transformed to the β form which has a lower density. Because of the change of volume the product becomes porous and can be easily crushed and leached.

Hydrated silicates. Most hydrated silicates have to be heated to about 500 "C so that the hydroxyl groups are expelled from the crystalline structure in the form of water vapor, leaving behind a porous solid having a large surface area that can be easily leached with dilute acids; the process is known as dehydroxylation:



Depending on their structure, some silicate minerals when dehydroxylated are also accompanied by the formation of solid-solution containing silica in disordered structure of extremely small crystallite phase that is amorphous to X-rays. Such a product will show high reactivity towards leaching. However, if after dehydroxylation the temperature is allowed to rise, then at a certain temperature the disordered solid-solution will undergo crystallization and the amorphous phase disappears. This transformation is accompanied by:

- Appearance of a well-defined X-ray pattern.
- An exothermic effect which is irreversible on cooling.
- A decrease in surface area.
- The reactivity of the product is greatly decreased.

When the thermally treated silicates are attacked by dilute acids, the metal values go into solution leaving behind a skeleton of silica. When, however, concentrated acids are used, colloidal silica may form which causes filtration problems. Using concentrated acid is also not desirable because of problems encountered in later steps such as neutralization and washing.

ALUMINUM SILICATES

North America produces about 50% of the world's aluminum, yet must import more than 90% of the raw material needed, although there is abundant domestic resources of aluminum-bearing silicates raw materials such as clay, shale, anorthosite, nepheline, and fly ash from power plants (Table 16.3). There is also aluminum-bearing non-silicate raw material such as alunite and dawsonite. That is why there is extensive research underway to recover alumina from these non-bauxitic sources. None of the numerous processes that have been proposed so far has proved economically competitive with the Bayer Process using imported bauxite. Russia has the only aluminum industry based partly on non-bauxite raw materials, namely a nepheline syenite that contains apatite in the Kola peninsula. This operation was possible because of the large production of apatite for fertilizer, and the production of Portlant cement as a co-product.

Alumina from clays

Dilute acids are effective only in solubilizing clay if the clay is preheated at 400 °C to expel the combined water. For example, to render kaolinite, the main clay mineral, attacked by dilute acids, it is heated at 400–800 °C to convert it to metakaolin:

Table 16.3: Analysis of alumina-bearing materials.

	Bauxite %	Clay %	Shale %	Anorthite %	Nepheline %	Fly ash %
Al_2O_3	55–60	34	23	20–35	23–28	24–32
SiO_2	3.5	45	58	45.55	45.60	45–51
Fe_2O_3	2–25	2.6	6	1–3	1–3	7–11
TiO_2	1–5	2.4	1	< 1	0.2	1
CaO	0.2–0.6		2	5–15	1–3	1–5
MgO			5	1	0.1	1–4
$Na_2O + K_2O$	0.02		2–15	18	4–6	10–30
H_2O	10–30	13		< 1	trace	nil

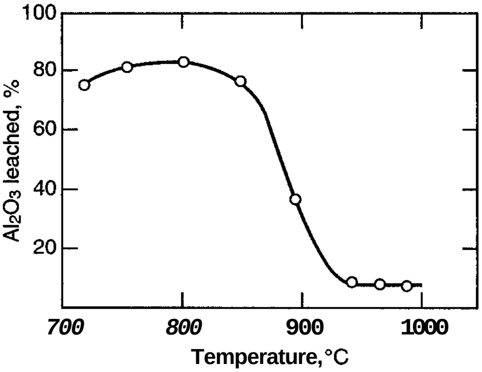


Figure 16.2: Effect of preheating temperature on the dissolution of Al_2O_3 from clay by H_2SO_4 (Zivan et al., 1983).

$$\underset{\text{kaolinite}}{Al_2(Si_2O_5)(OH)_4} \rightarrow \underset{\text{metakaolin}}{Al_2O_3 \cdot 2SiO_2} + 2H_2O$$

Metakaolin which is an amorphous aluminum silicate can be leached with acid to extract aluminum selectively leaving behind crystalline SiO_2:

$$Al_2O_3 \cdot 2SiO_2 + 6H^+ \rightarrow 2Al^{3+} + 2SiO_2 + 3H_2O$$

The temperature of dehydration is critical since at 900–1050 "C, metakaolin undergoes crystallization, and in this form, alumina is insoluble in acids (Figure 16.2). Montmorillonite, $Al_2(Si_2O_5)(OH)_2 \cdot 2H_2O$, is another clay mineral. On heating, it first loses the free water at 100 "C then the combined water at 600 "C.

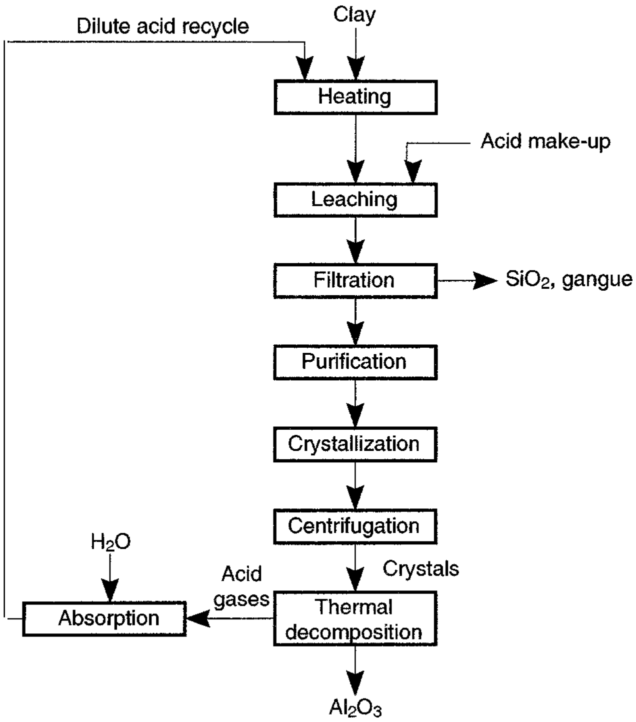


Figure 16.3: The recovery of alumina from clay.

The general scheme for treating clays is shown in Figure 16.3. The clay is first heated then leached with dilute acid. After filtering away the silica and gangue minerals, the solution is purified, then an aluminum salt is crystallized, separated by centrifugation, then decomposed to oxide. A variety of acids have been suggested, e.g., H_2SO_4, HCl, HNO_3, and H_2SO_3. The problems encountered are the following:

Purification. Chemical methods such as precipitation of iron as Prussian blue by calcium ferrocyanide, or solvent extraction are used for the removal of the last traces of Fe, Ti, Cr, and V, but such methods make the processes expensive.

Thermal decomposition. If H_2SO_4 is used for leaching and aluminum sulfate is crystallized, the cost of acid is low but the cost of decomposition of the sulfate to oxide is high. On the other hand, if HNO_3 is used for leaching and aluminum nitrate is crystallized, the cost of acid is high but the cost of decomposition is low (Table 16.4).

The economics of HCl leaching and aluminum chloride decomposition lies in between.

Acid recovery. When the aluminum salt is decomposed, the acid vapors must be collected and recycled. In case of sulfate, SO_2 may form because of the high temperature which necessitates its transformation to SO,. In case of nitrates, nitric oxide may also form which must be collected and transformed to HNO_3. To overcome the expenses in the second step of the H_2SO_4 process, it was proposed to convert aluminum sulfate to aluminum chloride by HCl:

$$Al_2(SO_4)_3 \cdot 18H_2O + 6HCl \rightarrow 2AlCl_3 \cdot 6H_2O + 3H_2SO_4 + 6H_2O$$

Aluminum chloride can then be decomposed more economically than the sulfate. H_2SO_4 generated during the conversion, and HCl formed during the decomposition are recovered and recycled.

Table *16.4:* Main decomposition reactions during the manufacture of alumina from clays.

Process	cost of acid	Decomposition reaction	Energy needed for decomposition
H_2SO_4	Low	$Al_2(SO_4)_3 \cdot 18H_2O \rightarrow Al_2O_3 + 3SO_3 + 18H_2O$	High
HCI	Medium	$2AlCl_3 \cdot 6H_2O \rightarrow Al_2O_3 + 6HCl + 9H_2O$	Medium
HNO_3	High	$2Al(NO_3)_3 \cdot 9H_2O \rightarrow Al_2O_3 + 6HNO_3 + 15H_2O$	Low

Alumina from nepheline

The production of Al_2O_3 from nepheline is a unique process used only in Russia. The source material is the waste from the beneficiation of apatite–nepheline rock, which contains enough Na_2O and K20 to convert its alumina content into aluminates. The feed material is mixed with limestone and calcined at 1250–1300 °C in a rotary kiln:

$$(Na,K)_2O \cdot Al_2O_3 \cdot 2SiO_2 + 4CaCO_3 \rightarrow (Na,K)_2O \cdot Al_2O_3 + 2Ca_2SiO_4 + 4CO_2$$

The sintered product is then crushed, ground, then leached with recycle NaOH solution. The filtrate is processed by CO_2 to precipitate $Al(OH)_3$ while the residue is made to cement. Some sodium carbonate and potassium carbonate are also recovered by crystallization from the leach solution after precipitating $Al(OH)_3$.

Alumina from anorthosite

Anorthosite, a solid solution of albite, $NaAl(Si_3O_8)$, and anorthite, $CaAl_2(Si_2O_8)$, is a potential source of aluminum. It is practically insoluble in most acids. However, when melted at about 1500 °C and the melt is quenched, the resulting amorphous material can be readily leached in dilute H_2SO_4 to dissolve aluminum.

Aluminum fluoride from clay

Fluorosilicic acid readily attacks clays at 70–80 °C to form either aluminum fluoride or aluminum fluorosilicate depending on the solid/liquid ratio:

$$Al_2(Si_2O_5)(OH)_4 + H_2SiF_6 \rightarrow 2AlF_3 + 3SiO_2 + 3H_2O$$

$$Al_2(Si_2O_5)(OH)_4 + 3H_2SiF_6 \rightarrow Al_2(SiF_6)_3 + 2SiO_2 + 5H_2O$$

In general the first reaction is preferable since it leads to a product needed by the aluminum industry. After filtering off the silica, the solution is evaporated to crystallize $AlF_3 \cdot 3H_2O$ which can be dried and calcined to AlF_3.

ASBESTOS TAILINGS

Canada produces about 35% of the world's asbestos, 82% of which comes from the Province of Quebec. Great interest has been expressed recently in the production of magnesium and its compounds from the asbestos tailings. Quebec produces about 1.5 million tons of asbestos and rejects about 20 million tons of tailings per year. The amount accumulated over the years is estimated at 600 million tons. A typical tailings analysis is given in Table 16.5. The material is already finely ground; the tailing piles represent a health hazard especially when the wind blows, and therefore they need regular attention to prevent excessive dust in the surroundings that may cause cancer in the lungs.

Table **16.5:** Typical analysis of asbestos tailings from Quebec.

	%
MgO	39
SiO_2	37
Fe	6
Ni	0.2–0.3
Co	0.02–0.03
Cr	0.1
H_2O	13

Table **16.6:** Forms of nickel in the asbestos tailings from Quebec.

	%
Silicate	67
Ni_3Fe alloy	30
Sulfide (Fe, Ni)S	3
Total	100

Table **16.7:** Separation of a magnetic fraction from asbestos tailings.

	Tailings feed	Nonmagnetic fraction	Magnetic fraction
Weight	100	80	20
MgO	40.8	42.9	26.0
SiO_2	39.0	35.8	21.8
Fe_2O_3	7.4	2.1	42.5
Cr_2O_3	0.19	0.10	0.62
NiO	0.38	0.25	0.45
Loss on ignition	15.5	16.7	8.3
Total	103.27	97.85	99.67

Mineralogically, the tailings are mainly serpentine which is a hydrated magnesium silicate. They represent also an appreciable nickel reserve. Nickel is mainly in isomorphous substitution with magnesium and the remaining is in form of a magnetic alloy Ni_3Fe and the sulfide pentlandite (Table 16.6). Since the tailings contain magnetic components (Ni_3Fe alloy and Fe_3O_4), it is possible to subject it to magnetic separation to obtain a concentrate rich in nickel and iron (Table 16.7), the serpentine can then be leached to recover magnesium. The tailings can also be melted with carbon in an electric furnace to produce a molten silicate phase that can be blown by air to form mineral wool for insulation and an iron–nickel alloy

The treatment of asbestos tailings is similar to that of clay for alumina production. To render serpentine soluble in dilute acids, it must first be heated to about 675 °C to drive off the combined water and to obtain a porous product with large surface area. The leach solution can be best purified by precipitating the impurities at pH 7 using MgO. The purified solution can then be subjected to crystallization. Hydrochloric acid is the preferred acid for leaching:

$$Mg_6Si_4O_{10}(OH)_8 + 12HCl \rightarrow 6MgCl_2 + 4SiO_2 + 10H_2O$$

because the crystals obtained can be dehydrated to get $MgCl_2$ for metal production, or decomposed to get MgO for refractories (Figure 16.4):

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

BERYLLIUM ORES

The major beryllium raw materials are beryl (anhydrous silicate) and bertrandite (hydrated silicate); rypical analyses of these materials are given in Table 16.8.

Table 16.8: Typical analysis of beryllium raw materials.

	Beryl concentrate %	Bertrandite ore %
BeO	8–10	0.5–1.4
Al_2O_3	17–18	8–10
SiO_2	58–60	53–64
$Na_2O + K_2O$	1–2	2–7
CaO + MgO	2–4	2–12
Fe_2O_3	1–3	1–2
MnO_2	—	0.2–1.3
ZnO	—	0.3–0.7
CaF_2	—	4.7–8.3
CO_2	—	0.2–7.9
Rare earth oxides	—	0.05
U_3O_8	—	0.008–0.03
H_2O	—	—

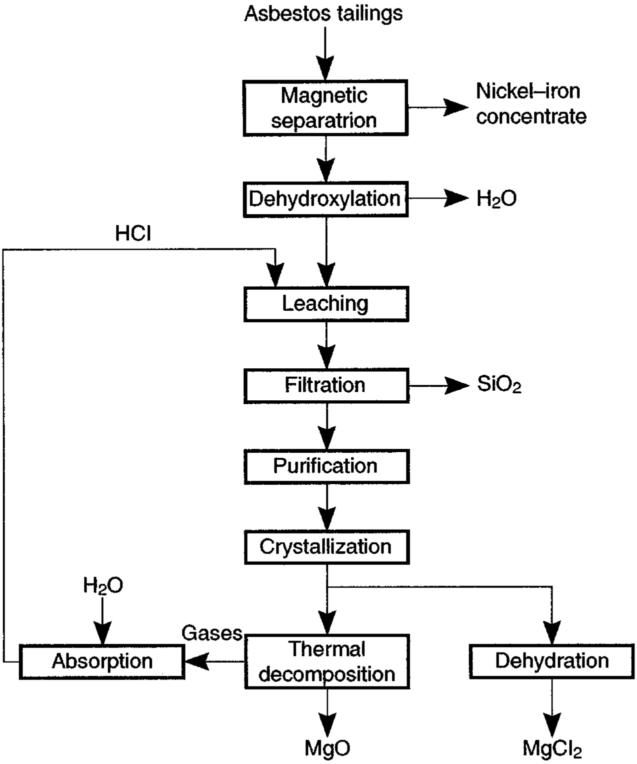


Figure 16.4: A possible route for the treatment of asbestos tailings.

Beryl

Beryl is composed of hexagonal silicate rings connected together by Al^{3+} and Be^{2+} ions as shown in Figure 16.5. It is a highly refractory mineral that is not attacked by concentrated acids. When, however, it is melted (m.p. 1627 °C) and the molten mass is rapidly quenched in water, an amorphous glassy product is obtained from which beryllium can be leached by dilute acids leaving a porous siliceous matrix:

$$Be_3Al_2(Si_6O_{18}) + 12H^+ \rightarrow 3Be^{2+} + 2Al^{3+} + 6SiO_2 + 6H_2O$$

Table 16.9 gives an analysis of a leach solution.

Table 16.9: Typical analysis of sulfuric acid leach solutions of beryllium raw materials.

	Beryl concentrate g/L	Bertrandite ore g/L
Be	11	0.4–0.7
Al	25	4–7
Fe	2	1.5
Mg	—	3–5
H_2SO_4	50	1

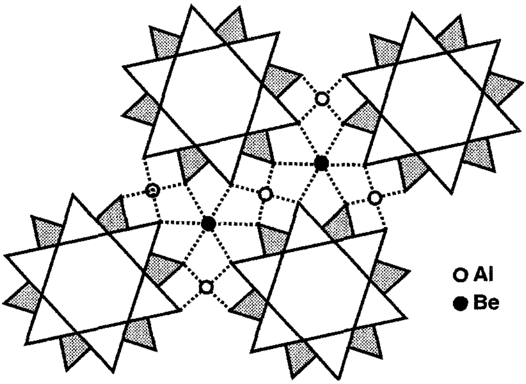


Figure 16.5: The structure of beryl. Triangles connected together to form the six-membered rings are the SiO_4 tetrahedra. The hatched rings are at a lower level.

Bertrandite

Large deposits of bertrandite-containing clays are found at the Spor Mountain in Utah. The ore is readily leached by dilute sulfuric acid:

$$Be_4(Si_2O_7)(OH)_2 \cdot nH_2O + 8H^+ \rightarrow$$
$$4Be^{2+} + 2SiO_2 + (n+5)H_2O$$

Aluminum and iron minerals are also solubilized (Table 16.9). Since these are about ten times the concentration of beryllium, the leach solution is treated by organic solvents to separate beryllium.

OTHER SILICATES

Spodumene

Spodumene is a lithium aluminum silicate; it is a hard mineral of 3.15 density which occurs in nature in the alpha form and is not attacked by hot concentrated H_2SO_4. However, when it is heated at 1100 "C, it is converted to the beta form which has a density of 2.4. When the hot beta form is rapidly cooled, then due to the volume change accompanying the phase transformation, the product can be easily crushed to a fine powder and will react readily with hot concentrated H_2SO_4:

$$2LiAl(Si_2O_6) + 8H^+ \rightarrow 2Li^+ + 2Al^{3+} + 4SiO_2 + 4H_2O$$

Pollucite

Pollucite is a cesium aluminum silicate having the formula $CsAl_4(Si_9O_{28})\cdot H_2O$. A chemical analysis of the most important pollucite ores is given in Table 16.10. Leaching is carried out by 14.4 M H_2SO_4 at 120 "C for 2 hours, then filtering while hot to remove the silica. The solution is then cooled to 0 "C to crystallize cesium alum, $Cs_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$. Cesium can then be separated from aluminum and recovered either as cesium sulfate or cesium chloride.

Table 16.10: Chemical **analysis** (in %) of pollucite ores.

	Maine, U.S.A.	Bikita, Rhodesia	Manitoba, Canada
CS	8.2	22.4	25.5
Rb	0.2	0.8	0.8
Na	4.9	1.8	1.1
K	*1.4*	**1.3**	1.0
Li	0.2	0.3	0.3
SiO_2	57.8	48.8	49.0
Al	11.7	10.5	8.8

Siliceous and granitic rocks

Some clays contain a small percentage of uranium. In these cases uranium does not form a mineral, but occurs dispersed in the silicate phase, probably in isomorphous substitution with another metal ion in one of the minor constituent minerals. In Sweden, uranium was recovered on a commercial scale from siliceous shale deposits containing only 0.02% uranium. The shale was leached with sulfuric acid. Before the discovery of large uranium ore deposits, much work was done to investigate the possibility of recovering uranium from granitic rocks. Such rocks contain about 10 ppm uranium, and it was concluded that it might be feasible to process such rocks for uranium recovery.

Zinc silicate ores

Minor zinc silicate ores are treated for the recovery of zinc. Willemite, Zn_2SiO_4, and hemimorphite, $Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$, dissolve completely in dilute sulfuric acid, e.g.:

$$Zn_2SiO_{4(s)} + 2H_2SO_{4(aq)} \rightarrow 2ZnSO_{4(aq)} + Si(OH)_{4(aq)}$$

Chapter Seventeen

Chlorides and Sulfates

Nonferrous Metals From Pyrite Cinder 375
The chloride route. 375
The sulfate route 376

NONFERROUS METALS FROM PYRITE CINDER

Pyrite is mainly used for the manufacture of sulfuric acid. It is oxidized in fluidized bed reactors whereby the following reaction takes place:

$$2FeS_2 + {}^{11}/_2O_2 \rightarrow 4SO_2 + Fe_2O_3$$

While SO_2 can be readily converted to SO_3 and then to H_2SO_4, iron oxide (called cinder) cannot be used directly for manufacturing iron because of the presence of impurity metals. Table 17.1 shows analysis of cinder. As a result, methods have been developed to purify the cinder and at the same time to recover the nonferrous metals present. The recovery of nonferrous metals from the cinder is achieved by two routes: the chloride and the sulfate processes.

Table 17.1: Typical analysis of pyrite cinder.

Main components, %		Trace metals, ppm	
Fe	54–58	Co	300–1500
Gangue	6–10	Ag	25–50
Cu	0.8–1.5	Au	0.5–1.5
Zn	2.0–3.5	Cd	40–100
S	2.5–4.0	Tl	15–45
Pb	0.3–0.7	Ni	10–1500
		Mn	300–3000

The chloride route

In this route, the nonferrous metals are transformed into water-soluble chlorides by heating with a solid chloride. At low temperature, the chlorides remain in the residue while at high temperature they are volatilized.

- *DK Process.* This process has been used in Germany for nearly a century at the Duisburger Kupferhutte in Duisburg[1]. The pyrite cinder is mixed with NaCl and heated continuously in a multiple hearth furnace at 800 °C to transform nonferrous metals into water-soluble chlorides. Each batch requires about 2 days for leaching in vats. The concentrated leach solution obtained in the first 15 to 20 hours is sent for copper recovery, while that subsequently obtained, being poor in metal content, is recycled. The residue, called purple ore, now a high-grade iron ore (61–63% Fe), is sintered and delivered to the blast furnace.
- *Kowa-Seiko Process.* This is a Japanese process in which the cinder is mixed with calcium chloride, palletized, then heated in a rotary kiln at 1100 °C to volatilize nonferrous metal chlorides (Table 17.2). These are scrubbed in water from the exit gases and the solution treated for metal recovery.

Table 17.2: Data on the treatment of pyrite cinder by Kowa Seiko Process.

	Dry pellets, %	Heated pellets, %	Volatilization, %
Cu	0.47	0.04	91
Pb	0.18	0.01	92
Zn	0.59	0.01	97
As	0.05	0.05	—
S	0.61	0.03	96.5
Fe	59.2	61.5	—
Au[a]	0.94	0.05	95
Ag[a]	33.6	7.00	80

a. g/t

The sulfate route

This route is mainly used for the recovery of cobalt from the cinder. It is based on a careful temperature control during the oxidation of pyrite. If the temperature is kept at 550 °C, cobalt in the pyrite will be converted to sulfate and therefore can be leached directly from the cinder with water. At least two plants are using this process:

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[1] Operations ceased in the 1980s.

- At the Bethlehem Steel plant, Sparrows Point, Maryland, the hot pyrite cinder is quenched with water to give a slurry containing 6–8% solids. When the solids are filtered off, the solution contains 20–25 g/L Co; it is processed further for metal recovery. In the cinder, the Fe:Co ratio is 50:1; in solution it is 1:1. This plant supplies the only domestic source of cobalt in U.S.A.
- In Finland at the Outokumpu Company plant, the sulfated pyrite cinder contains 0.8–0.9% Co and other nonderrous metals. It is leached with water to get a solution at pH 1.5 analyzing 20 g/L Co, 6–8 Ni,'7–8 Cu, 10–12 Zn, and trace amounts of iron, which is treated for metal recovery.

Part Four

Treatment of Leach Solutions: Concentration, *Purification*

Chapter Eighteen

General Aspects

Scope. 381
Distribution Ratio *384*

SCOPE

Leach solutions are sometimes concentrated and/or purified before metal recovery by one of the following methods[1]:

- Adsorption on activated charcoal
- Ion exchange
- Solvent extraction.

Adsorption on activated charcoal and ion exchange processes are conducted in columns filled with charcoal and ion exchange resins, respectively (Figure 18.1). The circuit involves two steps: loading of the desired metal and unloading, with water-washing after each step to remove the entrained solution. After the unloading step, the column is ready again for loading.

In solvent extraction the leach solution is mixed with an immiscible organic solvent so that the desired metal ion in the aqueous phase is transferred to the organic phase (Figure 18.2). The two phases are then allowed to separate. The process is then repeated by contacting the loaded organic phase with an aqueous solution now capable of transferring the desired metal ion back to the aqueous phase. The aqueous phase so obtained is a pure and concentrated solution suitable for metal recovery while the stripped organic phase is suitable for recycle.

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[1] Purification of leach solutions by the selective precipitation of the impurities is discussed in Part Five.

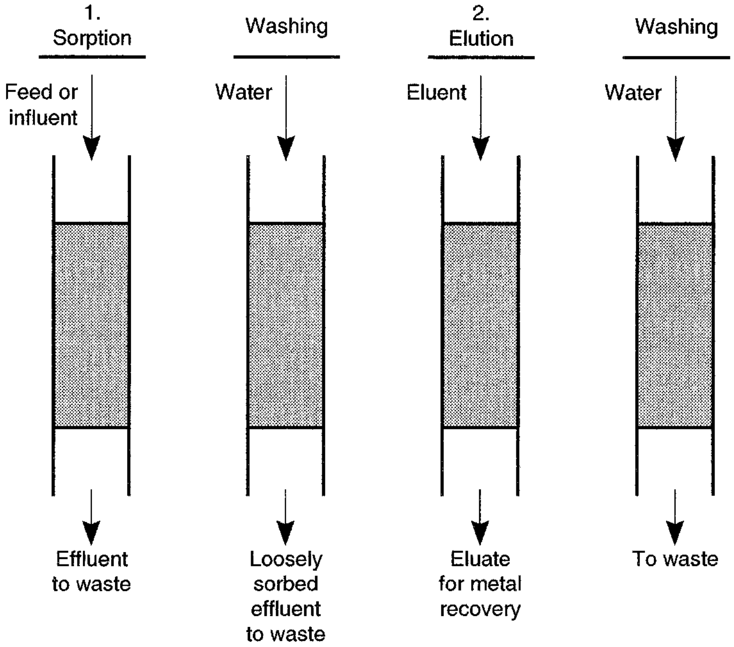


Figure 18.1: Sequence of operations in adsorption and ion exchange processes.

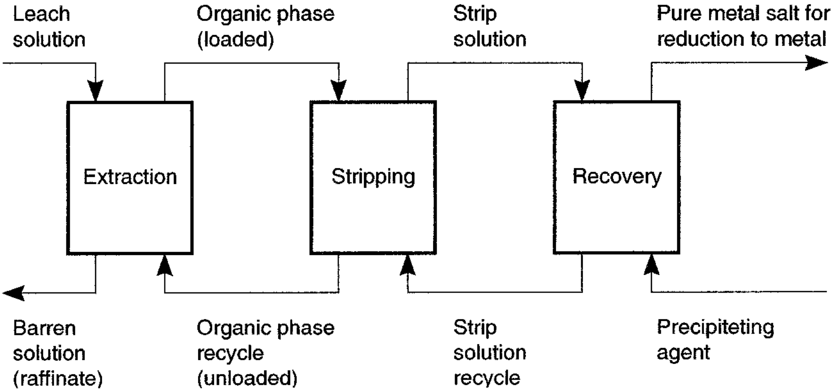


Figure 18.2: General scheme in solvent extraction.

Adsorption on activated charcoal is used mainly for concentrating gold and silver from cyanide leach solution. It is a cheap but a slow method for treating such dilute solutions. It can also be used for turbid solutions or pulps thus saving an expensive filtration step. Ion exchange is used mainly for uranium concentration from leach solutions and also for separating the individual members of the lanthanides. It is a relatively expensive operation, most suitable for dilute solutions usually operated batchwise or semi-continuously, but has the advantage of being used in turbid solutions thus saving an expensive filtration step. Solvent extraction is a continuous process, operates only on clear and relatively concentrated solutions. Its cost is moderate and used extensively for a large variety of metals. Adsorption is a physical process, ion exchange is physico-chemical, solvent extraction is a chemical reaction between the metal species and the organic molecule. Table 18.1 gives a comparison between the three processes.

Table 18.1: Comparison between the different concentration–purification processes.

	Adsorption on activated charcoal	Ion exchange	Solvent extraction
Maximum efficiency	dilute solution	dilute solution	concentrated solution
Speed	slow	slow	rapid
Capacity	low	high	high
Clarity of solution	clear or turbid	clear or turbid	clear
Method of operation	batch or semi-continuous	batch, semi-continuous, or continuous	continuous
cost	low	high	moderate
Main application	gold and silver from cyanide solution	uranium lanthanides	U, Cu, Zn, Be, B, V, Cr, Fe, Co, Ni, Zr, Hf, Nb, Ta, Mo, W, As, Pt-metals, Au, Th, Pu, lanthanides.
Mechanism	physical	physico-chemical	chemical

Concentration–purification processes may be applied in two ways:

- *Enrichment.* Removing the metal values selectively from the leach solution leaving behind the impurities. For example, the recovery of uranium by ion exchange or solvent extraction, and the recovery of gold by adsorption on activated charcoal.
- *Purification.* Removing the impurities from the leach solution leaving behind the metal values. For example, removal of iron from aluminum chloride solution in the recovery of aluminum from clay, or the removal of arsenic from copper sulfate electrolyte in the electrolytic refining of copper by organic solvents.

DISTRIBUTION RATIO

When the aqueous phase containing the metal ion to be removed is equilibrated with the solid or the immiscible liquid solvent, and the two phases are analyzed, the ratio of concentration in the two phases is called the distribution ratio:

$$D = \frac{\text{Concentration of metal ion in solid or in solvent}}{\text{Concentration of metal ion in aqueous phase}}$$

The higher the value of *D* the more efficient is the transfer. The plot of the concentration of metal ion in solvent or in solid adsorbent at constant temperature versus that in the aqueous phase is the distribution isotherm (Figure 18.3). The slope of the curve at any point equals *D*. It can be seen that *D* is not a constant value but varies with the experimental conditions; in dilute solutions the value of *D* is high and in concentrated solutions it is low.

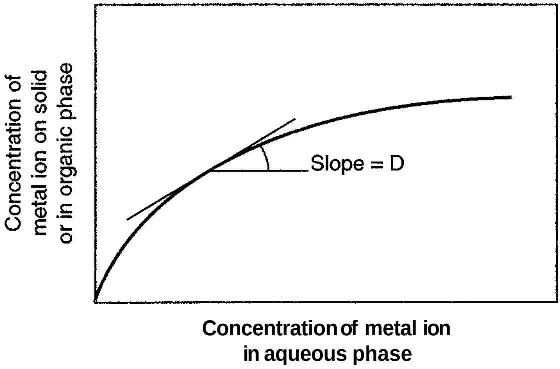


Figure 18.3: Distribution isotherm.

Chapter Nineteen

Adsorption on Activated Charcoal

Activated Charcoal 385
  Preparation 386
  Structure 388
  Properties 388
Mechanism of Adsorption 392
  Adsorption isotherms 392
  Effect of temperature 395
  Effect of organic solvents 396
  Effect of foreign ions 398
  Effect of time 398
Desorption 399
Engineering Aspects 399
  Column process 400
  Carbon-in-pulp process 400
  Carbon-in-leach process 400
Summary 403

ACTIVATED CHARCOAL

Activated charcoal was first applied in metallurgy in connection with gold recovery by the chlorination process. When this process was displaced by cyanidation, charcoal was also used for the new process[1]. In both cases gold was recovered from the gold-laden carbon by burning the carbon to ashes and melting to bullion, which was an expensive and wasteful process. This disadvantage, coupled with the major advances that were made in the technology of gold recovery by precipitation with zinc dust at that time, led to abandoning the process utilizing activated carbon. In the early 1950s, however, interest in the metallurgical application of activated carbon was revived when a pro-

---

1. The mechanism in the two cases is different: in chloride medium, the process is precipitation by reduction (see chapter 25), while in cyanide medium it is an adsorption phenomenon.

cedure was developed for the elution of gold and silver adsorbed on carbon granules, which allowed re-use of the carbon, and the utilization of the process as a concentration–purification step. This led to a wide-spread application of this technology.

The adsorption of metal ion by activated charcoal is slight as compared to ion exchange resins and is usually favorable only to anions and not to cations; however, activated charcoal is a much cheaper material. To increase the adsorptive capacity of coal it is sometimes pretreated with acids to impart ion exchange properties to its surface. Sulfonated coals or coals oxidized by nitric acid are available commercially as cationic exchangers.

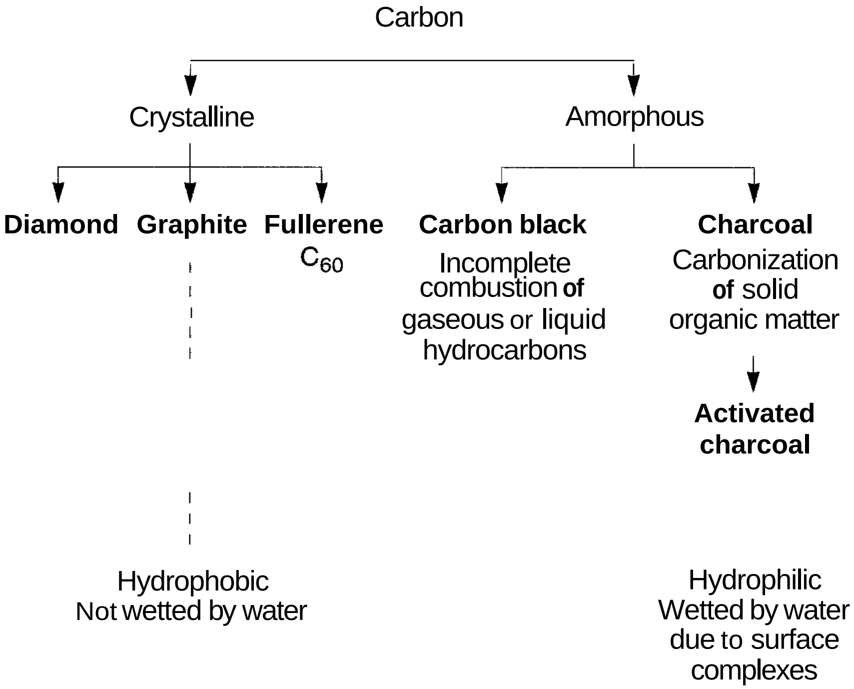


Figure 19.1: Varieties of carbon.

Preparation

There are two varieties of carbon (Figure 19.1): *Crystalline,* these are diamond, graphite, and fullerene, and *amorphous,* these are the carbons in which the crystal size is so small that it does not give an X-ray diffraction pattern. This variety is of two types, chemically similar but different in physical aspects'[1]:

- *Carbon blacks.* These are nonporous fine particles of carbon prepared by the incomplete combustion of *gaseous* or *liquid* carbonaceous material, e.g., natural gas, acetylene, oils, resins, tar, etc., in a limited supply of air. Lamp black and acetylene black are typical of this group. They are used as pigments, in the rubber industry, and in ink manufacture.
- *Charcoals.* These are prepared by heating of *solid* carbonaceous material such as coal, wood, nut shells, sugar, and synthetic resins at about 600 °C in the absence of air, to volatilize the component elements other than carbon — a process known as "Carbonization". Such charcoals have low porosity, but when heated at 400–800 °C for a limited time with air, chlorine, or steam, a highly porous material is produced (Figure 19.2). Such porous material is called "activated charcoal", and is used as an adsorbent in the chemical and the metallurgical industry, usually in the form of pellets about 2 mm in diameter.

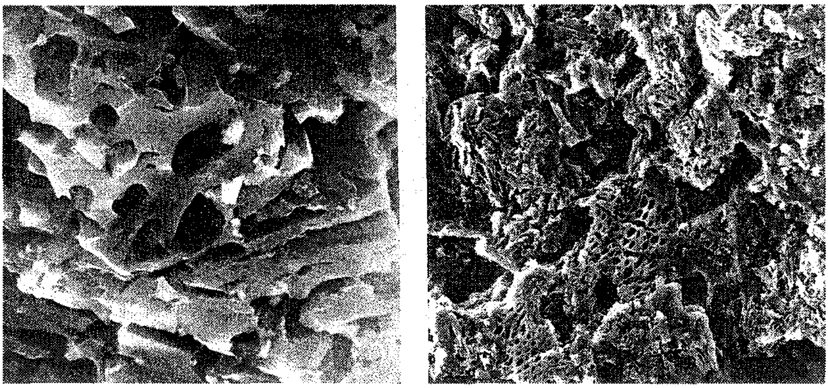


Figure 19.2: Electron micrographs of typical activated carbon showing the porous structure.

In the activation step the small pore structure of the coke is developed by burning away some of the remaining material to create new

---

[1] The so-called *animal charcoal* or *bone-char* is produced by pyrolyzing bones. It is mainly calcium phosphate with ≈ 10% carbon; it is also used as an adsorbent.

pores and enlarge others. Charcoals activated at low temperature (400 °C) are abbreviated L-charcoals; those activated at high temperature (800 °C) are abbreviated H-charcoals. After activation, H-charcoals must be cooled in an inert atmosphere; otherwise they will be converted to the L-type.

Structure

The structure of activated charcoal is essentially like graphite, i.e., carbon atoms covalently bonded in planar hexagonal arrays with weak van der Waals' bonds between the planes, but the structure is considerably disordered and the separation between the layers is greater than that found in graphite. Graphite fractures easily along the planes; in this process no covalent bonds are broken but rather the layers are detached due to overcoming the van der Waals' forces. Hence the new surface exposed is hydrophobic, i.e., it is not wetted by water. The surface properties of activated charcoal is, however, different from that of graphite (or coal) for the following reasons:

- The large surface area and the high porosity due to the activation process.
- The presence of organic surface groups formed during the activation process which render the surface hydrophilic, i.e., it is wetted by water.

As a result, activated charcoal may be considered to possess a polar surface.

Properties

The properties of activated charcoal depend primarily on the temperature of activation. Table 19.1 gives some data on charcoals prepared from sucrose by activation at different temperatures. From this it can be seen that activated carbons contain appreciable amounts of hydrogen and oxygen. These are thought to be chemically bound in the form of "surface complexes". Activated carbon should, in fact, be regarded as a *complex organic polymer* and not merely as an amorphous form of the element carbon. Figure 19.3 shows some of the organic surface groups identified on activated charcoal. L-charcoals are not commonly used because of their low surface area.

Table 19.1: Effect of activation temperature on the properties of sugar carbon activated by oxygen (Garcen and Weiss, *1955)*.

	Activation temperature			
	400°C	*550°C*	*650°C*	*800°C*
	L-charcoal			H-charcoal
Analysis [%]				
Carbon	*75.7*	*85.2*	*87.3*	*94.3*
Oxygen	*19.0*	*10.4*	*7.4*	*3.2*
Hydrogen	*3.2*	*2.7*	*2.1*	1.5
Ash	*0.7*	*1.3*	*1.4*	(1.2)
Surface Area (m^2/g)[a]	*40*	*400*	*390*	*480*
pH of Water Suspension	*4.5*	*6.8*	*6.7*	*9.0*
Adsorption (μequiv./g)				
NaOH	*340*	*159*	*158*	*23*
HCI	*39*	*155*	*169*	*265*

a. Determined by BET method.

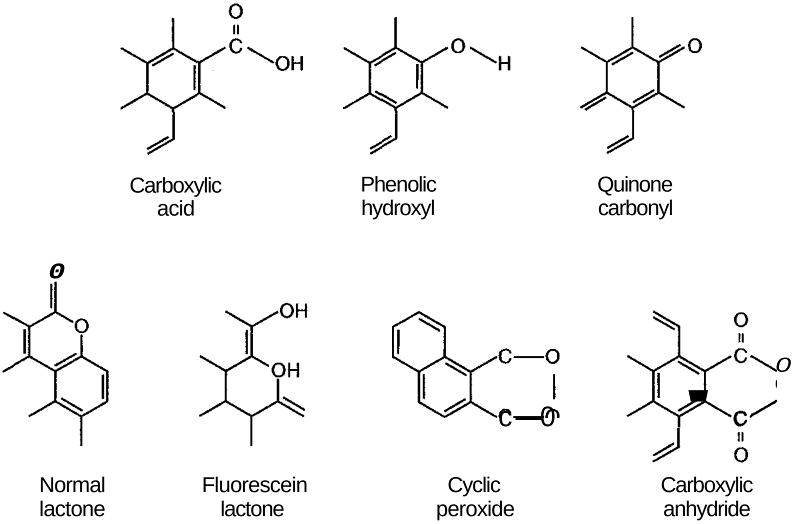


Figure **19.3:** Structure of some surface oxides that have been proposed as being present on the surface of activated carbon.

Sugar charcoal prepared at 550 °C has roughly 30 atoms of hydrogen and 9 of oxygen for every 100 atoms of carbon. Charcoal prepared at 800 "C has about 20 atoms of hydrogen and ***6*** of oxygen for every 100 atoms of carbon. The ash content of charcoal increases with increasing temperature of activation, since during this process more volatile matter is removed. The ash, even if present to the extent of only a few units, can profoundly alter the adsorbing characteristics of the carbon. Ash components are K_2O, Na_2O, CaO, MgO, Fe_2O_3, P_2O_5, SO_3, Cl^-. Ash can be removed from charcoals by washing with concentrated HCl or HF, and then by water. Charcoals with minimum ash content are those made from sucrose. The most important properties of activated charcoal can be summarized as follows:

- *Action of distilled **water.*** Activated charcoal when shaken with distilled water changes the pH either on the acidic or basic side depending on the method of activation of the charcoal. As a result, the charcoal has the capacity to adsorb alkali or acid, respectively. However, this phenomenon does not take place in absence of *oxy*gen. Thus a carbon activated at 950 °C, thoroughly outgassed in a high vacuum at this temperature, and subsequently cooled in an inert atmosphere, does not adsorb mineral acids from a dilute deaerated solution. Adsorption appears to be a function of the oxygen pressure (Figure 19.4). Also, when oxygen is bubbled through a suspension of charcoal in dilute acid and then the suspension is filtered, H_2O_2 will be found in the filtrate. H-charcoal yields more peroxide than L-charcoal. The formation of H_2O_2 can be due to the reduction of oxygen:

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

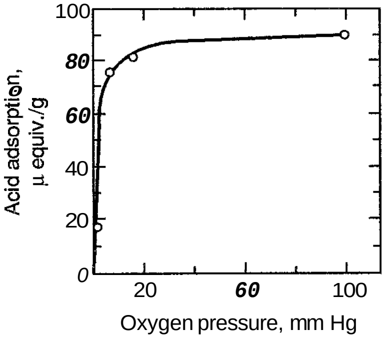


Figure 19.4: Effect of oxygen on the adsorption of acid on activated charcoal (Frumkin et al., 1931).

Since the electrons are supplied by the charcoal, it will acquire a positive charge. To maintain electrical neutrality on the surface of the charcoal, OH– ions or other anions in solution are attracted to the surface resulting in their adsorption. As a result of the presence of H_2O_2, some charcoals catalyze the oxidation of Fe^{2+} to Fe^{3+}, and sulfurous acid to sulfuric acid. The above reaction also explains why H-charcoal when shaken with distilled water changes the pH to the basic side. This pH change plays an important role when charcoal is in contact with aqueous solutions as explained below.

- *Reaction with metal ions.* In absence of complexing agents and at low pH, no sorption of metal ions takes place. However, when neutral or weakly acidic solution of metal ions ($pH > 4$) such as mercury, copper, cobalt, nickel, or lead are contacted with charcoal, sorption takes place due to precipitation since aqueous suspensions of charcoals are usually alkaline (H-charcoal). One kilogram charcoal sorbs about 2 g metal ion. This is the basis of decontaminating surface waters containing metal ions by activated charcoal.

- *Reducing properties.* L-charcoals readily reduce Au(III), Ag(I), and Hg(II) salt solutions to metals at ambient temperature. For example:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

$$Au^{3+} + 3e^- \rightarrow Au^0$$

Overall reaction:

$$4Au^{3+} + 3C + 6H_2O \rightarrow 4Au^0 + 3CO_2 + 12H^+$$

This was the basis of the early method of gold recovery from chlorine leach solution. Acid solutions of $KMnO_4$ are decolorized by charcoal, and MnO_2 is precipitated. Potassium chromate is also reduced.

- *Other properties.* Some charcoals have oxidizing properties, e.g., they liberate iodine from acidified potassium iodide solution. This has been attributed to the presence of hydrogen peroxide when the charcoal is immersed in solution. Addition reactions may take place in which two atoms are added to one double bond, e.g., in the chemisorption of bromine. The treatment of charcoal with hydrogen gas at 150–200 °C develops an appreciable amount of surface acidity. Substitution reactions take place when an L-charcoal is heated in a stream of chlorine; considerable amounts of

HCl are produced and the resulting carbon contains sorbed chlorine.

Activated charcoals are semiconductors, but this property is gradually lost as the carbon is heated to temperatures exceeding 600–700 "C. A carbon prepared at 3000 "C becomes a metallic conductor as is graphite. The mechanical strength of charcoals increases when prepared above 700 "C.

MECHANISM OF ADSORPTION

Adsorption is considered to be due to the fact that the interatomic forces acting upon a surface atom are fewer than those acting upon an atom in the bulk of the solid. There is, therefore, a net resultant force acting upon a surface atom in the direction of the bulk (Figure 19.5). The surface will thus possess a degree of unsaturation and will adsorb the molecules or ions in its proximity.

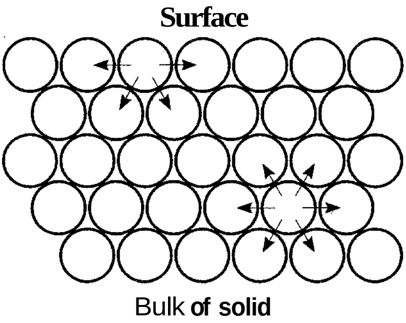


Figure 19.5: Interatomic forces acting on surface atoms as compared to those in the **bulk** of the solid.

Adsorption isotherms

The phenomenon of adsorption was first studied in connection with the behavior of solids when in contact with gases. In many processes, it was found that the amount of gas w adsorbed by unit mass of adsorbing material varies with the pressure of the gas. The relation was expressed empirically as:

$$w = kp^{1/n}$$

where p is the pressure of the gas, k and n are constants ($n > 1$). This relation is known as *Freundlich adsorption isotherm* after its discoverer. The plot of log w against log p gives a straight line of slope $1/n$. The same relation was later found to apply also for solids, including activated charcoal, in contact with aqueous solutions containing a solute. In this case the relation becomes:

$$w = kC^{1/n}$$

where w is the amount of solute sorbed and C is its concentration, and the plot of log w against log C gives a straight line of slope $1/n$ (Figure 19.6). It can be seen that adsorption is effective only from dilute solutions since at high ion concentration in solution the quantity adsorbed is nearly constant.

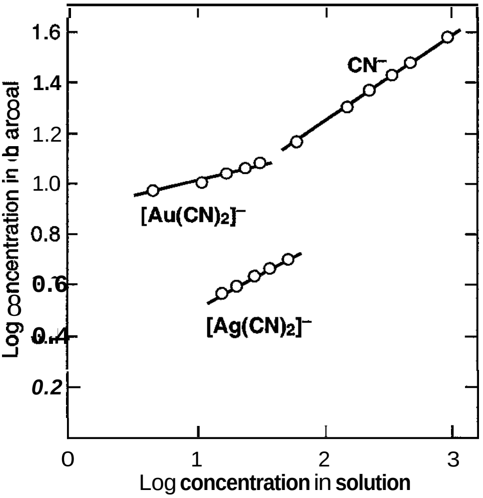


Figure 19.6: Adsorption of gold, silver, and potassium cyanide on activated charcoal (plotted from data by Gross and Scott, 1927).

The theoretical basis of Freundlich's equation was explained in 1916 by Langmuir as follows: Adsorption is achieved when the rate at which gas molecules are held to the surface equals the rate of their evaporation from the surface. According to the kinetic theory of gases, at a constant temperature, the rate at which the gas molecules will strike the surface is proportional to the pressure of the gas. If at any instant a fraction of the surface θ is already covered with gas molecules, the fraction (1 – @) of the surface will be bare. Assuming only a monomolecular layer adsorption, therefore, only those molecules striking the bare surface can be retained, hence:

Rate of adsorption of gas molecules = $kp(1-0)$

Rate of evaporation = $k'\theta$

At equilibrium the rate of adsorption will be equal to the rate of evaporation, i.e.:

$$kp(1-\theta) = k'\theta$$

$$\theta = \frac{kp}{kp + k'}$$

The amount of gas w adsorbed per unit mass of adsorbent is directly proportional to the fraction θ of the surface covered if the surface can become covered with a uniform layer of gas one molecule in thickness:

$$w = k''\theta$$

Inserting this value of θ in the above equation, then:

$$w = \frac{(kk''/k')p}{(k/k')p + 1} = \frac{k_1p}{k_2p + 1}$$

where k_1 and k_2 are constants. This equation is known as the *Langmuir adsorption isotherm.* It can be seen that when k_2P « 1, then the adsorption isotherm becomes:

$$w = k_1p$$

i.e., the extent of adsorption is directly proportional to pressure; this is the case at very low pressures. On the other hand, when k_2p » 1, then:

$$w = \frac{k_1}{k_2}$$

i.e., the amount of gas adsorbed at any temperature should reach a constant limiting value at high pressures. This condition arises when the surface is completely covered by a unimolecular layer of gas molecules. The amount of gas adsorbed, therefore, varies with a fractional power of the pressure which is in agreement with Freudlich isotherm:

$$w = kp^{1/n}$$

Effect of temperature

When the effect of temperature on adsorption was studied, it was found that some processes decreased with increasing temperatures while others increased. **As** a result two types of adsorption processes were identified: physical and chemical.

Physical adsorption. In this case, the amount adsorbed at equilibrium decreases with increased temperature because the process is slightly exothermic. This follows from van't Hoff's equation:

$$\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

when AH is positive, i.e., endothermic reaction then K_2 will be higher than K_1, and when AH is negative, i.e., exothermic reaction then K_1 will be higher than K_2, i.e., the amount adsorbed decreases with increasing temperature. Hence, reversibility can be readily achieved by increasing the temperature. In this type, the molecules or ions are held to the surface by weak forces of attraction that range from van der Waals' forces to hydrogen bond formation. Figure 19.7 shows the effect of temperature on the adsorption of silver from cyanide solution on activated charcoal.

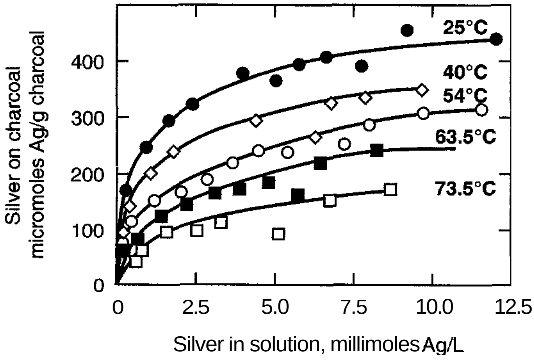


Figure 19.7: Adsorption isotherms for silver cyanide on activated charcoal (Dixon **et al.**, 1978).

Chemical adsorption. In this case, the amount adsorbed at equilibrium increases with increased temperature because the process is endothermic. This type is known as chemisorption; it is a chemical reaction that takes place on the surface of the solid and may involve ion exchange or precipitation. It is an irreversible process. In both cases an ion in solution displaces another in the crystal lattice of a solid in contact with the solution with or without a change in the structure. For example, the adsorption of fluoride ion on hydroxyapatite crystal:

$$Ca_{10}(PO_4)_6(OH)_2 + F^- \rightarrow Ca_{10}(PO_4)_6(OH)F + OH-$$

is not accompanied by a change in crystal structure (an ion exchange process) while the adsorption of silver ions on sphalerite crystals:

$$ZnS + 2Ag^+ \rightarrow Ag_2S + Zn^{2+}$$

is accompanied by a change in crystal structure (a precipitation process). Chemisorption may propagate from the surface into the bulk of the absorbent turning it into an ordinary heterogeneous reaction.

Effect of organic solvents

Acetone was found to decrease greatly the adsorption of gold cyanide complex on charcoal. More data can be inferred from desorption data that alcohols do not favor adsorption. It was found, for example, that methanol, ethanol, isopropyl alcohol, and acetonitrile increase the rate of desorption of gold from charcoal. For example, a 20% ethanol in an aqueous solution containing 0.1% NaCN and 1% NaOH at 93 °C readily desorbs charcoal loaded with gold while a similar solution without alcohol is desorbed with difficulty (Figure 19.8). Alcohol is adsorbed on the charcoal; a typical activated charcoal adsorbs about 12% of its weight ethanol when treated with the above mentioned desorbing solution. Desorption also increases with increased temperature (Figure 19.9).

The unfavorable effect of alcohols on adsorption can be explained by the low dielectric constant of these compounds which also decreases with increased temperature. The dielectric constant of a medium is related to its polarity and water molecules are highly polar. The force of electrostatic attraction between two oppositely charged particles is inversely proportional to the dielectric constant of the medium separating the charges. Thus, in the case of gold cyanide complex in water (high dielectric constant), the force of attraction between the negatively charged cyanide complex and the positively charged K^+ or Na+ is small and therefore the complexed gold ion is free to move and adhere to the charcoal; but in presence of alcohol (low dielectric constant) the reverse is true.

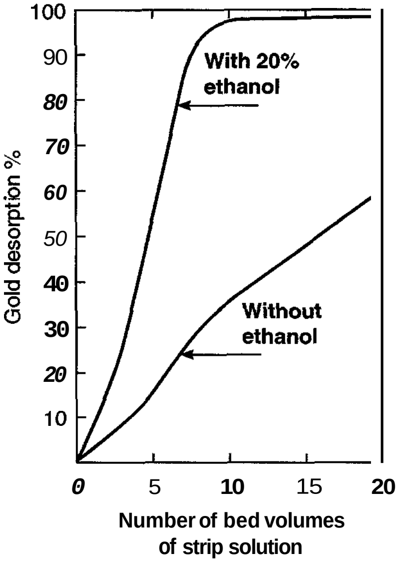


Figure 19.8: Effect of ethanol gold desorption. Conditions: 1% NaOH, 0.1% NaCN, temperature 93 "C (Heinen et al., 1976).

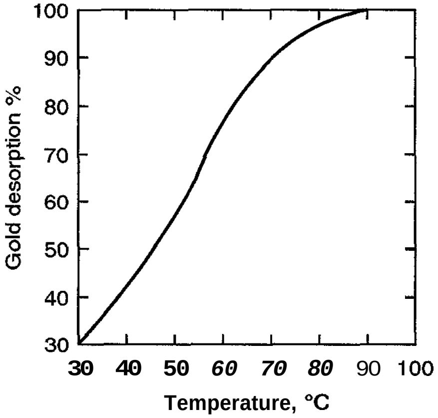


Figure 19.9: Temperature effect on desorbing gold with alkaline cyanide solution containing methanol. Conditions: 20% Methanol, 1% NaOH, 0.1% NaCN (Heinen et al., 1976).

Effect of foreign ions

Adsorption of gold from cyanide solution decreases with increased concentration of other anions in solution, e.g., CN^- or OH^- as shown in Figure 19.10. Because these anions are also adsorbed and hence they are competing with the positively charged charcoal surface. Positively charged ions, e.g., Na^+ or Ca^{2+} are not adsorbed and do not influence the adsorption of gold. However, $CaCO_3$ precipitates on charcoal because CaO is used to adjust the pH during leaching and the solution adsorbs CO_2 from the air thus favoring the precipitation of $CaCO_3$. It is also possible that calcium peroxide, CaO_2, precipitates due to the presence of H_2O_2 in the leach solution. Because of the blocking of the pores of charcoal by these precipitates, an acid leaching step is usually introduced during regeneration to dissolve the precipitates in the regeneration step.

Effect of time

The equation describing the kinetics of many adsorption processes is known as the *Elovich equation:*

$$W = K \log t$$

i.e., the plot of the amount adsorbed, W, against the logarithm of the time gives a straight line with a slope K. The rate of adsorption of gold and silver from cyanide solution on activated charcoal obeys this relation (Figure 19.11).

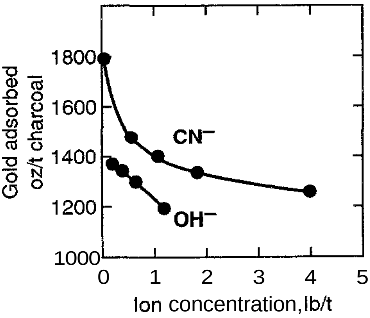


Figure 19.10: Effect of potassium cyanide and sodium hydroxide on gold adsorption on activated charcoal (plotted from data by Gross and Scott, 1927).

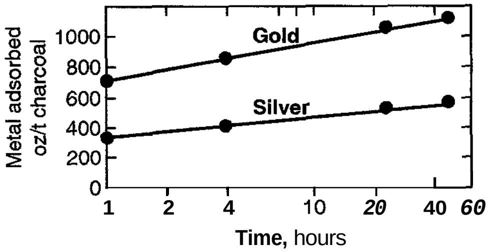


Figure 19.11: Adsorption of gold and silver on activated charcoal (plotted from data by Gross and Scott, 1927).

DESORPTION

While metal hydroxides or basic salts precipitated on charcoal in the sorption step can be dissolved by acids and desorbed, it is not possible to remove gold from gold-laden activated charcoal by acids because of the formation of insoluble gold cyanide:

$$[Au(CN)_2]^- + H^+ \rightarrow AuCN_{(ppt.)} + HCN_{(g)}$$

The usual way to desorb gold is by elution with a hot concentrated alkaline solution of sodium cyanide. The high temperature is necessary because the dielectric constant of water decreases with increasing temperature hence the electrostatic forces between charcoal and the gold cyanide complex decreases. High alkalinity and high concentration of cyanide are necessary for gold desorption because both OH– and CN^- ions are preferentially adsorbed.

Another desorption method is using an alcoholic solution of sodium cyanide. This is because alcohol has a lower dielectric constant than water. If the temperature is increased, the dielectric constant decreases further and elution becomes more favorable. This method, however, is not used in industry because of its expenses.

ENGINEERING ASPECTS

There is a variety of methods used industrially to recover gold from cyanide solution. Essentially they are all common in the following steps:

- Sorption of the gold cyanide complex on charcoal.

- Washing with water to remove the entrained solution.
- Desorption, usually with a solution of 0.2% NaCN and 1% NaOH at 90 °C.
- Acid washing to remove $CaCO_3$ precipitate.
- Washing the depleted charcoal with water to remove the entrained solution.
- Dewatering, activation by heating for 30 minutes at 700 °C in absence of air, then quenching and recycling.
- Two factors contribute to the choice of the adsorption process:
- Filtration properties of the pulp.
- Presence of organic matter in the ore.

As a result, the following processes are used:

Column process

Adsorption columns charged with granular activated charcoal are used when the ore can be filtered easily and clear solutions can be obtained. When the beds are saturated, they are desorbed, and the depleted carbon is then washed, dewatered, and activated.

Carbon-in-pulp process

This process is used to treat slimy ores, i.e., ores containing finely divided clay particles which are difficult to filter. In this process, the cyanide leaching pulp is agitated in tanks with the charcoal pellets (Figure 19.12). When adsorption is complete, the pulp is screened to separate the gold-laden pellets for washing and desorption. The process has the advantage of eliminating filtration which may be an expensive operation.

Carbon-in-leach process

This process is used to treat ores containing organic matter. Since organic matter may act as adsorbents, their presence renders the gold cyanide complex susceptible of being lost in the residue. Hence, granular activated carbon is added in the leaching tanks (Figure 19.13) so that it can adsorb the gold cyanide complex as soon as it is formed and more effectively than the organic matter. The charged carbon is then separated from the pulp by screening.

Adsorption and elution are slow processes. Typically it takes about 24 hours to adsorb gold from a solution containing about 10 ppm gold and 50 hours to elute. One ton activated carbon adsorbs about 10 kg gold. About 4 liters of solution per kilogram of carbon are sufficient for continuous operation. Gold and silver are recovered from the eluate by electrolysis using steel wool cathodes and the barren solution recycled to the sorption step. Gold and silver are recovered by melting the steel wool to a bullion. For the recovery of gold from cyanide solution using zinc, **see** chapter 25.

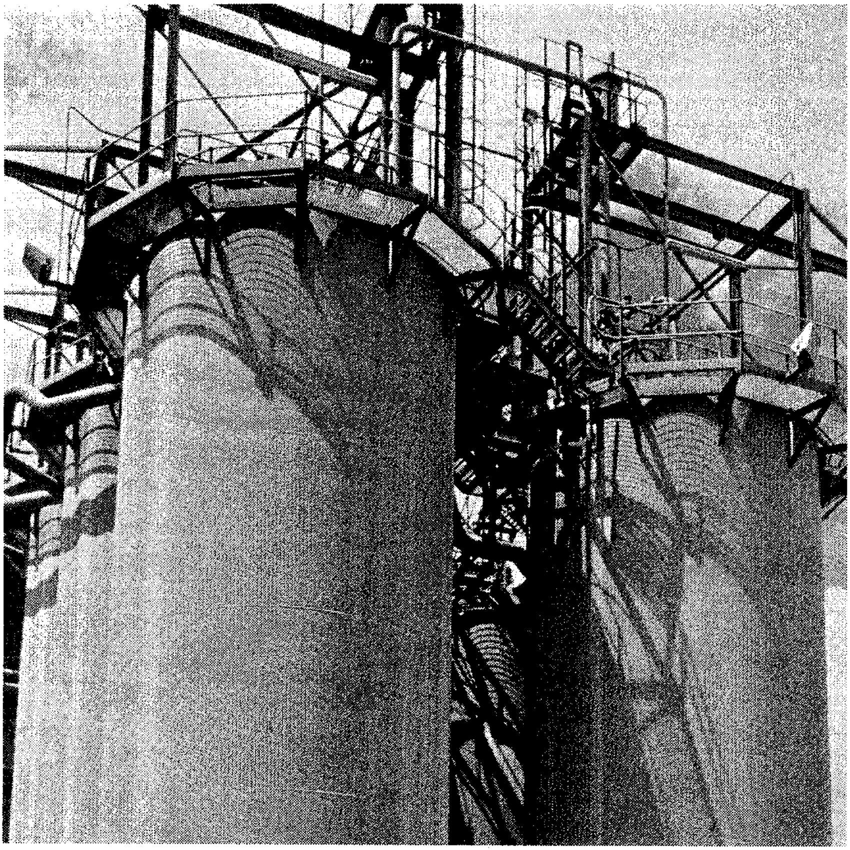


Figure 19.12: **A** carbon-in-pulp plant in South Africa.

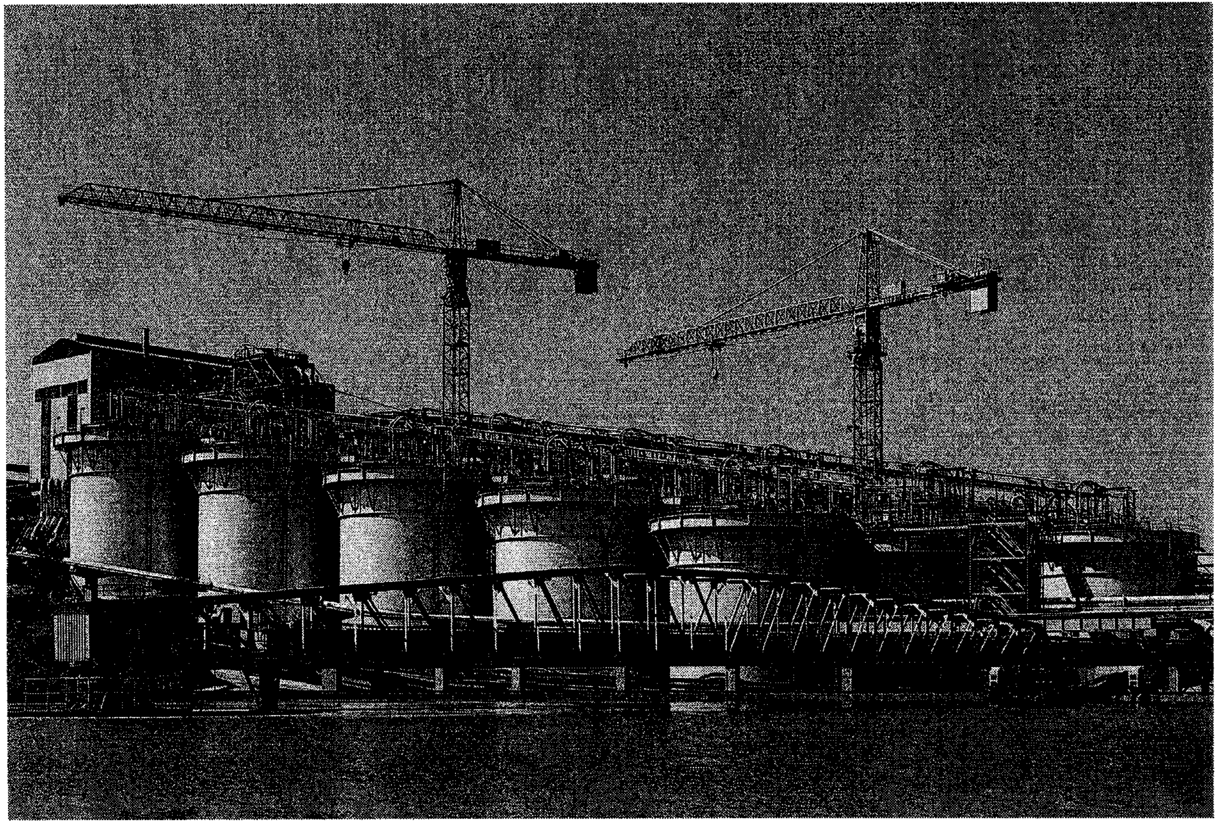


Figure 19.13: Carbon-in-leach plant at East Rand Gold and Uranium Company, South Africa.

SUMMARY

- Activated charcoal is different from coal and graphite in being hydrophilic, i.e., it is wetted by water. This is because of the organic surface complexes formed during activation. It has a large surface area and a high porosity.

- Adsorption of gold or silver cyanide complexes on activated charcoal is a physical process in which the amount adsorbed decreases with increased temperature. This is in contrast to chemisorption processes in which the amount adsorbed increases with increased temperature.

- Oxygen is necessary for adsorption processes on activated charcoal. It is reduced on the surface of charcoal by the reaction:

  $$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

  electrons being supplied by the charcoal. The charcoal thus acquires positive charge. **As** a result:

  - Uncomplexed metal ions in solution are precipitated as hydroxides from neutral or slightly acidic dilute solutions on the surface of charcoal due to the OH^- ions liberated, while the anions are attracted to the positively charged charcoal surface.
  - The negatively charged gold cyanide complex, $[Au(CN)_2]^-$, is attracted to the positively charged charcoal surface.

- Adsorption of gold and silver from cyanide solution by charcoal at equilibrium conditions follows Langmuir's adsorption isotherm, $W = kC^{1/n}$, where W is the amount of metal adsorbed by unit weight of charcoal in equilibrium with a solution of concentration C; k and n are constants ($n > 1$). The rate follows Elovich equation, $W = K' \log t$, where K' is a constant and t is the time.

- Adsorption of gold from cyanide solution by activated charcoal decreases when the solution contains an organic solvent of lower polarity than water since under these conditions the electrostatic forces of attraction decrease. Decreased adsorption with increased temperature may be also due to the decreased dielectric constant of the medium with increased temperature.

Chapter Twenty

Ion Exchange

General Principles 406
Methods and Equipment 407
    Columns 407
    Resin-in-pulp 408
    Continuous system 409
Ion Exchange Materials 411
    Inorganic 411
    Organic 412
    Membranes 415
    Specific resins 416
    Electron exchangers 417
Exchange Mechanism 417
    Ionization and association of ionogenic groups 417
    Exchange capacity 418
    Swelling 419
    Factors favouring swelling 420
    Importance of swelling 420
    Selectivity 421
    Effect of complexing agents in the aqueous phase 423
    Site sharing 423
    Effect of non-aqueous media 425
    Elution or regeneration 426
Properties 427
    Color change 427
    Fluorescence 427
    Infrared spectra 428
    X-ray diffraction 428
    Dissolution and precipitation of salts 428
    Ion exclusion 429
Applications 429
    Recovery of uranium from leach solutions 429
    Metal separations 431

The first attempts to utilize ion exchange phenomena was in the field of water softening around 1906, using natural and synthetic silicates. The improved properties of synthetic organic resins greatly broadened the application potential for ion exchange processes due to their stability and high capacity. The first attempts to apply ion exchange for metal recovery were in connection with recovery of copper from waste liquors of the cuprammonium rayon and brass industry, silver from photographic film manufacturing wastes, and chromium from electroplating wastes. Uranium was the first metal to be recovered from leach solutions by ion exchange on a large scale, and the great amount of research done in this field opened the doors to the wide possibilities of using ion exchange for recovering other metals from leach solutions.

The exchange process is especially useful in the treatment of very dilute solutions with metal ion concentration of the order of 10 ppm or less. For solutions with metal ion concentration above 1%, this method is generally not of value. The ion exchange phenomenon occurs in rocks, sands, soils, glass, wood, wool, cotton, and other materials.

GENERAL PRINCIPLES

An ion exchanger is a framework or a matrix which carries a positive or a negative electric charge. This is compensated by ions of opposite sign, called *counter-ions.* Ions of the same sign as that on the framework are called *co-ions.* The counter-ions are free to move within the framework and can be replaced by other ions of the same sign, while the fixed ions are not mobile. When the matrix carries positively charged ions, the exchanger is an *anion exchanger,* since it can exchange anions with the counter-ions. Similarly, a *cation exchanger* is capable of exchanging cations with its counter-ions. Exchange reactions are represented as follows:

Anionic: $R^+X^- + A^- \rightarrow R^+A^- + X^-$

or simply: $X^-_{(r)} + A^-_{(aq)} \rightarrow A^-_{(r)} + X^-_{(aq)}$

Cationic: $R^-Y^+ + B^+ \rightarrow R^-B^+ + Y^+$

or simply: $Y^+_{(r)} + B^+_{(aq)} \rightarrow B^+_{(r)} + Y^+_{(aq)}$

If the ions exchanged are different in valency, then charge and mass balances are preserved. For example, if A^{2-} is exchanged for X^- and B^{2+} for Y^+, then the equations can be represented as follows:

$$2X^-_{(r)} + A^{2-}_{(aq)} \rightarrow A^{2-}_{(r)} + 2X^-_{(aq)}$$

$$2Y^+_{(r)} + B^{2+}_{(aq)} \rightarrow B^{2+}_{(r)} + 2Y^+_{(aq)}$$

Ion exchangers can be compared to a sponge with counter-ions floating in the pores. When the sponge is immersed in a solution, the counter-ions can leave the pores and float out. In order to preserve electrical neutrality in the sponge, a stoichiometric number of other ions from the solution enters the pores (Figure 20.1). Dissolved electrolytes can be completely removed from aqueous solutions by exchanging all cations for H^+,and all anions for OH^-. This can be achieved in two-stage columns: One cationic and the other anionic, or a single column containing an intimate mixture of cation and anion exchanger particles.

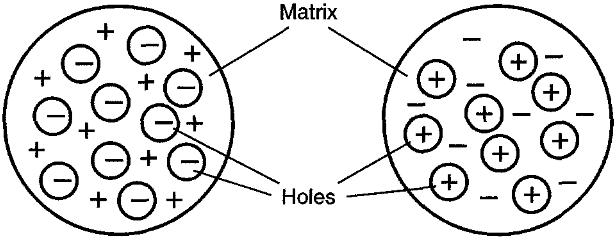


Figure 20.1: Sponge model of exchangers.

METHODS AND EQUIPMENT

Ion exchange processes may be conducted batchwise in columns, on a semi-continuous basis in resin-in-pulp system, or continuously in an elaborate system of columns.

Columns

Since ion exchange is an equilibrium operation, the degree of separation of two species that can be achieved in a single batch operation is limited by the value of the distribution coefficient (page 384). Repeated batch operations are tedious and consume considerable space. Separations are therefore carried out on columns which may be considered to consist of a large number of repeated batch equilibriums between the solution and the resin. Efficient operation of a column depends on flow rate of solution, particle size of resin, and column dimensions. Columns 2 m in diameter and 4 m high are in common use. To prevent channeling in the bed, the resin must be of the same particle size. Also, a space must be left at the top of the bed to allow the expansion of the resin during the exchange process.

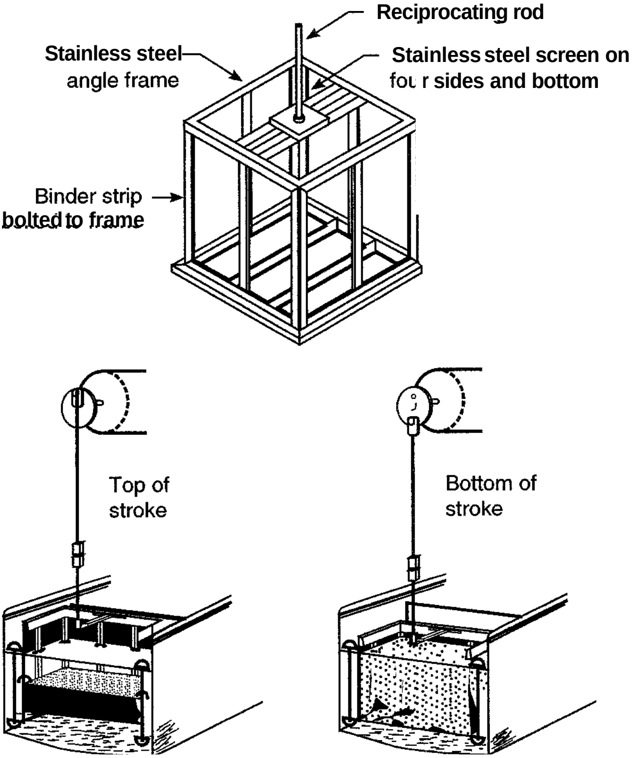


Figure *20.2:* Resin-in-pulp method for treating slimy ores.

Resin-in-pulp

In some ores the leach solutions are slimy and difficult to filter, and the production of clear leach liquors suitable for column operations is expensive and time-consuming. To meet these difficulties, a semicontinuous batch method has been devised; it is the resin-in-pulp method (RIP) (Figures 20.2 and 20.3). In this method, the unfiltered leach liquors are fed into tanks in which wire-mesh baskets, 28 mesh, or 0.6 mm openings, containing coarse-grade resin (10–20 mesh), are moved continuously up and down by a reciprocating mechanism, so that the resin bed expands on the downstroke through the pulp and is compressed again on the upstroke. The size of baskets is from 40 x 40 x 40cm to 180 x 180 x 180 cm, the top of the basket being left open.

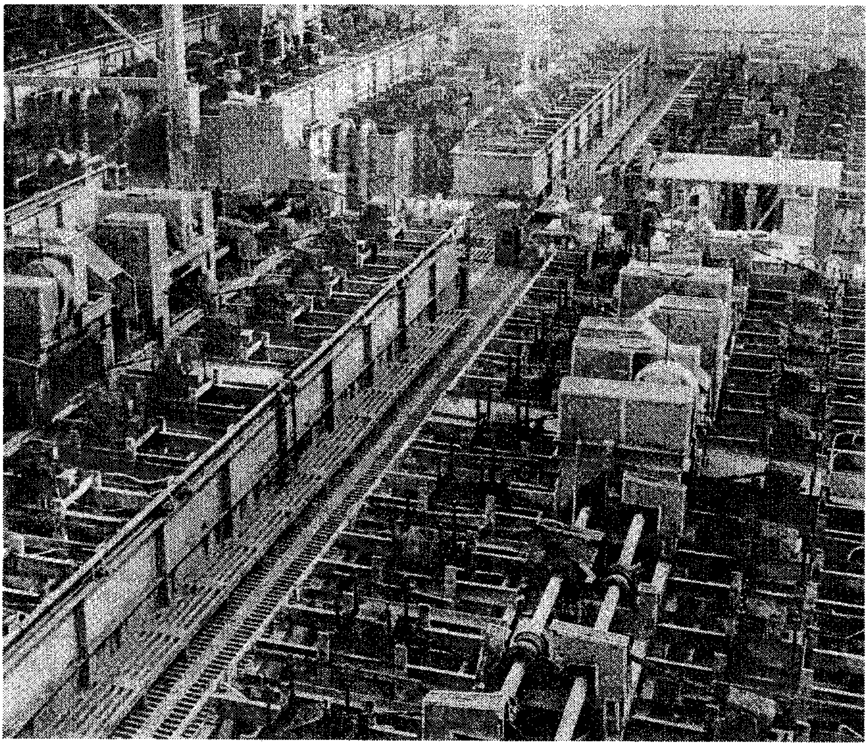


Figure 20.3: Resin-in-pulp plant for uranium. The Anaconda Company, Grants, New Mexico.

Continuous system

This system operates in counter-current fashion and can handle either clear or turbid solution. It is composed of three towers: The absorption column, the measuring chamber, and the elution column (Figure 20.4). The absorption column comprises a number of chambers separated by orifice plates, in each of which there is a measured volume of resin. The leach solution enters the bottom of the column and flows upwards through the resin and out at the top. The resin in the chambers is fluidized by the upward flow, but the flow is so regulated that it does not carry the resin up into the next chamber above. Likewise, the upward velocity does not allow resin to fall down into the chamber below. During operation samples are taken of the effluent and when breakthrough of ions is detected, the resin from the lowest chamber is discharged into the measuring column as a slurry. Following upon this, the resin in the next chamber above is transferred into the lowest chamber and in turn the resin in all the chambers above are transferred progressively from one chamber to the empty chamber below.

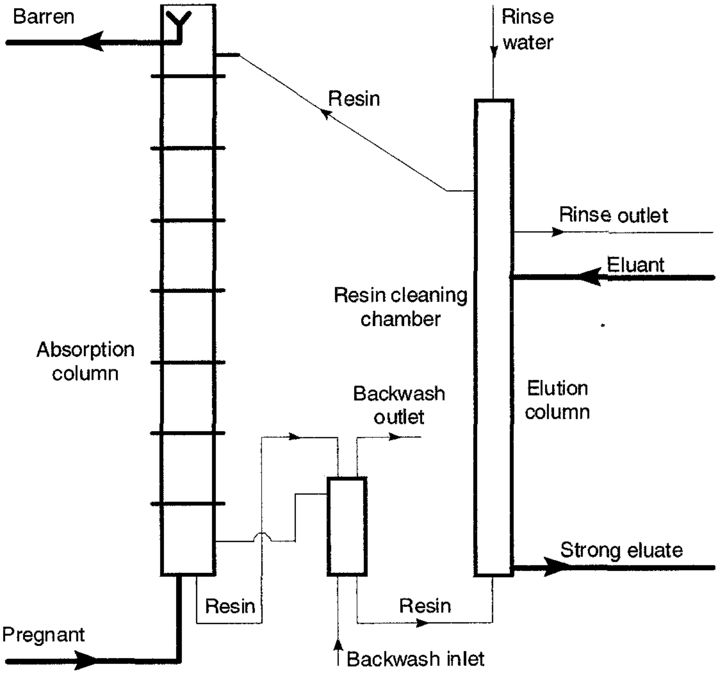


Figure *20.4:* Continuous ion exchange system.

When the uppermost chamber is empty, it receives freshly eluted resin from the elution column and the elution column is then ready to receive a batch of loaded and clean resin from the measuring chamber. The measured volume of resin in this chamber has in the meantime been backwashed to remove any suspended matter that may have attached itself to the resin. When this has been completed the resin is transferred in a fluidized manner into the bottom of the elution column. The resin is raised as a plug and a volume of resin equivalent to the amount introduced is then rinsed and transferred to the top of the absorption column.

ION EXCHANGE MATERIALS

Ion exchange materials may be inorganic or organic.

Inorganic

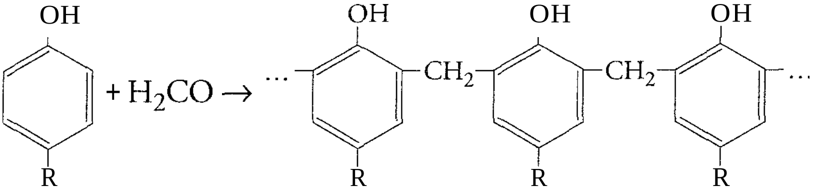
Inorganic materials are either natural or synthetic. Analite and chabazite belong to the group of naturally occurring aluminosilicate minerals known as zeolites. The zeolite lattice consists of SiO_4^{4-} and AlO_4^{4-} tetrahedra which have their oxygen atoms in common. Since aluminum is trivalent, the lattice carries a negative electric charge. This is balanced by alkali or alkaline earth cations which do not occupy fixed positions, but are free to move in the lattice framework. Due to the presence of these mobile positive ions, zeolites have the capacity to exchange cations.

Aluminosilicates with ion exchange properties have also been synthesized, e.g., by fusion of soda, kaoline, feldspar, etc., or by formation of gelatinous precipitates from aluminum sulfate–sodium silicate solution with NaOH, and drying. Hydrothermal methods have also been used, e.g., by crystallization at high temperature and pressure from aqueous solutions containing SiO_2, Al_2O_3, and alkali. This method is the one in use exclusively today: the products are very similar to the natural material and a variety of products can be prepared. Thus, silicon may be replaced by Fe, Mn, V, or P. Also, exchangers based on ZrO_2 and P_2O_5 are prepared by precipitating zirconium phosphate from zirconyl chloride solution by H_3PO_4. In this case also a variety of products can be prepared, e.g., zirconium may be replaced by Th, Sn, or Ti, and phosphorus may be replaced by As, Mo, or W.

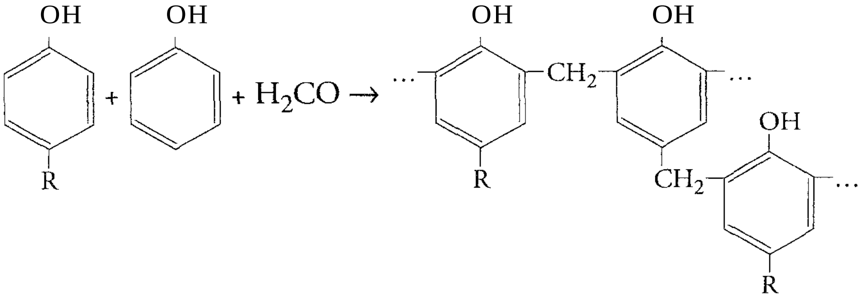
Organic

Organic exchangers used first were sulfonated coals. These are now superseded by synthetic resins. These consist of an elastic three-dimensional network of hydrocarbon chains which carry fixed ionic groups. The charge of the groups is balanced by mobile counter-ions. The introduction of groups such as $-SO_3^-H^+$ by sulfonation, i.e., reaction with concentrated H_2SO_4, makes the hydrocarbon macromolecule soluble in water. But ion exchange resins containing such groups are made insoluble by *cross-linking,* i.e., by interconnecting the various hydrocarbon chains. The degree of cross-linking determines the physical properties of the resin. The main methods of preparing these materials are the following.

- *Phenol formaldehyde resins.* Condensation of p-substitued phenol with formaldehyde yields linear polymers:

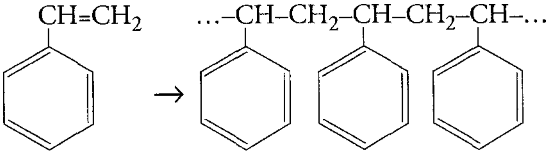


No cross-linking occurs because the para positions to OH groups are occupied, and the meta position is inaccessible to the aldehyde. However, if unsubstituted phenol is added to the mixture, a cross-linked polymer is obtained:

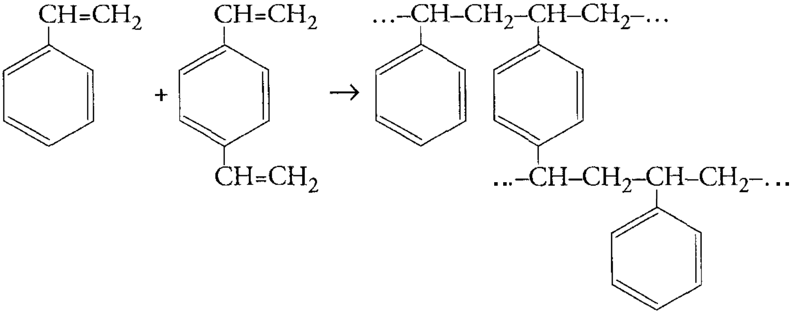


Thus the degree of cross-linking can be adjusted by varying the content of phenol in the reaction mixture. This method is, however, obsolete.

- *Polystyrene resins.* Polymerization of styrene yields linear polystyrene:



However, if divinyl benzene is added, a cross-linked matrix is obtained:

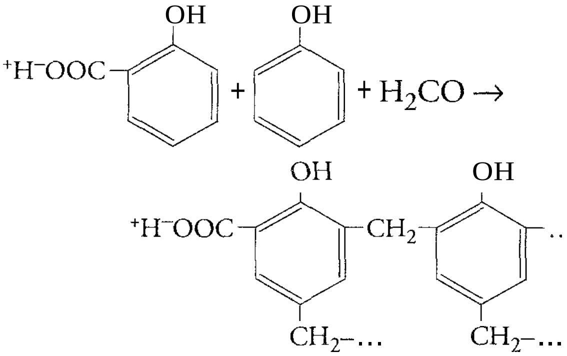


The degree of cross-linking can be adjusted by varying the divinylbenzene content in the reaction mixtures. Most resins are now prepared by this method and are chemically more stable. The functional groups, either anionic or cationic, are incorporated either in the monomer before polymerization, or into the polymer itself.

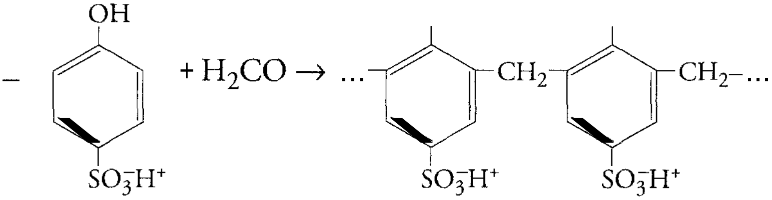
Types

There are four types of synthetic organic exchangers:

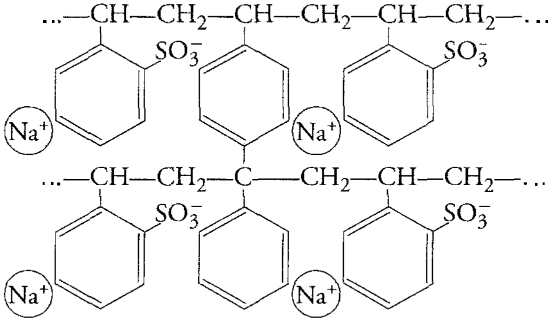
- Weak-acid cation exchangers, containing –COOH groups:



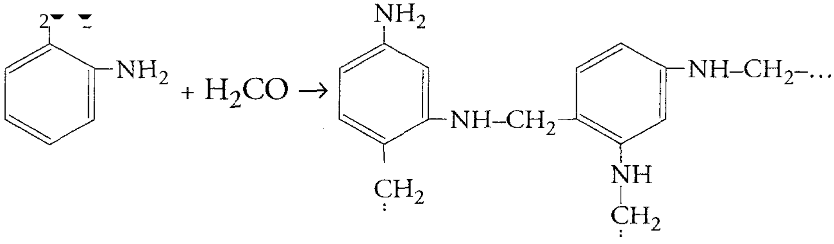
- Strong-acid cation exchangers, containing $-SO_3H$ groups:



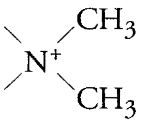
  - Sulfonation of addition polymers with divinyl benzene.

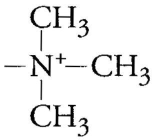


- Weak-base anion exchangers, containing amino groups, e.g.:



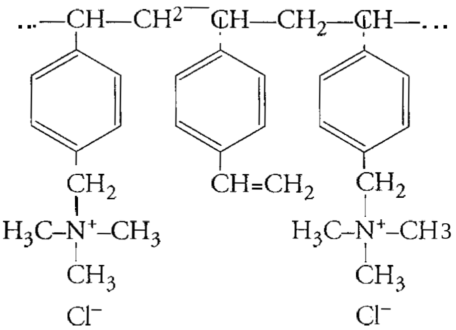
- Strong-base anion exchangers. The base strength of the resin can be increased by using substituted amines, e.g.:





$$-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-CH_3$$

An important resin used extensively in extractive metallurgy is Amberlite IRA *400:*



Membranes

These are synthetic organic resins prepared in the form of sheets. When an ion exchange membrane is in contact with an electrolyte solution, counter-ions will have no difficulty in passing through the membrane from one solution to the other. Co-ions, on the other hand, are excluded. It corresponds to the ideal semipermeable membrane. In a cell containing NaCl solution, the following processes take place when an electric current is applied as shown in Figure 20.5.

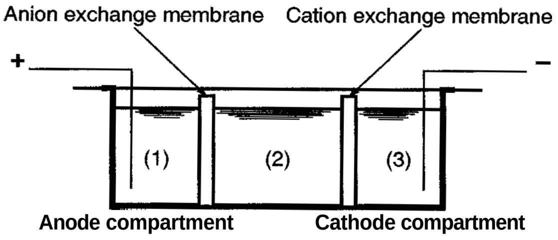


Figure 20.5: Ion exchange membrane.

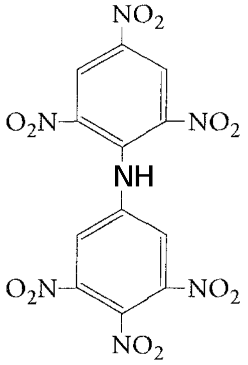
At the cathode: $H_2O + e^- \rightarrow {}^1/_2H_2 + OH-$

At the anode: $H_2O + 2H^+ + {}^1/_2O_2 + 2e-$

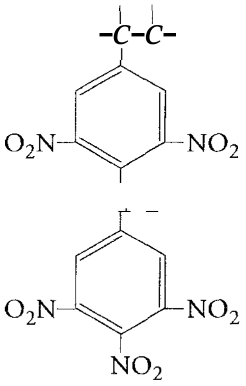
The electric current transfers the anions and cations out of compartment (2) into compartments (1) and (3) respectively. The net effect is deionization of solution (2), since cations in (1) and anions in (3) cannot migrate to compartment (2). Thus, in the cathode compartment, NaCl is converted to NaOH, and in the anode compartment, HCl is formed, or a salt can be converted into its acid and base components.

Specific resins

Resins having specific affinity for a certain metal ion have been prepared. For example, a resin based on nitrated and reduced polystyrene, having a structure similar to dipicrylamine, was prepared:



Dipicrylamine

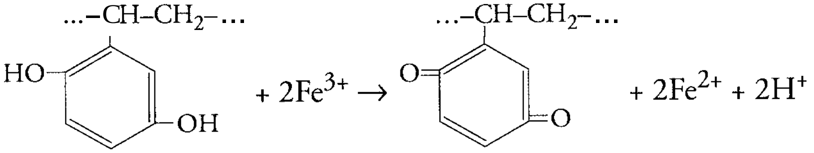


Dipicrylamine-based resin

This resin has an unusual affinity for potassium ion, and has been suggested as an exchanger for recovering potassium from seawater. The resin owes its selectivity to the presence of the specific organic precipitant for potassium, dipicrylamine. Other specific resins have been prepared. The problem with these resins, however, is the difficulty of elution and regeneration.

Electron exchangers

These are cross-linked polymers which carry a built-in reversible redox couple such as quinone–hydroquinine. They carry no fixed ionic groups and no counter-ions; therefore, no ion exchange takes place. But they are capable of oxidizing or reducing an ion in solution –– example: reduction of Fe^{3+} by a hydroquinone-type electron exchanger:



The resin can be regenerated by a strong reducing agent, e.g., Ti^{3+} ion, and reused. The process is irreversible in the sense that Fe^{2+} cannot regenerate the resin.

EXCHANGE MECHANISM

Ionization and association of ionogenic groups

Interaction between the counter-ions and the fixed ionic groups takes place. Thus, while strong-acid or strong-base resins are completely ionized, weak-acid and weak-base resins are not. The ionization of the latter two resins depends on the pH of the external solution. Weak-acid groups are not ionized at low pH, while weak-base groups are not ionized at high pH. Consequently, under these conditions, ion exchange is greatly decreased.

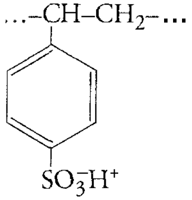
The ion exchanger prefers the counter-ion which forms the stronger ion pairs, or bonds, with the fixed ionic groups. Interactions of this kind are likely to occur if the fixed ionic groups are similar in structure to precipitating or complexing agents which react with the counter-ion. For example:

- Bond formation between carboxylic acid anions and H^+ ions.
- Resins with groups resembling dipicrylamine (precipitating agent for potassium) are highly selective for potassium.

Exchange capacity

- *The maximum capacity.* This is the number of ionogenic groups per one gram of resin free of sorbed solutes and solvents. The weight of a resin depends on its ionic form. The chloride form is used for an anion exchanger and not the OH– form, because it is more difficult to determine the dry weight of the latter. Drying of a resin is carried out at 50 °C under vacuum and overnight.

  Styrene–divinylbenzene copolymers, when completely monosulfonated and in the H^+ form, consist mainly of the units:

  Each unit, $C_8H_8O_3S$, has the formula weight 184.2 and carries one fixed ionic group. Accordingly, the capacity of the resin is approximately 10001184.2 = 5.43 milliequivalents/g.

- *The effective capacity.* This is the number of exchangeable counter-ions per specified amount of resin. It is the same as the maximum capacity for strong-acid and strong-base resins, because the resin is completely ionized, i.e., the number of exchangeable groups equals the number of ionogenic groups. But, it is lower for weak-acid and weak-base resins, because the resin is not completely ionized. The effective capacity for non-ionized resins depends on:
  - pH of the external solution because the weak-acid groups are not ionized at low pH, while weak-base groups are not ionized at high pH. Therefore, a weak-acid resin will sorb fewer Na+ ions from acid than from alkaline solution.
  - Concentration of external solution. For a non-ionized resin in the H^+ form, the exchange with Na+ is enhanced by increasing the concentration of Na^+ ions:

    $$H^+_{(r)} + Na^+ \rightleftharpoons H^+ + Na^+_{(r)}$$

    The strong affinity of such a resin for H^+ can only be overcome by increasing the concentration of the counter-ion in the external solution.

Resin capacity is determined experimentally by titrating the resin with an acid or a base.

Swelling

When a dry ion exchange resin is immersed in water, a considerable amount of water is taken up, and as a result, the resin swells. This swelling property is also known in natural gums (e.g., tragacanth, agar-agar, etc.). A resin swells to a limited degree only: an equilibrium is attained beyond which swelling does not proceed because the tendency to swell is counteracted by the elastic forces in the matrix. Natural and synthetic zeolites do not swell to any appreciable extent because the lattice is not elastic. A resin tends to swell for the following reasons:

- The fixed and the counter-ion tend to solvate.
- The highly concentrated ionic solution inside the resin has a tendency to be diluted when in contact with water due to osmosis'.
- Neighboring fixed ionic groups repel one another electrostatically, and thus tend to stretch the chain of the matrix. Repellence depends on the dielectric constant of the medium in which the resin is immersed. Thus, in a dry resin, it is different from that of a resin immersed in water.

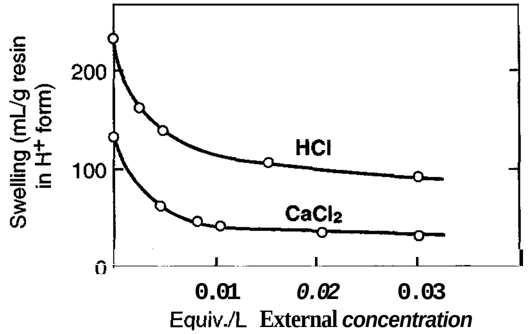


Figure 20.6: Effect of concentration of external solution on the swelling of the resin (Samuelson, 1963).

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1. Osmosis (Οσμος in Greek means to push) is the diffusion of water through a serni-permeable membrane from a dilute solution (a region of high water concentration) to a more concentrated solution (a region of a lower water concentration).

Factors favouring swelling

- Low degree of cross-linking
- High exchange capacity, since more ionic groups are involved inside the resin.
- Large and strongly solvated counter-ions. A resin in Cs^+ form expands when Cs^+ ion is replaced by Rb^+, and expands further when Rb^+ is replaced by K^+, Na^+, or Li^+. This sequence is the same as that of hydrated ionic volumes. The ionic volumes of hydrated ions increase from Cs^+ to Li^+, i.e., the reverse of unhydrated ions.[1]
- Complete ionization inside the resin. Weak-acid resins swell less in H^+ form than in alkali ion form; weak-base swell in free-base than in chloride form. The opposite holds for strong-acid and strong-base.
- Low concentration of the electrolyte in the external solution favours increased swelling (Figure 20.6), since an increase in concentration reduces the osmotic pressure difference between the interior of the resin and the aqueous phase, or the driving force for the solvent uptake gets smaller.

Importance of swelling

Swelling is of considerable practical importance, especially for column operation. High pressures are usually developed inside the bed, and unless precautions are taken, a column may burst, or movements in the bed may take place causing channeling. A resin in a swelled state is under strain and can be compared with a spring under tension. Therefore, any factor that lessens this strain is favoured by the resin. Also, the resin in its swollen state has maximum selectivity because of the tendency to relax. The resin will, therefore, be ready to exchange its counter-ions for others if this exchange causes relaxation.

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[1] When the radius of the cation is large, the positive charge on the nucleus is far from the water molecules, therefore less attractive to water. Although Li^+ is the smallest of the alkali ions, yet it has the lowest attraction to H_2O molecules in aqueous solution because it is the most strongly hydrated.

Selectivity

An ion exchanger exchanges its counter-ions in preference for other ions in solution for certain physical and chemical reasons. The basis of preference in dilute solution in cationic resins is as follows:

- A counter-ion of higher charge is preferable since a highly charged ion is strongly attracted to the fixed ions. Thus, Th^{4+} would replace La^{3+}, La^{3+} replaces Ca^{2+}, and Ca^{2+} replaces Na^+.
- For similarly charged ions, the one with the smaller solvated volume is preferable since it decreases swelling, and thus the elastic matrix would relax, i.e., it contracts. The selectivity of the alkali ions, for example, is of the order $Li^+ < Na+ < K^+ < Rb^+ \leq Cs^+$, i.e., Cs^+ is more preferred by the resin than Li^+ (Figure 20.7). Also, $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ and $F^- < Cl^- < Br^- < I-$. This sequence is the same as that of the decreasing radii of hydrated ions.
- The counter-ion that interacts more strongly with the matrix, e.g., by bond formation or electrostatic attraction, is preferable. Thus, carboxylic acid anions prefer H^+ as counter-ions, and picrylamine resin prefers potassium ions.
- Selectivity is enhanced by decreasing the concentration of the external solution (Figure 20.8), because in dilute solutions the swelling will be maximum and the resin tends to relax.

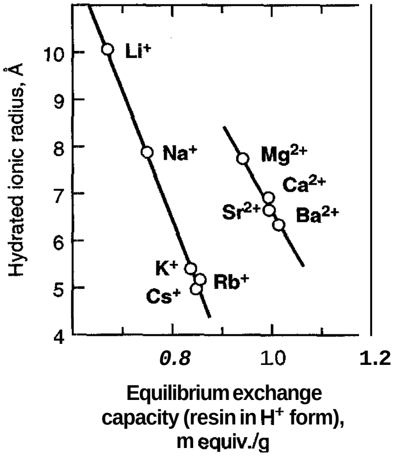


Figure *20.7:* Effect of ionic radius on ion exchange (Nachod and Wood, *1945).*

- Increasing cross linking of the resin increases the selectivity. Large counter-ions may be sterically excluded from the narrow pores of the exchanger.

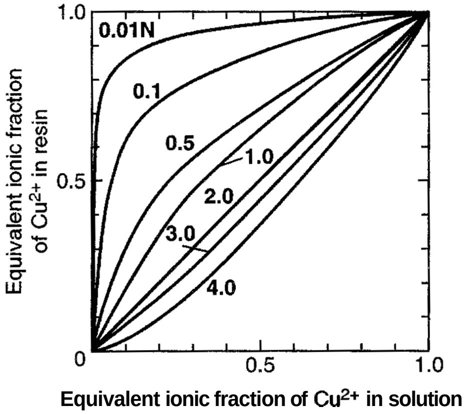


Figure *20.8:* Cu^{2+}–Na^+ exchange on Dowex 50-X8 in Na^+ form at various total normalities of the external solution ($CuCl_2$ + NaCI); the preference for the ion of higher valency increases with dilution of the solution (Rao and David, 1957).

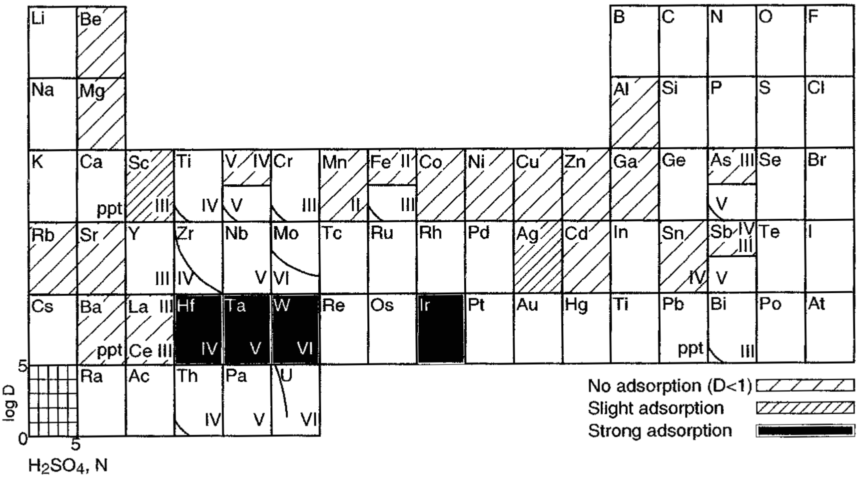


Figure 20.9: Sorption of metal ions from H_2SO_4 solution by anion exchange. Plotted from data by Danielsson (1965) and Samsahl (1963).

Effect of complexing agents in the aqueous phase

The distribution coefficients for a large number of metal ions in a variety of acids at different concentrations are available (Figures 20.9 to 20.12). It can be seen that with increasing acid concentration, the value of D changes greatly. The reason for this is the presence of two effects which may strengthen or oppose each other, depending on the chemical properties of metal ion and the acid in question:

- In dilute acids, the resin swells more than in concentrated acids and therefore ion exchange is enhanced.
- With increasing acid concentration, complexing action takes place.

Site sharing

Uptake of sulfuric acid may take place by the following mechanism:

$$\begin{matrix} R^+ \\ R^+ \end{matrix} > SO_4^{2-} + H_2SO_4 \rightarrow \begin{matrix} R^+HSO_4^- \\ R^+HSO_4^- \end{matrix}$$

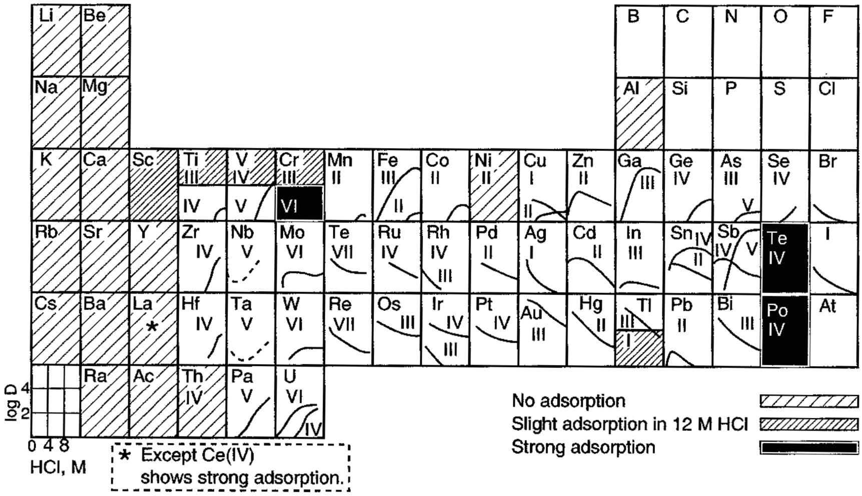


Figure 20.10: Sorption of metal ions from HCl solution by anion exchange resin (Kraus and Nelson, 1956).

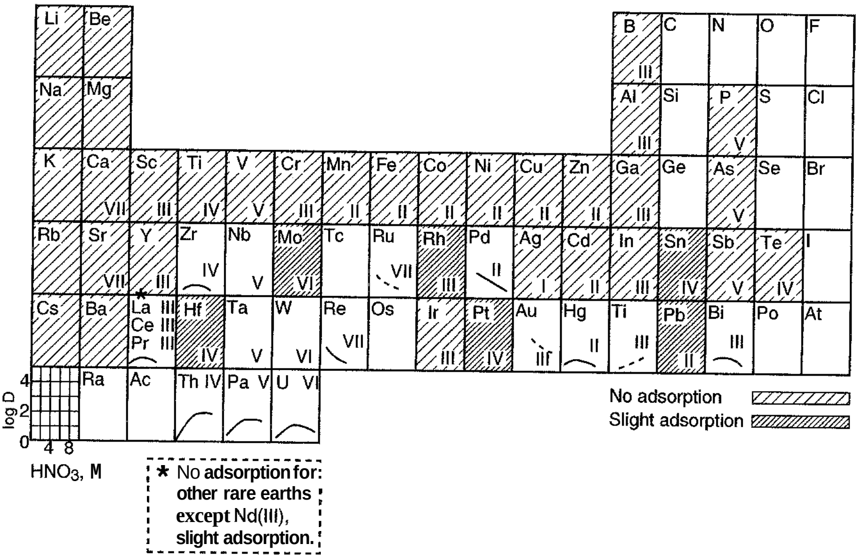


Figure 20.11: Sorption of metal ions from HNO_3 solution by anion exchange resin (Buchanan and Faris, *1962).*

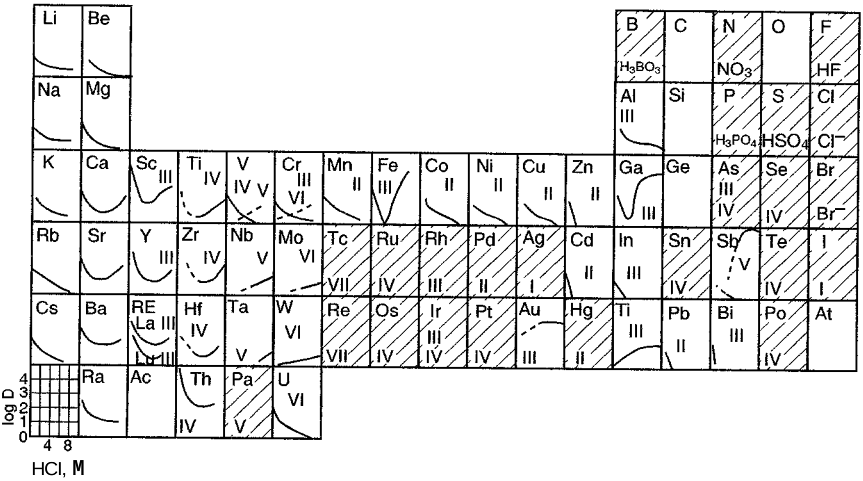
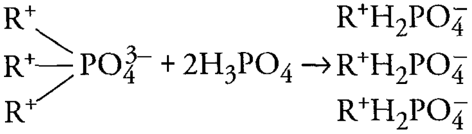


Figure 20.12: Sorption of metal ions from HCl solution by cation exchange resin; *D* < 1 for shaded areas (Nelson et **al.**, *1964).*

Similarly, the uptake of phosphoric acid:



$$\begin{matrix} R^+ \\ R^+ \\ R^+ \end{matrix} PO_4^{3-} + 2H_3PO_4 \rightarrow \begin{matrix} R^+H_2PO_4^- \\ R^+H_2PO_4^- \\ R^+H_2PO_4^- \end{matrix}$$

The sorbed acids can be eluted from the resin by washing with water. In this way, an acid can be separated from its salt. For example, H_2SO_4 can be separated from Na_2SO_4 by passing the mixture over a strong anion exchanger in SO_4^{2-} form; the acid is sorbed while Na_2SO_4 is not.

Effect of non-aqueous media

The use of organic solvents in ion exchange operations has been extensively studied to improve separations in analytical chemistry and eventually in metal recovery. For example, it is practically impossible to elute silver and gold cyanide complexes from strong-base anion exchange resins, but when acetone is added to an eluting agent such as HCl, elution takes place readily. In explaining this phenomenon it is necessary to recall polarity, dielectric constant, and osmosis. The reason is that acetone is less polar than water and therefore causes less swelling in the resin. The behaviour of a resin in non-aqueous media can be summarized as follows:

- Resins usually swell more strongly in polar than in non-polar solvents. Thus a resin swells more in water than in a less polar solvent like methanol or ethanol, and does not swell at all in non-polar solcents such as benzene and kerosene. However, if the solvent interacts with the organic constituents of the matrix then the situation may be reversed. For example, weak-acid resins in H^+ form swell more strongly in methanol than in water because of the strong affinity of the carboxylic acid groups for the alcohols.
- Swelling also depends on the solvation of ions which is different in non-aqueous media from that in water. The less polar the solvent the weaker is the solvation of the ions. Thus, in water, cation exchangers in Li+ form swell more strongly than the other alkali-ions forms, since Li+ has the highest solvation tendency. This tendency is reversed in alcohols because of low solvation.

- Swelling depends on the dielectric constant of the solvent which has a dual effect:
  - Low dielectric constant increases swelling since the electrostatic repulsion between the fixed ions becomes stronger.
  - Low dielectric constant tends to decrease swelling because of increased electrostatic interaction between ions of opposite charged, so that ion pair formation and association is increased, and the osmotic activity of the resin is reduced.

Thus, weak-acid resin in the alkali ion forms swells more strongly in water than in alcohols, since dissociation is more complete and the osmotic and electrostatic forces are more important. On the other hand, strong-base resins swell more strongly in alcohols than in water because the ionic form has little effect, but the affinity of the organic structural groups for the organic solvent is stronger.

Elution or regeneration

On loading a resin in A form with counter ion B, the resin should have preference for the ion B. Strong preference of the resin for the ion B is, however, undesirable in the elution step because of the difficulty of regenerating the resin. Moderate preference is the best compromise.

Selectivity of the resin can be reversed in such a way that equilibrium is favourable in both the sorption and the elution steps. From a dilute solution, Ca^{2+} and Mg^{2+} are preferentially taken up by a resin in the Na+ form because of the higher charge of the former. However, the exchanger can be regenerated with concentrated NaCl solution.

Sometimes, it is more convenient to elute in one step and regenerate that resin in another. For example, a weak acid resin loaded with Cu^{2+} or Ni^{2+} can be eluted easily with a strong acid because of the strong affinity of $-COO^-$ group for H+,and then converted to Na^+ by treatment with NaOH for regeneration. One-step elution with, for example, NaCl is not practical because of the stronger affinity of the resin for Cu^{2+} and Ni^{2+} than for Na^+. Further, it is not possible to use such resin in the H^+ form to sorb Cu^{2+} or Ni^{2+} from solution because the resin prefers the H^+ ion rather than the other ions.

In column operation, the ions with the strongest affinity for the exchanger are accumulated in the first layers of the column near the inlet. The ions are also most strongly retained by the exchanger in the regeneration step. In such cases counter-current regeneration has the advantage of avoiding forcing the most strongly preferred ion through the whole column. Further, if any suspended matter is retained on the top of the bed, it can be easily removed in the first fraction of counter-current eluate.

Poisoning. A resin is said to be poisoned when it becomes incapable of exchanging with the ions it normally exchanged. This results when certain impurity ions in solution are attached to the resin but not removed with the eluting agent, thus they build up and gradually decrease the capacity of the resin. For example, in the recovery of uranium from sulfuric acid leach solution by anion exchange resins, traces of molybdate, vanadate, and silicates are attached to the resin together with the uranyl sulfate complex. On eluting the resin, only uranium is eluted. The build up of other anions with time causes “poisoning”. To restore the resin, other eluting agents have to be used to remove these poisons.

PROPERTIES

Color change

Color of ion exchange resins changes with the nature of counter-ion. For example, the anion exchanger Amberlite IRA *400* is golden brown color in SO_4^{2-} form, lemon yellow in SO_3^{2-} form, and bright red when charged with V(V).

Fluorescence

Synthetic resins fluoresce in ultra-violet light and the fluorescence depends on the ion loaded. For example, an anionic resin in the sulfate or chloride form fluoresce strongly but when the same resin is exchanged with uranium, it is no longer fluorescent. The phenomenon was suggested for controlling the loading and elution cycles in processes using ion eschange resins.

Infrared spectra

Infrared spectrophotometry offers a mean for studying the interaction between metal ions and the active groups in ion exchange resins. The infrared spectrum of a resin is composed of two parts: lines characteristic of the matrix, and lines characteristic of the counter-ions. For example, Dowex 1 × 10 in sulfate form shows the characteristic lines of SO_4^{2-} ions as well as those of the matrix. When magnesium and lithium chloride solutions are passed through the resin and then the resin washed with water and dried, the lines characteristic of SO_4^{2-} ions disappear and new lines due to Cl^- ions appear instead, thus showing that SO_4^{2-} ions were exchanged for Cl^- ions.

X-ray diffraction

In certain cases it is possible by means of X-ray diffraction studies to identify the form in which a metal is sorbed by a resin. For example, beryllium is held by anionic resins as a fluoro complex when beryllium sulfate solution is passed through the resin in the fluoride form.

Dissolution and precipitation of salts

Insoluble salts such as AgCl and $BaSO_4$ can be solubilized by the addition of an ion exchange resin. Such salts when suspended in water dissociate to an extremely small extent, e.g., $AgCl \rightleftharpoons Ag^+ + Cl^-$. When a resin in H^+ form is added, the equilibrium is strongly shifted to the right due to the uptake of Ag^+ ions from solution by the resin, thus resulting in the solubilization of AgCl.

The uptake of a counter-ion by the resin can be enhanced by removing the competing counter-ion from the solution by precipitation. For example, passing NaCl solution over a resin in the Ag^+ form causes precipitation of AgCl:

$$Ag^+_{(r)} + Na^+ + Cl^- \rightarrow Na^+_{(r)} + AgCl_{(precipitate)}$$

Application: Desalting of seawater in emergency cases.

Ion exclusion

This is a convenient method for separating nonelectrolytes from electrolytes. No ion exchange takes place; the column acts as a sorbent only. When, for example, glycerine is to be separated from a sodium chloride solution, the solution is passed through a column of a cation exchanger in the Na^+ form, or an anion exchange in the Cl^- form. Glycerine is sorbed in the column, while NaCl passes through. By washing with pure water, the loosely sorbed NaCl is removed first, then glycerine, and the column is again ready for use. This particular example of separating glycerine is of technical importance, since such a mixture is a by-product of the soap industry.

APPLICATIONS

Ion exchange in extractive metallurgy is used for the recovery of metal values from leach solution, e.g., uranium and the separation of closely related metals, e.g., cobalt and nickel, hafnium and zirconium, niobium and tantalum, and the lanthanides.

Recovery of uranium from leach solutions

Uranium exists in sulfate solution as the uranyl ion UO_2^{2+}, as the uncharged complex $UO_2(SO_4)$, as well as the anionic complexes $[UO_2(SO_4)_2]^{2-}$ and $[UO_2(SO_4)_3]^{4-}$ depending on the amount of SO_4^{2-} ion in solution. It can, therefore, be sorbed by cationic as well as anionic resins. Sorption by the anionic resins has the advantage in that only a few metals form anionic complexes and are sorbed together with uranium, for example, ferric ion, arsenates, chromates, vanadates, permanganates, and molybdates. Sorption of ferric ion and vanadium(V) can be eliminated by reduction to ferrous and vanadium(III) (e.g., by adding SO_2) since the ferrous ion and vanadium(III) are not sorbed.

Sorption of uranium from H_2SO_4 leach solution is a function of SO_4^{2-} concentration because of its influence on the uranium anion formed. Under equilibrium conditions, the amount of uranium sorbed increases when the ratio $[SO_4^{2-}]/[U]$ is less than 2. Above this ratio, excess SO_4^{2-} competes with the uranium sulfate complex for resin sites, resulting in decreased sorption. Hydrogen ion concentration also plays an important role. At pH values below 1.5 there are not sufficient SO_4^{2-} ions to furnish the uranium sulfate complexes since HSO_4^- ions are predominant. At pH above 6, uranium precipitates. When the leach solutions contain phosphates or arsenates, precipitation of uranium may take place at a pH value lower than **6.** Therefore, the optimum pH is usually 2 to 2.5.

Tetravalent uranium is much less sorbed by the resin than the hexavalent. Uranium can also be sorbed from carbonate leach solutions by anion exchangers, due to the existence of the carbonate complex $[UO_2(CO_3)_3]^{4-}$.

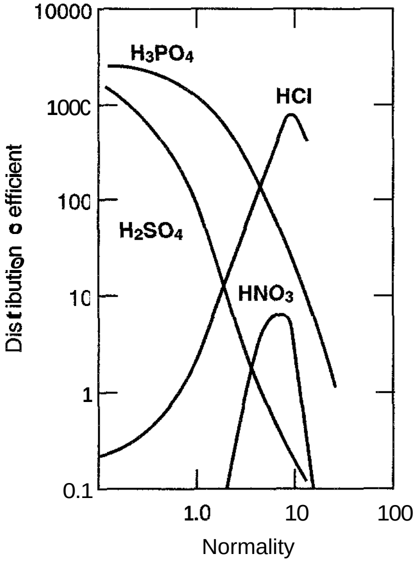


Figure 20.13: Sorption of uranium on anion exchange resins from different acids (Bunney et al., 1959; Freiling et al., 1959).

The sorption of uranium from different acid media on anion exchange resin is shown in Figure 20.13. These diagrams show that uranium can be sorbed by the resin from dilute solution of H_2SO_4 and H_3PO_4 but not from dilute solutions of HCl and HNO_3. That is why these last two acids are used as eluating agents. When sorbed from sulfuric acid leach solution, elution of uranium is preceded by a sulfate band as shown in Figure 20.14, which could be discarded in order to prevent contamination of the eluate build up of SO_4^{2-} in the recycled eluent.

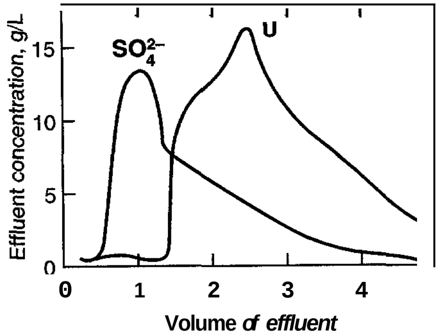


Figure *20.14:* Elution of uranium sulfate complexes by 0.9M NaCl (Grinstead et al., 1956).

Metal separations

To separate two or more metal ions from solution, one of the following methods can be used:

- ***Selective sorption.*** This is usually achieved by adjusting the aqueous phase such that the uptake of one of the ions is more favorable than the other. For example, by choosing the proper pH, concentration of the aqueous phase, the addition of a complexing agent, the addition of an oxidizing or a reducing agent, etc. Separation of thorium and uranium can be achieved from dilute sulfuric acid solution, using an anionic resin: Uranium is sorbed while thorium (and the lanthanides) is not (Figure 20.15). Sometimes, it may be possible to select a resin such that when the solution is passed through the column, one of the ions is retained while the other is not. For example, iron(III) can be separated from aluminum by using an anionic resin. Iron forms anionic complexes in 9 M HCl, while aluminum does not. Similarly, to separate cobalt from nickel, HCl is added to make the solution 8 M. Cobalt forms the anionic complex:

  $$Co^{2+} + 4Cl^- = [CoCl_4]^{2-}$$

  while nickel does not.

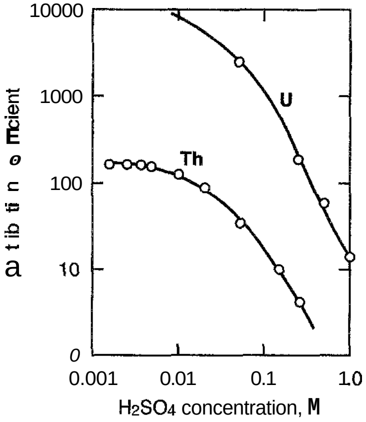


Figure 20.15: Separation of thorium and uranium on anionic resin Dowex 2 x 8SO_4^{2-} (Jangida et al., 1956).

- *Selective elution.* In this method, the desired ions are retained on the column, but in the elution step, an eluant is so chosen that it removes only one of the ions, and does not affect the other. Figure 20.16 shows, for example, the separation of the transition metals, manganese to zinc, by selective elution with HCl. Also, hafnium and zirconium nitrates in 2 M HNO_3 are sorbed on a cation exchange resin, and then with 1.5 M H_2SO_4 to remove hafnium (Figure 20.17). Anion exchange was also applied for separating these two metals based on sorption of the complex fluorides $[ZrF_6]^{2-}$ and $[HfF_6]^{2-}$. Elution is carried out with a mixture of 0.2 M HCl and 0.01 M HF, in which case zirconium is eluted first. Separation of niobium and tantalum is based on sorption of the chloride complexes on anionic resin in a mixture of 9 M HCl and 0.05 M HF; elution is done with the same medium.

- *Chromatographic elution.* Sometimes, the same eluent desorbs the two ions, but at different rates, and it is possible, therefore, to **get** one kind of ion in the first fraction of eluent and a second in a later fraction. To control the separation of the ions during elution, it is usually necessary to collect small fractions of the effluent at short periods of time and analyze them, or in some cases the effluent is continuously analyzed. The separation of the lanthanides is usually done by this method. The lanthanides are very similar chemically and therefore their separation by ion exchange was one of the most outstanding achievements in extractive metallurgy.

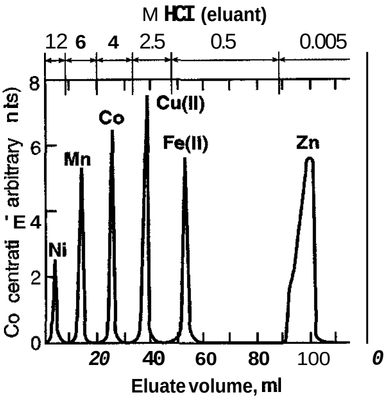


Figure 20.16: Separation of transition metals Mn to Zn by selective elution with HCI; resin: Dowex 1 (Kraus and Moore, 1953).

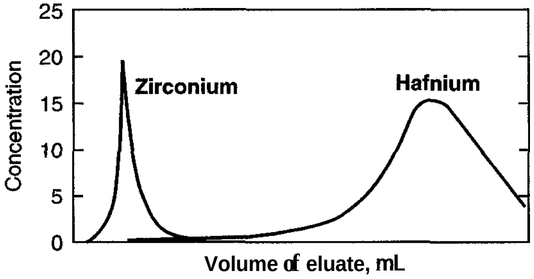


Figure **20.17:** Separation of hafnium and zirconium from HNO_3 medium, by cationic exchanger (Benedict et al., *1954).*

When the acid leach solution containing the lanthanides is allowed to flow through a cation exchange resin bed in hydrogen or ammonium form, they will be sorbed by the resin. However, the resin has no selectivity for one of the lanthanides as compared with the other, and therefore practically no separation can be achieved. In order to separate the different metals, use is made of their different affinities toward complexing agents in solution. When a buffered solution of some negative ion species, which forms a stable complex with the lanthanides, is passed through the column, a competition for the lanthanide ions between the aqueous phase and resin phase will be set up. When equilibrium conditions are maintained, an individual lanthanide ion continuously exchanges between the complexing ion and the resin. The positive ion in the complexing solution replaces the lanthanide ions at the rear edge of the band, so that the lanthanide band is driven down the resin bed. Because the stability constants of the lanthanide complexes differ appreciably from one lanthanide to another, the most stable complex moves faster down the column.

Different complexing agents were used as eluents for example, 5% citric acid adjusted at pH 3 by ammonium hydroxide, 0.1% citric acid adjusted at pH 5–8 by ammonium hydroxide, 1 M lactate at pH 3, and 0.26 M ethylene diamine tetraacetic acid (EDTA) at pH 3.6. Uniform rate of elution has been obtained by continuously varying the pH of the eluent. The eluent at pH 3.19 was neutralized at a predetermined rate with 1 M lactic acid buffered with ammonia to pH 7 to give a rate of change of pH of +0.1 unit/hour. Figure 20.18 shows the sharp separation resulting from the gradual change in pH during elution.

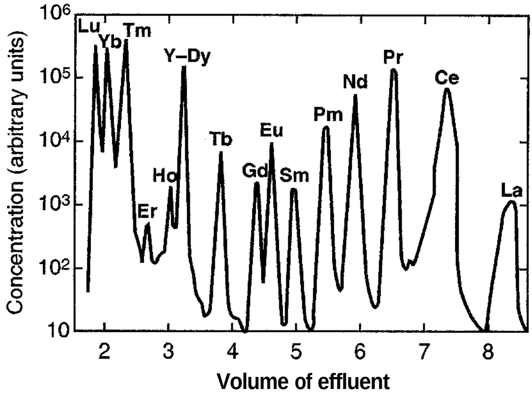


Figure 20.18: Separation of the lanthanides from cationic exchanger (Dowex 50) with 1 M lactate, pH initially 3.19, increasing continuously at 0.107 unit/hour, flow rate 0.4 mL/cm^2·min (Nervik, 1955).

In the separation of the lanthanides, the concentrate is dissolved in hydrochloric acid and diluted with water to make up the feed solution for the cation exchange columns 1.5 m long x 15 cm diameter in the ammonium form. The solution of the chlorides is loaded on four columns which are connected together in series. The sorbed band is first washed with distilled water, then eluted with 0.1% citrate solution at pH 8 at a flow rate of 0.1–1.2 L/min into a series of six similar columns. Under these conditions, the front of the adsorbed band advances at the rate of about one resin bed per day. The light lanthanides are sorbed on the first two columns, and the heavy lanthanides are concentrated on the last two columns, while the bulk of yttrium and a considerable portion of terbium and dysprosium are concentrated on the two middle columns. Each set of two columns is further fractioned by elution through a series of eight smaller columns (1.5 m long x 10 cm diameter) at a much smaller flow rate of 0.5 L/min. Each of these small columns is loaded with a pure metal, then separately eluted in a container. The pure lanthanide is recovered from the solution by precipitation with oxalic acid. Individual lanthanides **up** to 99.99% purity from monazite are produced on a commercial scale based on elution with EDTA (Figure 20.19).

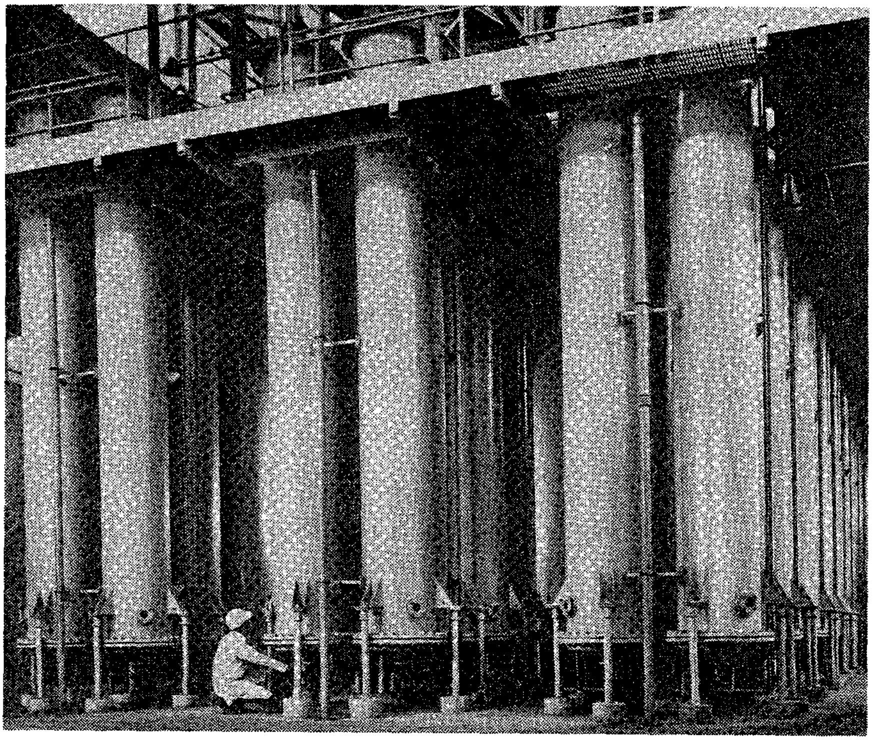


Figure 20.19: Ion exchange columns for the separation of the lanthanides at Michigan Chemical Corporation, St. Louis, Michigan.

Chapter Twenty-one

Solvent Extraction

Introduction 438
Engineering Aspects.. 439
  Equipment 439
  Distribution and stripping coefficients 442
  Phase ratio 444
  Percent extraction 445
  Separation and enrichment factors 445
  Multiple extractions.. 447
  Extraction isotherms 449
  Solvent loading.. 450
  Counter-current extraction.. 450
Extractants 453
  Ethers and their derivatives.. 455
  Alcohols.. 458
  Aldehydes 459
  Ketones 460
  Oximes 463
  Quinolines 468
  Organic acids 469
  Phenols 473
  Esters 474
  Amines and amine oxides 481
  Organic sulfides and sulfoxides 487
  Other extractants 488
Mechanism of Extraction 489
  Ion pair transfer 489
  Ion exchange.. 489
  Chelation 490
  Extraction by mixed solvents 491
  Effect of temperature 494
The Organic Phase 495
  Nature of the extracted species.......................... 496
  Polymerization of extractant.......................... 497
  Role of diluents 497
  Effect of extractant concentration 499

Third-phase formation 501

The Aqueous Phase 502

Effect of metal ion concentration........................ 502

Effect of foreign ions 502

Complex formation in the aqueous phase..................503

Effect of pH 507

Effect of ion hydration 507

Extraction of inorganic acids 508

Extraction of water 511

Applications... 512

Recovery 513

Separation... 520

Purification.. 525

Production of pure phosphoric acid...................... 525

Literature Guide 525

Monographs 525

Periodicals... 526

Selected review articles 526

Local Conferences 527

The International Solvent Extraction Conferences 527

INTRODUCTION

Extraction by organic solvents is a chemical process in which metal species in the aqueous phase react with an organic reagent to form an organometallic *complex;* thus. the metal species leave the aqueous phase and enter the organic phase. The metal in the organic phase is not bound to carbon atoms as in organometallic *compounds* but to oxygen. nitrogen. sulfur. or hydrogen by a coordination (dative) bond. Stripping is the reverse chemical reaction.

Solvent extraction was used for the first time in hydrometallurgy in connection with rhe Manhattan Project for the production of atomic bomb. A plant was constructed in USA for the preparation of high-purity uranyl nitrate solution. In this plant. high-grade uranium concentrate was dissolved in HNO_3, and uranium was selectively extracted by ether then stripped by water to give a concentrated solution of pure uranyl nitrate. This was followed gradually by developing methods for other high-priced metals such as plutonium. thorium.

niobium, tantalum, zirconium, hafnium, boron, beryllium, and finally molybdenum. The second step took place in the 1960s when solvent extraction was applied for the first time to extract a relatively cheap metal — copper. At present, solvent extraction technology is widespread, well accepted, and highly efficient. Table 21.1 gives a summary of the historical development in this field.

ENGINEERING ASPECTS

Equipment

Only clear filtered solutions can be extracted by organic solvents, although considerable work has been attempted on extraction from slurries. The following equipment are in common use:

Mixer settlers

These are composed of a mixing chamber where the aqueous and organic phases are mixed together by a rotating impeller, and a settling chamber where the mixed phases are given enough time to separate (Figure 21.1). Each such unit composes a stage. The apparatus is very efficient but its principal disadvantage is the large space required per stage. Usually many stages are used (3 to 5) and are operated in counter-current in the extraction as well as in the stripping steps. Sometimes, a washing step is inserted between extraction and stripping to remove loosely bound metal ions (Figure 21.1). Mixing action may be conducted in a centrifugal pump.

Columns

These are of numerous designs.

- ***The packed column.*** This is the simplest design; it consists of a vertical tower packed with ceramic or platic rings for increasing the surface area of contact between the aqueous and organic phases. The organic phase is introduced at the bottom and the aqueous phase near the top. Separation of the phases takes place at the top (Figure 21.2).

Table 21.I: Historical development of solvent extraction processes in hydrometallurgy.

1842	The French chemist Péligot observed that uranyl nitrate is soluble in diethyl ether and used this property for separating uranium from other constituents from pitchblende.
1942	The Mallinckrodt Chemical Works operated a uranium refinery for the US Atomic Energy Commission (The Manhattan Project) based on Péligot's observation. Separation of plutonium.
1951	The US Bureau of Mines in cooperation with the US Atomic Energy Commission started a production scale operation to separate hafnium from zirconium by solvent extraction. The basic process used was developed by the Oak Ridge National Laboratory.
1953	The National Lead Company used tributyl phosphate as the extractant, and subsequently the Mallinckrodt plant was converted to the use of this reagent.
1955	Dow Chemical Company and Oak Ridge National Laboratory developed a process for extracting uranium from wet process phosphoric acid.
1956	Uranium and vanadium recovery from sulfuric acid leach solutions using alkyl phosphoric acids and aliphatic amines. Solvent extraction used at US Bureau of Mines for separating niobium from tantalum.
1959	Solvent extraction applied for thorium and tungsten.
1960	Scandium recovery by Vitro Chemical Co., Salt Lake City. Recovery of boron from Searles Lake, California, by solvent extraction.
1963	Recovery of beryllium from low-grade ores in Utah by Brush Beryllium Company.
1965	Molybdenum Corporation of America commercial plant for separating rare earths at Mountain Pass, California.
1968	Removal of molybdenum from uranium circuits. First commercial plant for copper recovery by solvent extraction (in Miami, Arizona).
1970	Falconbridge's process for nickel recovery in Norway.
1971	International Nickel (U.K.) process for recovery of gold and platinum metals.
1970s	Numerous commercial plants for copper recovery by solvent extraction.
1973	Cobalt extraction at Metallurgie Hoboken, Belgium.
1975	Germanium extraction at Metallurgie Hoboken, Belgium.
1976	Recovery of zinc from pyrite cinder by solvent extraction at Bilboa, Spain.
1980	Removal of arsenic from solution in the electrolytic refining of copper.

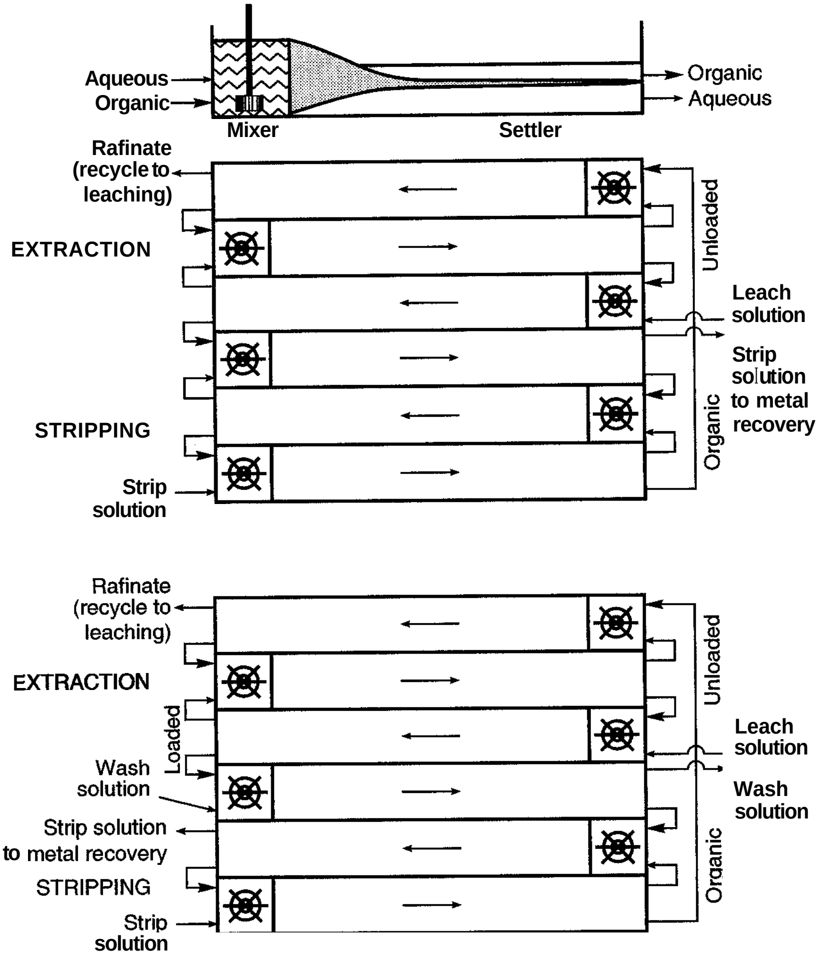


Figure 21.1: Solvent extraction in mixer-settler, elevation and plan. Lower circuit includes a washing step.

- *Pulse column.* Another type of columns is that with screen partitions instead of packing. Efficiency of contact may be improved by introducing a pulsating action in the column (Figure 21.2). In this column, the two phases are dispersed in each other by pulsating action through the screens. The pulsating action is supplied by leading a pulse leg from the bottom of the column to a reciprocating pump. The pulsating action forces the two phases through the holes in the plates, forming bubbles. They rise (or fall) to the next plate, where they coalesce to await the next pulse.

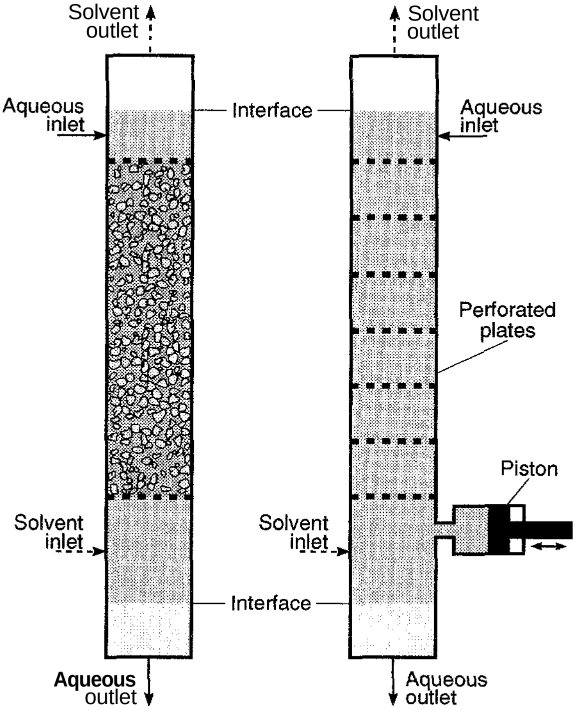


Figure 21.2: Solvent extraction in columns. Left: packed column. Right: pulsating column with sieves.

- *Rotating-disk column.* This consists of a vertical tower with annular disks attached to the tower shell, and circular rotor disks attached to an axial vertical shaft (Figure 21.3). Each rotor disk is spaced vertically midway between adjacent stator disks. Rotation of the central shaft provides controlled dispersion of the two phases in countercurrent flow. Separation takes place at the top of the tower.

Distribution and stripping coefficients

The transfer of metal ions from an aqueous to an organic phase is measured by the distribution coefficient D, which is defined as follows:

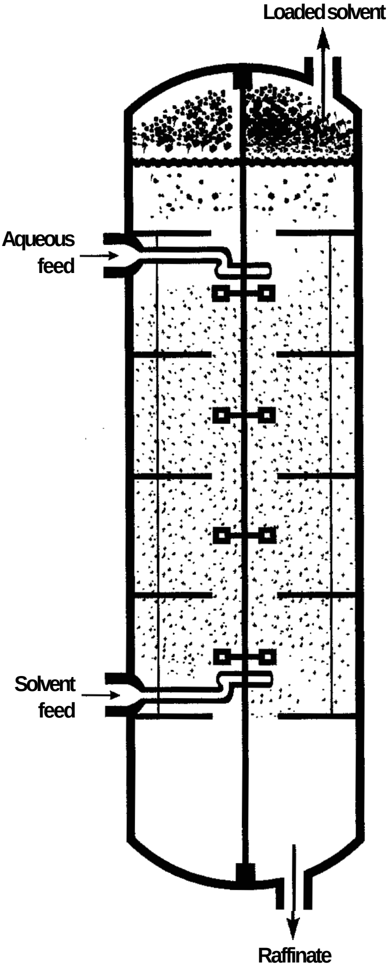


Figure 21.3: Extraction in a column with a rotating shaft.

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

'The higher the value of D at equilibrium, the higher is the extractability of the metal ions in question by that particular extractant. The stripping coefficient is defined by:

$$D' = \frac{\text{Concentration of metal in aqueous phase}}{\text{Concentration of metal in organic phase}}$$

The higher the value of D' at equilibrium, the higher is the tendency of the metal ion to be transferred to the aqueous phase. The stripping coefficient is the inverse of the distribution coefficient D. Stripping agents depend on the nature of the extraction mechanism.

In the stripping process, two purposes are achieved:

- Recovery of the metal values from the loaded organic phase.
- Regeneration of the extractant for recycle.

Stripping can be carried out in one of the following ways:

- Back-washing the organic phase.
- Precipitation of metal values directly from the organic phase.
- Selectively, when the organic phase is loaded with more than one metal. In this case, different stripping agents are used consecutively.

The extraction or distribution coefficients are usually determined by shaking the organic and aqueous phases in a separating funnel for few minutes then allowing the two phases to separate. Each phase is then analyzed and the value of distribution coefficient calculated.

Phase ratio

The volume ratio of the two phases is called the phase ratio; it plays an important role in the extraction process. A low organic/aqueous ratio although advantageous from the theoretical point of view (see page 448) is sometimes undesirable because it may lead to high solvent losses. On the other hand, a high organic/aqueous ratio requires a large inventory of solvent, which may be a financial burden.

During extraction, it is often that the two phases change volume due to the transfer of metal species from one phase to the other or due to the solubility of one phase in the other. This change in volumes should be taken into consideration when calculating the distribution coefficient. Change in volume due to the solubility of one phase in the other can be minimized by equilibrating the organic phase with water before extraction.

Percent extraction

If the original weight of the solute in the aqueous phase is w, and after extraction it is decreased to w_1, then:

$$D = \frac{(w - w_1)/V_o}{w_1/V_a}$$

where V_o is the volume of the organic phase and V_a is that of the aqueous phase. From this equation, it follows that:

$$\frac{w_1}{w} = \frac{V_a}{V_o D + V_a}$$

Therefore:

$$\text{Percent extraction} = \frac{w - w_1}{w} \times 100\%$$

$$= \left(1 - \frac{w_1}{w}\right) \times 100\%$$

$$= \frac{D}{D + V_a/V_o} \times 100\%$$

Figure 21.4 shows a plot of this relation when $V_a/V_o = 1$

Separation and enrichment factors

When two metal ions are to be extracted from an aqueous solution by an organic solvent, the separation factor, β, of the two metal ions is defined by:

$$\beta = \frac{D_A}{D_B}$$

where D_A and D_B are the distribution coefficients of the two metals. In order that separation is possible, β must not equal 1. The enrichment factor, E, is given by:

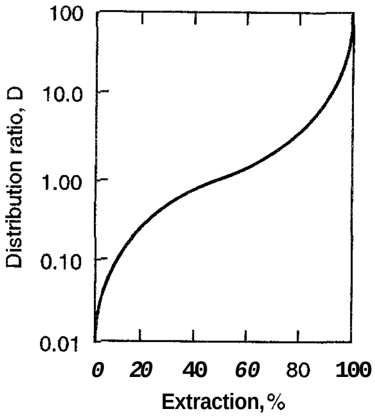


Figure 21.4: Relation between the distribution ratio D and the percent extraction for aqueous to organic ratio of unity.

$$E = \frac{\text{Percent extraction of A}}{\text{Percent extraction of B}}$$

$$= \left(\frac{D_A}{D_A + V_a/V_o} \times 100\%\right) \div \left(\frac{D_B}{D_B + V_a/V_o} \times 100\%\right)$$

$$= \beta \times \frac{D_B + V_a/V_o}{D_A + V_a/V_o}$$

To have a high enrichment, therefore, not only the separation factor must be high, but also the aqueous/organic ratio should be taken into consideration — the volume of organic phase should be as small as possible compared to the aqueous phase. For example, if a solution containing equal amounts of ions A and B is extracted by an organic solvent and the distribution ratio for each component was $D_A = 10$ and $D_B = 1$, respectively, therefore $\beta = 10$. The enrichment factor can be calculated at two aqueous/organic ratios using the above equation:

- When $V_a/V_o = 1$:

Percentage of A transferred to organic phase =

$$\frac{10}{10+1} \times 100\% = 90.9\%$$

Percentage of B transferred to organic phase =

$$\frac{1}{1+1} \times 100\% = 50\%$$

$$E = \frac{90\ 9}{50} = 1.8$$

- When $V_a/V_o = 10$:

Percentage of **A** transferred to organic phase =

$$\frac{10}{10+10} \times 100\% = 50\%$$

Percentage of B transferred to organic phase =

$$\frac{1}{1+10} \times 100\% = 9.09\%$$

$$E = \frac{50}{9.09} = 5.5$$

It can be seen, therefore, that the enrichment factor increases with increased V_a/V_o.

Multiple extractions

If V_a = volume of aqueous phase containing w grams of solute, V_o = volume of organic phase, and after the first extraction, w_1 = weight of solute remaining in aqueous phase, then the equilibrium concentration in aqueous phase = w_1/V_a, and the equilibrium concentration in organic phase = $(w-w_1)/V_o$. Therefore:

$$D = \frac{(w-w_1)/V_o}{w_1/V_a}$$

$$\frac{Dw_1}{V_a} = \frac{w-w_1}{V_o}$$

$$Dw_1 \times V_o = V_a w - V_a w_1$$

$$(V_a + DV_o)w_1 = V_a w$$

$$w_1 = \frac{wV_a}{V_a + DV_o}$$

$$= w \times \frac{1}{1 + DV_o/V_a}$$

After the second extraction, w_2 = weight of solute remaining in aqueous phase; the equilibrium concentration in aqueous phase = w_2/V_a, and the equilibrium concentration in organic phase = $(w_1 - w_2)/V_0$.

$$D = \frac{(w_1 - w_2)/V_o}{w_2/V_a}$$

$$w_2 = w_1 \times \frac{1}{1 + DV_o/V_a}$$

$$= w \times \left(\frac{1}{1 + DV_o/V_a}\right)^2$$

After n extractions,

$$w_n = w \times \left(\frac{1}{1 + DV_o/V_a}\right)^n$$

where w_n = weight remaining in aqueous phase after n extractions, or:

$$\frac{w_n}{V_a} = \frac{w}{V_a} \times \left(\frac{1}{1 + DV_o/V_a}\right)^n$$

$$C_n = C_i \times \left(\frac{1}{1 + DV_o/V_a}\right)^n$$

where C_n = concentration after n extractions, and C_i = initial concentration in aqueous phase.

If the value of V_a is kept constant while V_o is varied such that nV_o = constant, then with a certain total volume of an organic phase, it is always advantageous to use small portions of V_o and a large value of n than the inverse. For example, if C_i = 1 g/L, V_a = 100 mL, D = 10, and the total volume of the organic phase available is 100 mL, then it is more efficient to use 10-mL portions of the organic phase and make 10 extractions than to make a single extraction with 100 ml since this procedure results in the minimum concentration of metal ion in the aqueous phase, C_n, as can be seen from Table 21.2.

Table 21.2: Effect of organic phase volume, V_o, and the number of stages, n, on C_n, the residual concentration of metal ion in aqueous phase after n extractions. Initial concentration, $C_i = 1$ g/L, volume of aqueous phase $V_a = 100$ mL, distribution ratio $L >= 10$.

V_o mL	n	Total organic volume $= nV_o$	C_n g/L
100	1	100	0.09
50	2	100	0.02
25	4	100	0.007
10	10	100	0.001

Extraction isotherms

Extraction data may be represented in two ways: Percentage extraction as a function of a certain variable like acid concentration, pH, etc., or in form of extraction isotherms. The extraction isotherms are the plot of the concentration of the metal ion in aqueous phase versus its concentration in the organic phase when the two phases are in equilibrium. Such a plot is useful, since at each point it directly displays the concentrations in both phases and consequently the distribution coefficients can be evaluated. Extraction isotherms may be constructed in two ways:

- An aqueous phase of a certain volume containing a known amount of metal ion is contacted with an organic phase of a certain volume until equilibrium is reached: the concentration of metal ions in both phases is then determined. The process is repeated at least five times with variable volumes of the organic phase. Figure 21.5 shows the isotherm for copper extraction from an aqueous phase containing initially 3 g/L Cu and the organic–aqueous phase was varied 5:1, 3:1, 2:1, 1:1, 1:2, and 1:8.

- The process is repeated as in the previous case but keeping the organic–aqueous ratio constant and varying the initial metal ion concentration in the aqueous phase.

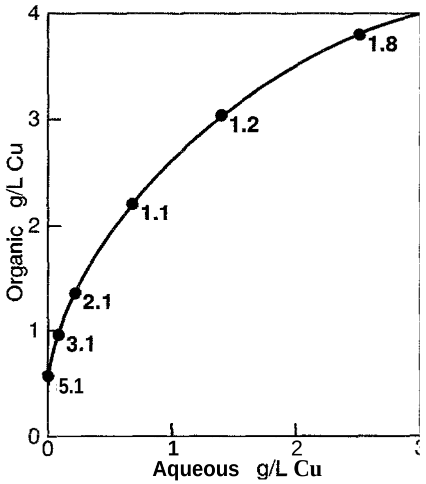


Figure 21.5: Extraction isotherm of copper from a sulfate solution containing 3 g/L Cu by LIX (Henkel Corporation).

With the addition of an operating line based on the volume ratio of the two phases, the extraction isotherm provides a McCabe–Thiele diagram for a stagewise of extraction in a countercurrent system, as will be described later.

Solvent loading

The extraction isotherm also shows that with increasing concentration of the metal ion in the aqueous phase, a limiting concentration is reached in the organic phase. There is usually a simple relation between the number of moles of the extractant and that of the metal ion at saturation. This relation determines the stoichiometry of the reaction and the nature of the extracted species in the organic phase. For example, in Figure 21.6, 0.1 M extractant is saturated with 0.05 M UO_2^{2+}, i.e., 0.5 mole metal ion saturates 1 mole of extractant (see also "The Organic Phase" on page 495).

Counter-current extraction

Complete extraction of a solute in a single stage can be achieved only by using an infinitely large volume of solvent. Multistage extraction is therefore used, since it permits essentially complete recovery using a limited volume of the solvent. In the countercurrent process, the aqueous feed and organic phase flow in opposite directions. Thus, the fresh extractant contacts nearly barren raffinate, while the nearly saturated extractant contacts fresh aqueous feed.

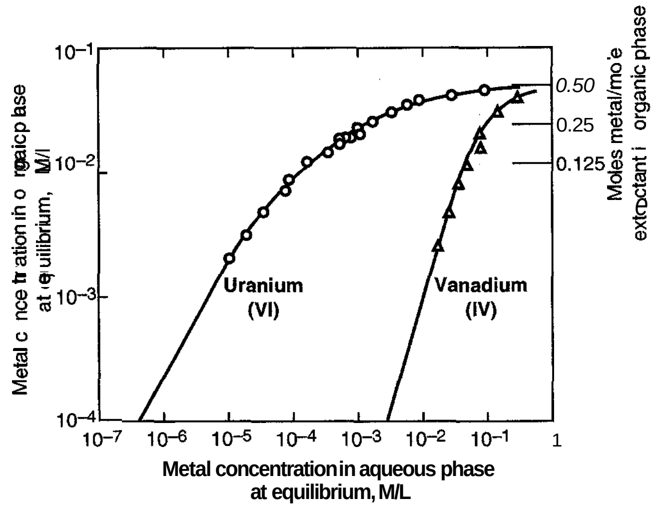


Figure 21.6: Metal extraction from 0.5 M sulfate solutions with 0.1 M D2EHP in kerosene (Blake et al., 1958).

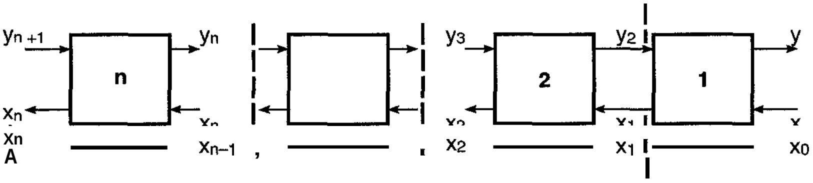


Figure 21.7: Counter-current extraction.

The aqueous flow volume is designated by A, and the corresponding organic flow volume by O (Figure 21.7). The concentration of the extractable species are x and y in the aqueous and organic phases, respectively. The mass balance over n stages is:

$$Ax_0 + Oy_{n+1} = Ax_n + Oy_1$$

$$Oy_1 = A(x_0 - x_n) + Oy_{n+1}$$

$$y_1 = \frac{A}{O}(x_0 - x_n) + y_{n+1}$$

This is an equation of a straight line of slope, *A/O.* The composition of the organic phase leaving the first stage (y_1) is a linear function of the composition of the aqueous phase leaving the *n*th stage (x_n). The values x_0 and y_{n+1}, the composition of aqueous and organic phases before countercurrent contacts, are constants. This straight line is the operating line in the McCabe–Thiele diagram.

A McCabe–Thiele diagram is useful for estimating the number of theoretical stages required to obtain specified results in a solvent extraction system. The operating line is based on mass balance. Hence, the concentration of solute in the aqueous feed entering any stage, and the organic phase leaving any stage, are coordinates of points on the operating line. Since the operating line is straight, it is fixed by any two points. Alternatively, it can be established by only one point and the ratio of aqueous to organic feed that determines the slope of the line.

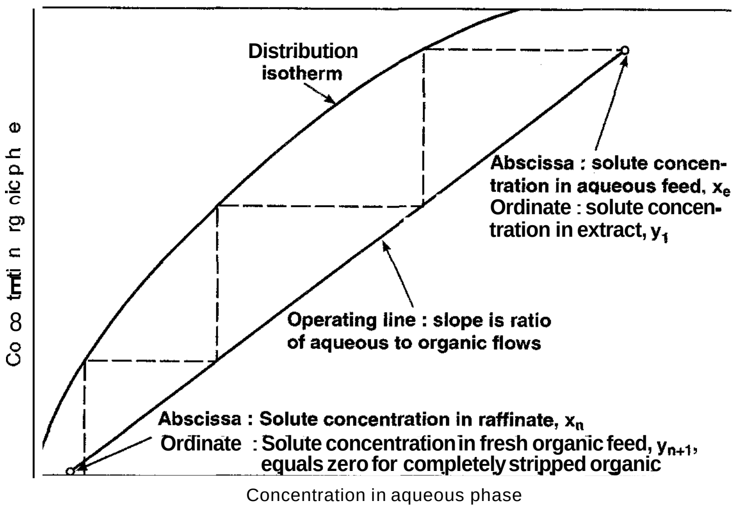


Figure 21.8: McCabe–Thiele diagram.

In constructing the diagram, as illustrated in Figure 21.8, theoretical or ideal stages are "stepped off' by extending a horizontal line from the upper extremity of the operating line to intersect the distribution isotherm, and then a vertical intercept to the operating line, and so forth, until the other extremity of the operating line is intersected. Alternatively, a vertical intercept can be made initially from the lower extremity of the operating line. Each cycle or “step” is termed an ideal or theoretical stage. An ideal stage is a contact stage in which equilibrium between the two phases is achieved, and hence it corresponds to a stage efficiency of 100%. The intersection of each pair of vertical and horizontal lines with the operating line indicates the solute content of the aqueous raffinate leaving an ideal stage and the organic feed entering that stage.

EXTRACTANTS

An ideal extractant should fulfill the following requirements:

- Selectivity
- High extraction capacity
- Easily stripped
- Separates easily from water, i.e.:
    - Density is appreciably different
    - Low viscosity
    - High surface tension
- Safe to handle, i.e.:
    - Non-toxic
    - Non-flammable
    - Non-volatile
- Stable during storage or when in contact with acids or alkalies, i.e., does not hydrolyze during extraction or stripping.
- Cheap

Table 21.3: Physical properties of common diluents.

Group	Compound	Molecular weight	Boiling point °C	Density at 20 °C	Viscosity at 20 °C cp	Spontaneous ignition temperature °C	Dipole moment $\mu \times 10^{18}$ esu	Dielectric constant at 20 °C
Aliphatic hydrocarbons	n-Hexane	86.18	68	0.6594	0.326	260	0	1.890
	Kerosene	—	200–260	0.795	—	85	—	—
	Naphtha	—	150–215	0.775	—	—	—	—
Aromatic hydrocarbons	Benzene	78.11	80.1	0.8787	0.652	590	0	2.284
	Toluene	92.13	110.6	0.8669	0.590	568	0.36	2.438
	o-Xylene	106.16	144	0.8968	0.810	501	0.6	2.568
	m-Xylene	106.16	139	0.8684	0.620	563	—	2.374
	p-Xylene	106.16	138	—	0.648	564	0	2.270
Hydroaromatics	Cyclohexane	84.16	81	0.7791	1.0	270	0	1.890
Substituted hydrocarbons	Chloroform	119.38	61.2	1.4916	0.58	[a]	1.02	4.806
	Carbon tetrachloride	153.82	76.1	1.5942	0.969	[a]	0	2.238
	Carbon disulfide	76.14	45	1.2628	0.37	[a]	0	2.641

a. Non flammable

In practice, however, it is not possible to find an extractant fulfilling all these requirements, and therefore a compromise is usually made. An extractant is seldom used in pure form; it is usually diluted with a cheap organic solvent in order to improve its physical properties, such as its viscosity, density, etc. This organic solvent, called *diluent*, has no capacity to extract metal ions from solution, i.e., it is inert. However, as will be seen later, it affects the extracting power of the extractant. The solution of the extractant in the organic solvent composes the organic phase and is often referred to as the solvent. Beside fulfilling most of the requirements of an extractant, a diluent should be insoluble in water. Hydrocarbons and substituted hydrocarbons are therefore the most commonly used diluents (Table 21.3).

Kerosene is a refined petroleum product composed of a complex mixture of aliphatic, naphthenic, and alkyl aromatic hydrocarbons. Naphthenic compounds, also called naphthenes, are saturated cyclic hydrocarbons such as cyclopentanes and cyclohexanes. The actual composition of kerosene varies widely depending on the crude oil from which it is produced and the method of preparation, but generally aliphatic hydrocarbons in the C_9 to C_{16} range predominate. The aromatic molecular types predominate in the aromatic fraction: indanes, diphenyls, methylnaphthalenes, and tetralin.

While diluents should be insoluble in water, the solubility of extractants in water may vary greatly. Tributyl phosphate, for example, is practically insoluble while a chelating agent like acetyl acetone is completely soluble. Extraction by chelation is characterized by the fact that although the extractant (i.e., the chelating agent) may be soluble, yet the metal chelate is insoluble in water but completely soluble in the diluent.

Ethers and their derivatives

Ethers are light, volatile, and highly flammable liquids having the general formula R–0–R'. The most commonly used ethers are shown in Table 21.4. Many metal ions are extracted by diethyl ether from HF, HCI, and HNO_3 solutions, but not from H_2SO_4. Isopropyl ether extracts iron from phosphoric acid. The extracting power of ethers decreases with increasing molecular weight. Ethers are miscible in aqueous solutions containing high HCl concentration. Ethers are susceptible to oxidation, forming peroxides which are liable to explode on distillation. It is therefore essential that water be present when ether solutions containing nitrates are being evaporated. Figure 21.9 shows extraction of some metal ions from HNO_3 solution by diethyl ether.

Carbitols. These are mono- or dialkyl ethers of diethylene glycols; they are derived from ethylene oxide and monoalkyl ethers of ethylene glycol, e.g., dibutyl carbitol which is used in extracting gold from HCl solution, and uranium and plutonium from HNO_3 solution.

Chlorinated ethers. These are colorless liquids much less volatile than diethyl ether, less soluble in water, and non-flammable at ordinary temperature; that is why they are more preferable than unchlorinated ethers. A typical chlorinated ether is β,β′-dichlorodiethyl ether (Table 21.4).

Crown ethers. These are molecules with ring structure containing oxygen (Figure 21.10).

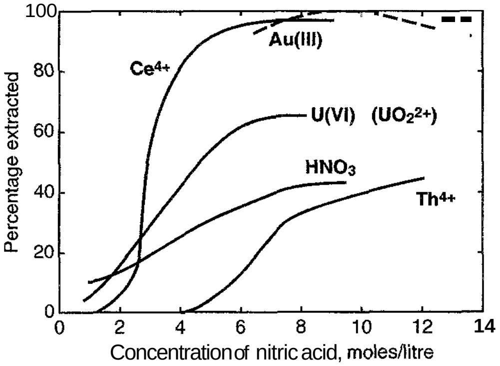


Figure 21.9: Extraction of some metal ions from nitric acid solution by diethyl ether.

Table 21.4: Physical properties of some ethers

	Diethyl ether	Isopropyl ether	Diethylene glycol dibutyl ether[a]	β,β′-dichloro-diethyl ether
Formula	$[C_2H_5]_2O$	$[(CH_3)_2CH]_2O$	$C_4H_9O(C_2H_4O)_2C_4H_9$	$[ClCH_2CH_2]_2O$
Molecular weight	74	102	218	143
Boiling point ("C)	34.6	68.5	256	178.0
Flash point ("C)	−45.0	—	127	75.6
Solubility in water (%)	7.5	1.2	0.3	1.0
Solubility of water in ether (%)	1.3	0.57	1.4	—
Specific gravity	0.717	0.7245	0.8853	1.222
Viscosity at 20 °C (centipoise)	0.23	—	2.39	2.06

a. **Known** industrially as dibutyl carbitol, produced by Union Carbide.

Table 21.5: Alcohols.

Alcohol	Formula	Boiling point °C	Specific gravity	Solubility at 20 °C (%)	
				in water	water in
Primary amyl alcohol	$C_5H_{11}OH$ (mixed isomers)	133	0.8134	1.7	9.2
2-Ethylhexanol	$C_4H_9CH(C_2H_5)CH_2OH$	184.3	0.8340	0.07	2.6
1-Octanol	$CH_3(CH_2)_7OH$			0.03	
n-Butyl alcohol (Propylcarbinol)	$CH_3(CH_2)_4OH$	117.3			
Secondary butyl alcohol (Methylethylcarbinol)	$CH_3CH_2(CH_3)CHOH$	99.5			
Isobutyl alcohol (isopropyl carbinol)	$(CH_3)_2CHCH_2OH$	108			
Tertiary butyl alcohol (Trimethyl carbinol)	$(CH_3)_3COH$	83 (m.p. 25 °C)			

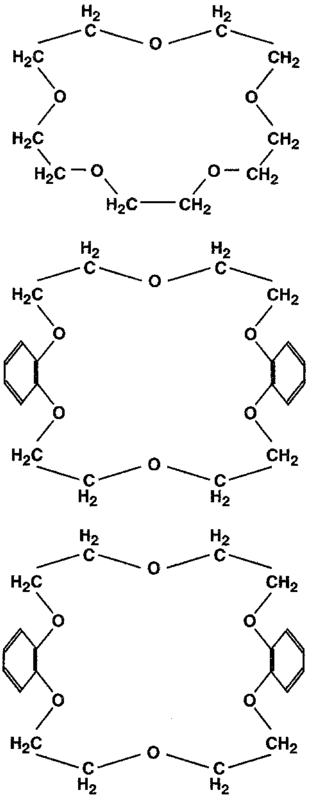


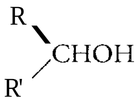
Figure 21.10: Crown ethers.

Alcohols

Monohydric alcohols may be primary, secondary, or tertiary:

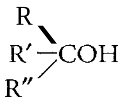
$R{-}CH_2OH$

Primary



$R(R')CHOH$

Secondary



$R(R')(R'')COH$

Tertiary

The lower members are soluble in water, and the solubility decreases with increasing molecular weight. The solubility of n-octyl alcohol (or 1-octanol), $CH_3(CH_2)_7OH$, is 0.03 g in 100 g water. It is used, for example, in separating cobalt from nickel. Table 21.5 gives data on some alcohols, and Figure 21.11 shows the extraction of cobalt and nickel by octyl alcohol.

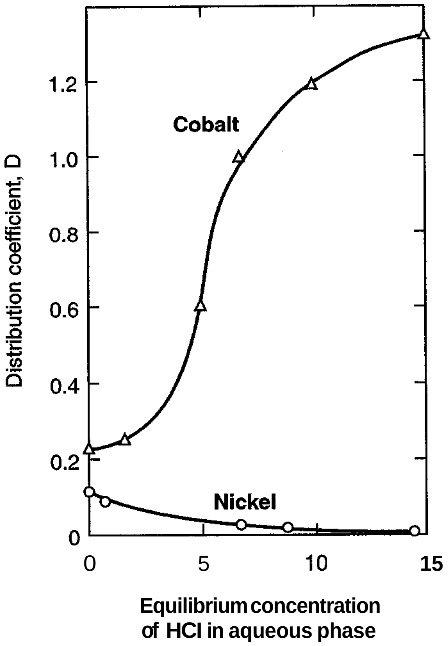
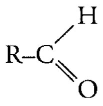


Figure 21.11: Extraction of cobalt and nickel by octyl alcohol (Gindin et al., 1960).

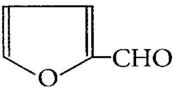
Aldehydes

These are the products of oxidation of monohydric primary alcohols and have the general formula:



$$R{-}C\overset{H}{\underset{O}{\ }}$$

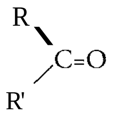
A commonly used aldehyde is furaldehyde or furfural:



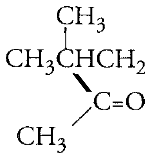
It is a colorless, pleasant-smelling liquid, b.p. 162 °C, density 1.1598, and solubility in water 9 % by volume. It is produced in large quantities as a by-product of the agricultural waste industry; cheap and non-poisonous, it is already used in purifying lubrificating oils.

Ketones

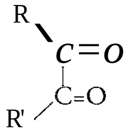
Ketones are products of oxidation of secondary alcohols. Mono ketones, or simply ketones, have the general formula shown below.



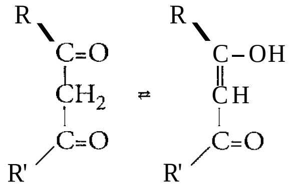
Monoketone
(or simply ketone)



Example: hexone

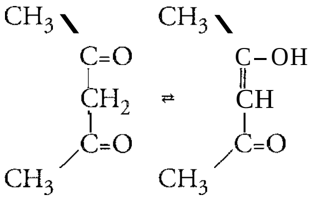


Alpha diketone

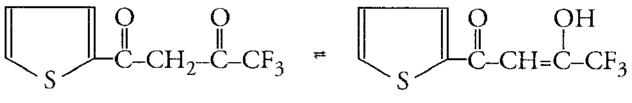


(keto) (enol)
Beta diketone

A commonly used ketone is methyl isobutyl ketone, known as hexone (Table 21.6). Diketones exist in the alpha and beta forms. They are prepared by the condensation of ketones with esters. Beta diketones exist in the keto and enol forms and therefore possess an acidic hydrogen atom. An important diketone is acetyl acetone, also known as 2,4-pentanedione, and its derivative thenoyl trifluoro acetone:



(keto) (enol)
Acetyl acetone



(keto) (enol)
Thenoyl trifluoro acetone

Table 21.6: Ketones.

Ketone	Formula	Boiling point (°C)	Specific gravity	Solubility at 20 °C (%)	
				in water	water in
Methyl isobutyl ketone[a]	$CH_3COCH_2CH(CH_3)_2$	116.2	0.8020	1.9	1.6
Methyl isoamyl ketone	$CH_3COC_2H_4CH(CH_3)_2$	144.9	0.8132	0.54	1.28
Diisobutyl ketone	$(CH_3)_2CHCH_2COCH_2CH(CH_3)_2$	169.4	0.8076	0.05	0.75
2,4-Pentanedione	$CH_3COCH_2COCH_3$	140.4	0.9753	16.6	4.5

[a] Known industrially as **hexone.**

Methyl isobutyl ketone will extract cobalt from thiocyanate solution while di-isobutyl ketone will not. Hexone is used for extracting uranium, plutonium, zirconium, hafnium, and niobium–tantalum separations. Extraction data is shown in Figures 21.12 and 21.13.

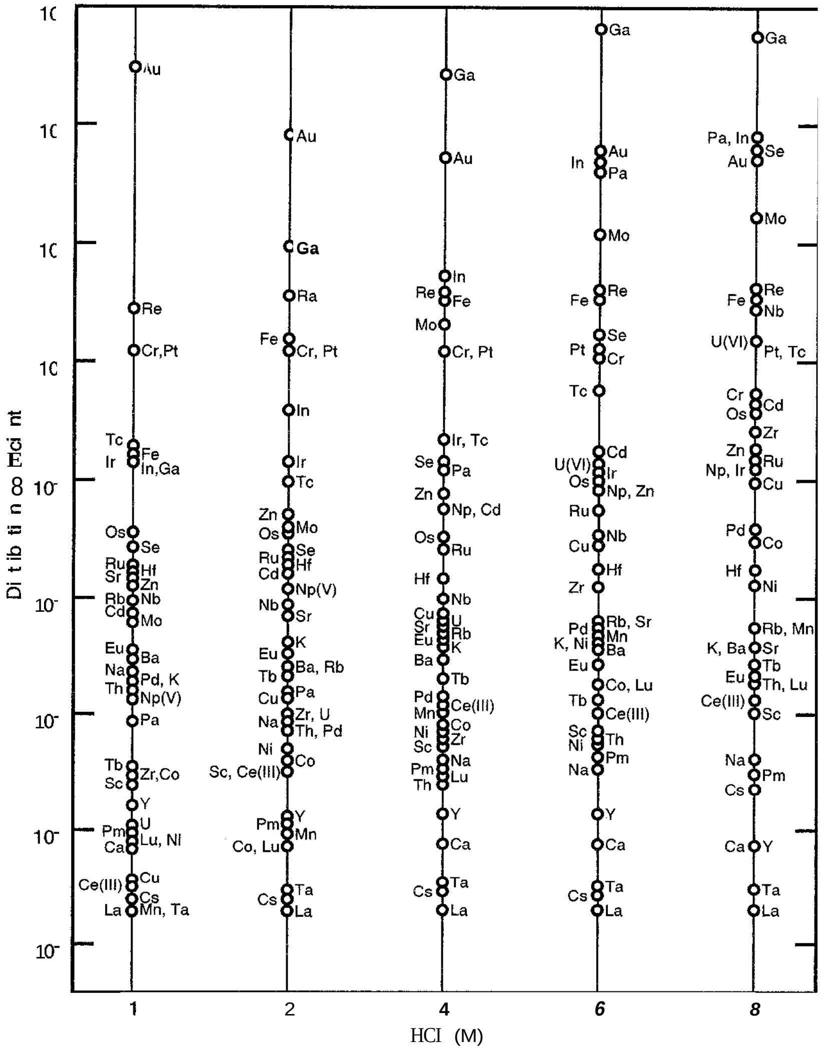


Figure 21.12: The extraction of metals from hydrochloric acid solutions with methyl isobutyl ketone (Marcus and Kertes, 1969).

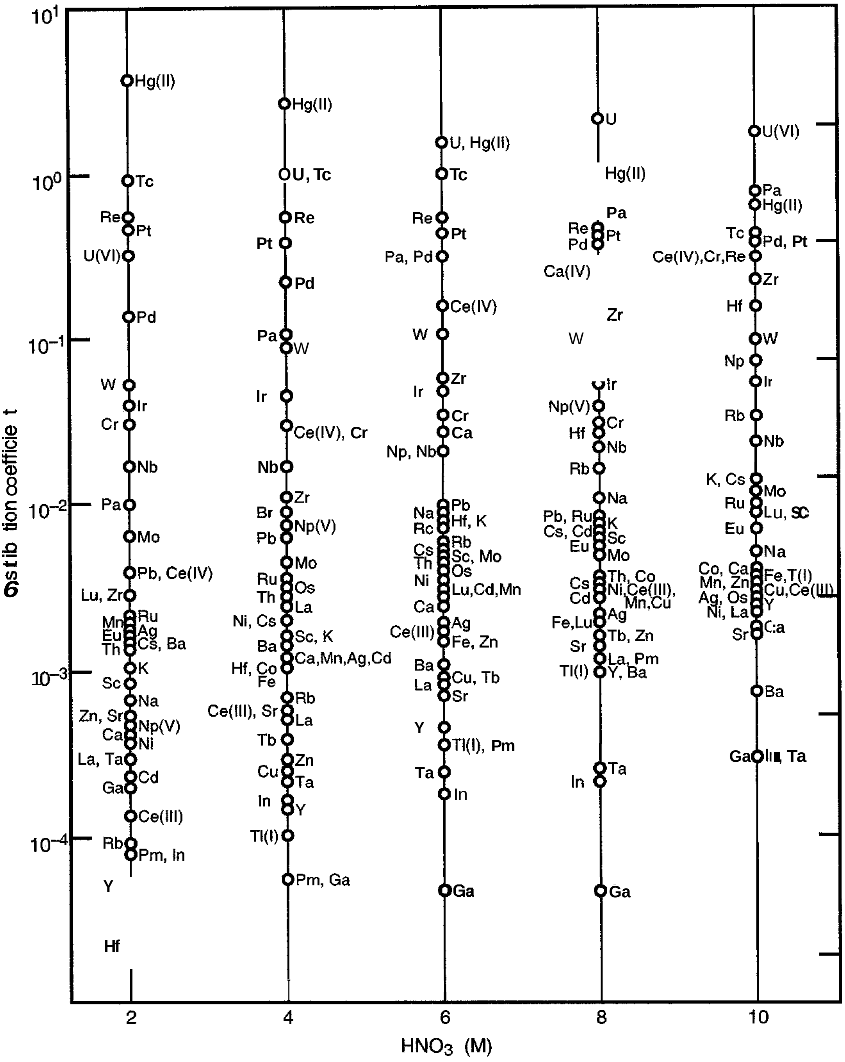
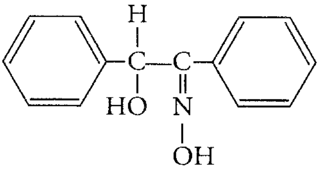


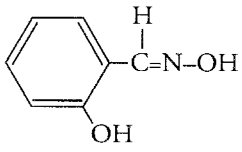
Figure 21.13: The extraction of metals from nitric acid solutions with methyl isobutyl ketone (Marcus and Kertes, *1969)*.

Oximes

Oximes, i.e., compounds containing the group =N–OH, have been used for many years in analytical chemistry as precipitants for metals. The α-hydroxyoximes are well known as specific for precipitating copper, e.g.:

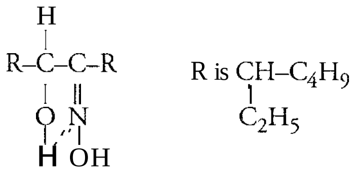


α-Benzoinoxime



Salicylaldoxime

Hydroxyoximes. 5,8-diethyl-7-hydroxy-6-dodecanone oxime is used in extracting copper from leach solutions, under the trade name LIX-**63** introduced to the market by General Mills Corporation, now Henkel Corporation.



LIX *63*

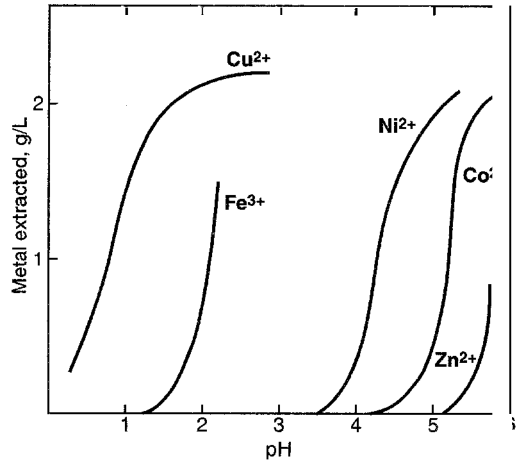


Figure 21.14: Extraction of some metal ions with LIX-64N as a function of pH (Henkel Corporation).

Hydroxybenzophenone oximes. These are more efficient than the hydroxyoximes, also introduced by Henkel (Table 21.7). Other groups of similar structure were introduced by Imperial Chemical Industries (Acorga extractants), and by Shell (SME group); they are also shown in Table 21.7. The commercial products are usually mixtures and not pure compounds, For example, LIX-64 and LIX-70 contain some LIX-63. Table 21.8 gives some data on LIX-65N while Figures 21.14 and 21.15 give data on LIX-64N.

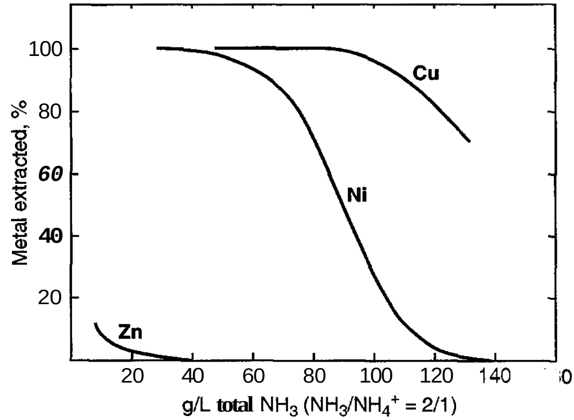
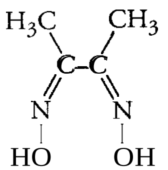
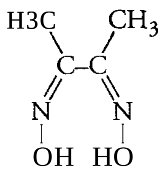


Figure 21.15: Extraction of metal ions from ammoniacal solution by LIX-64N (Henkel Corporation).

Dioximes. These are compounds containing the $(=N{-}OH)_2$ group, e.g., dimethyl glyoxime. They have also been known for many years as chelating agents for metals. Dimethyl glyoxime is specific for nickel; it exists in three configurations:



Anti-isomer



Syn-isomer

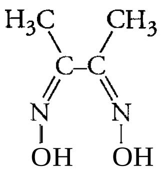
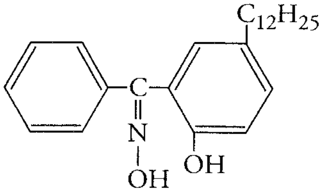
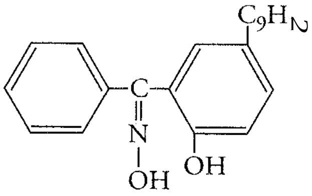
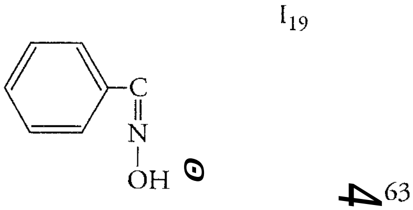


Table 21.7: Hydroxybenzophenone oximes.

Trade name	Chemical name	Formula
LIX-64 (Henkel)	2-Hydroxy-5-dodecylbenzophenone oxime	 + LIX 63
LIX-64N	LIX 65N + 1% by volume LIX 63	
LIX-65N (Henkel)	2-Hydroxy-5-nonylbenzophenone oxime	
LIX-70 (Henkel)	2-Hydroxy-3-chloro-5-nonylbenzophenone oxime	
LIX-71	LIX 70 + LIX 65N	
LIX-73	LIX 70 + LIX 65N + LIX 63	

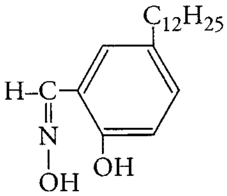
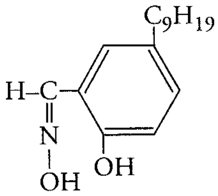
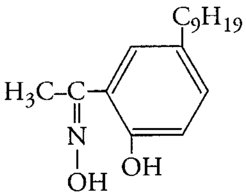
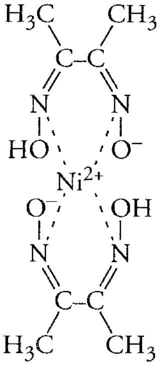
Trade name	Chemical name	Formula
LIX-860 (Henkel)	5-Dodecylsalicyl aldoxime	
Acorga P50 (ICI)	5-Nonyl salicylaldoxime	
SME 529 (Shell)	2-Hydroxy-5-nonyl acetophenone oxime	

Table 21.8: Physical properties of LIX-65N Henkei Corporation

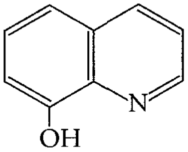
Appearance	Amber liquid
Specific gravity	0.899
Viscosity at 30°C	45 Centipoise
Pour point (ASTM)	–36 °C
Flash point (ASTM)	85 °C
Fire point (ASTM)	92 °C



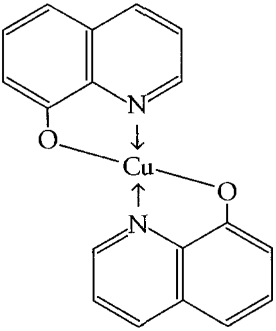
Only the anti configuration is capable of forming the stable complex with nickel. Like the dioximes, the hydroxyoximes can exist in two forms: anti-isomer and syn-isomer. It was proved that only the anti-isomer is an active extracting agent, the synisomer (about 50% of LIX) being inactive.

Quinolines

8-Hydroxyquinoline, also known as oxine, is a colorless solid, m.p. 75 °C, slightly soluble in water:

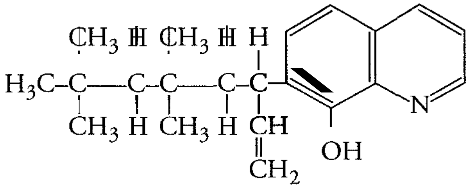


8-Hydroxyquinoline



8-Hydroxyquinolinecopper complex

Keelex-100 is β-alkenyl-8-hydroxyquinoline:

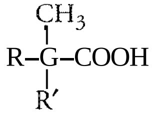


It is marketed by Ashland Chemicals for the extraction of copper. It is a liquid having a density 0.9985 at 25 "C, flash point over 90 "C, pour point **3** °C, and viscosity 764 centipose. It has a copper loading capacity of 0.7 g Cu per 1 volume percent. Keelex-120 is composed of 20% volume of Keelex-100 in para-nonyl phenol. Figures 21.16 and 21.17 give extraction data by Keelex-100.

Organic acids

Many organic compounds exhibit acidic properties; only those which contain the carboxyl group and are of metallurgical interest are mentioned here:

- *Fatty acids,* RCOOH. Also known as carboxylic acids; the low members are soluble in water and the solubility decreases with increasing molecular weight. Numerous acids have been suggested as extractants, e.g., palmitic, $CH_3(CH_2)_{14}COOH$, and stearic, $CH_3(CH_2)_{16}COOH$. Others are in use under the trade name Versatic acid:



$$R-\overset{CH_3}{\underset{R'}{G}}-COOH$$

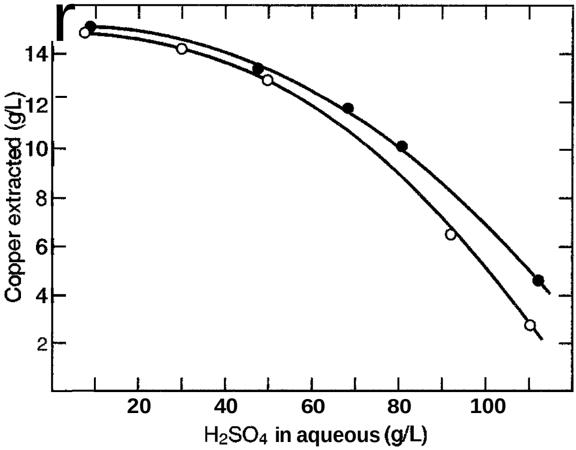


Figure 21.16: Extraction of copper from H_2SO_4 solution by Keelex at 45 °C and organic: aqueous ratio 1:1. Initial copper concentration 15.55 g/L. ● 20% Keelex 100 and 10% nonylphenol. ○ 20% Keelex 100 and 20% nonylphenol.

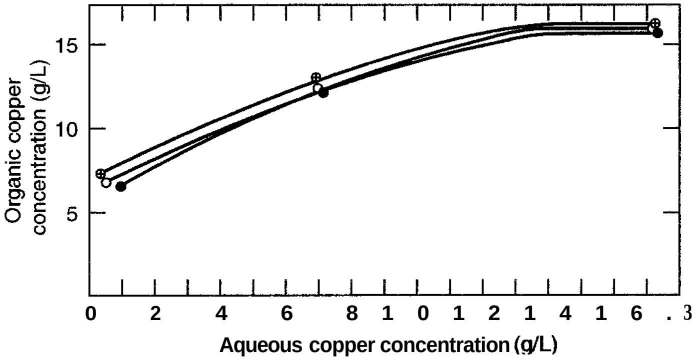
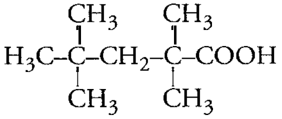


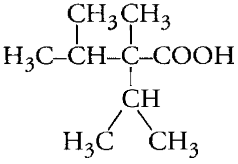
Figure 21.17: Extraction of copper from H_2SO_4 by Keelex at 35–38 "C. Aqueous phase 33.6 g/L Cu and 13.5 g/L H_2SO_4. ⊕ 20% Keelex 100 and 10% nonylphenol-Solvesso 150. ○ 20% Keelex 100 and 10% isodecanol-Solvesso 150. ● 20% Keelex 100 and 10% nonylphenol-Escaid 100.

For example, in Versatic acid 911, R is C_4 and R' is C_5 chains. Versatic acid 9 is a mixture:



$H_3C-C(CH_3)_2-CH_2-C(CH_3)_2-COOH$

56%



27%

Versatic 10 is derived from C_9 olefin and is highly branched at the alpha position. Alpha-substituted acids, e.g., α-bromo lauric, $CH_3(CH_2)_9CHBrCOOH$, and α-bromo myristic (C_{14}) have also been suggested because of their increased strength. Solubility data of some Versatic acids are given in Table 21.9, while Figures 21.18 to 21.21 give extraction data.

Table 21.9: Solubility of some carboxylic acids in water at pH 4.

Acid	Solubility g/L
Versatic 9	0.25
Versatic 10	0.07
Versatic 911	0.10

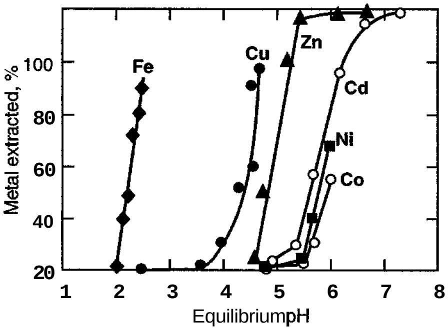


Figure 21.18: Extraction of some metal ions from H_2SO_4 solution by Versatic 9 (Spitzer et al., 1966).

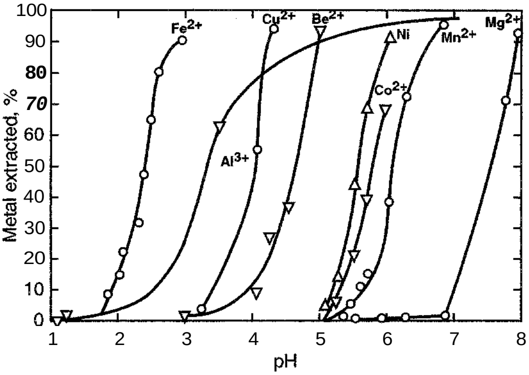


Figure 21.19: Extraction of metal ions from sulfate medium by Versatic 10 (Shell Chemicals).

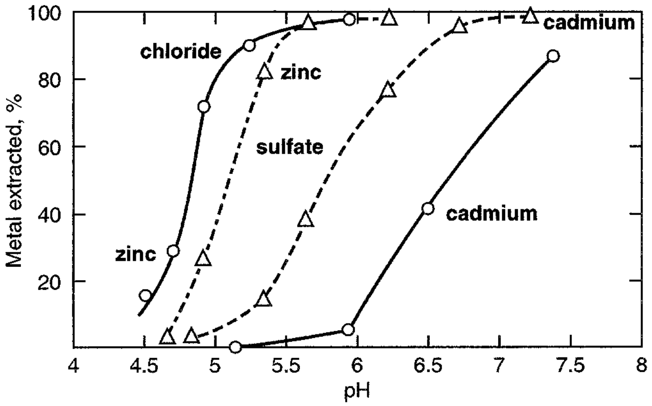
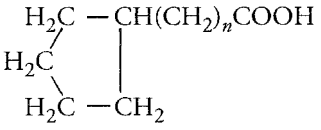


Figure 21.20: Extraction of zinc and cadmium by Versatic 10 from sulfate and chloride media (Spitzer et al., 1967).

- *Naphthenic acids.* These are carboxylic derivatives of cycloparaffin hydrocarbons, having a structure as shown:



They are derived from crude petroleum oils and have a variable composition. The molecular weight varies from 170 to 330. Figure

21.22 shows extraction data for a commercially available naphthenic acid.

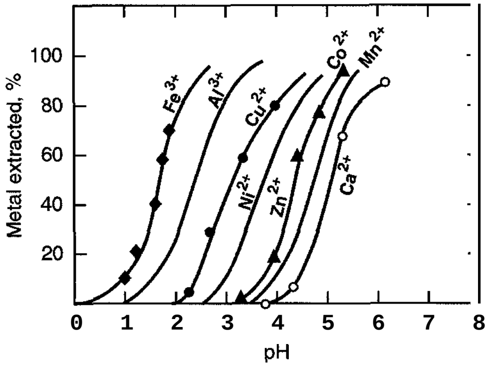


Figure 21.21: Extraction of some metal ions from H_2SO_4 solution by a-bromo lauric acid (Blumberg and Metzer, 1965).

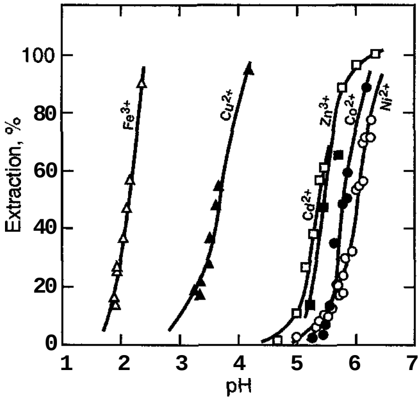
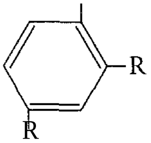
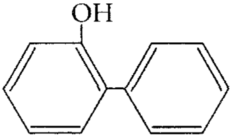
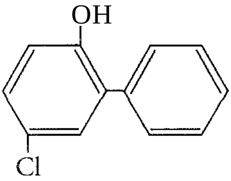
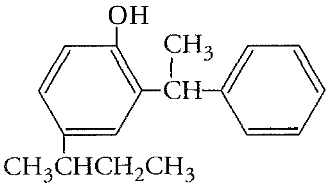
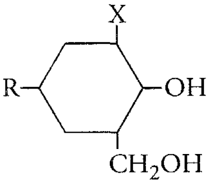


Figure 21.22: Extraction of some metal ions with naphthenic acid (Fletcher and Flett, 1965).

Phenols

Phenols, in which a hydroxyl group is attached to an aromatic nucleus, are more strongly acidic than alcohols. Table 21.10 shows some phenols of metallurgical interest. Polyol is used on commercial scale for boron extraction.

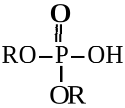
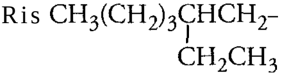
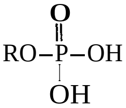
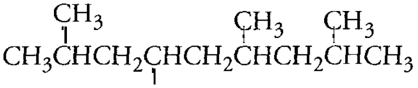
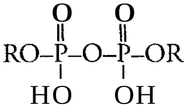
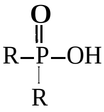
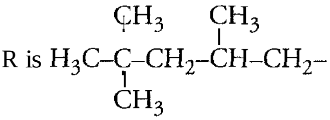
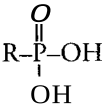
Table **21.10:** Phenols suggested as extractants.

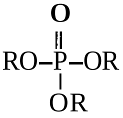
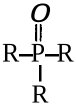
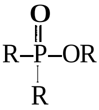
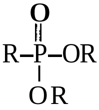
p-Dodecyl phenol	 R = Dodecyl (mixed isomers)
o-Phenyl phenol	
4-Chloro-2-phenyl phenol	
4-sec-Butyl-2(α-methyl benzyl) phenol	
Polyol	

Esters

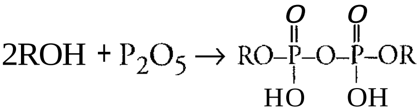
Esters are formed by the reaction of alcohols with inorganic acids. Those used in extractive metallurgy are derived from phosphoric acid and can be classified into acidic or neutral esters (Table 21.11). Phosphoric acid is introduced in the form of P_2O_5 or $POCl_3$. A mixture of products is generally obtained, and compounds formed from the hydrolysis of the products are common. Moreover, dehydratation of the alcohol by P_2O_5 may take place, giving unsaturated hydrocarbons or olefins in the reaction mixture. Thus, an alkyl phosphoric acid such as octyl pyrophosphoric acid (OPI'A) was found to be composed of at least seven components.

Table 21.11: Organic phosphorus compounds.

	Group	Example	Abbreviation
Acidic	Dialkyl phosphoric acid  $RO{-}\overset{\overset{O}{\parallel}}{\underset{\underset{OR}{\vert}}{P}}{-}OH$	Di (2-ethylhexyl) phosphoric acid  R is $CH_3(CH_2)_3\underset{\underset{CH_2CH_3}{\vert}}{C}HCH_2{-}$	D2EHPA
	Monoalkyl phosphoric acid  $RO{-}\overset{\overset{O}{\parallel}}{\underset{\underset{OH}{\vert}}{P}}{-}OH$	Dodecyl phosphoric acid R is (1,2-methylpropyl)-3,5-dimethyl hexyl phosphate  $CH_3\overset{\overset{CH_3}{\vert}}{C}HCH_2\underset{\vert}{\overset{\overset{CH_3}{\vert}}{C}}HCH_2CHCH_2\overset{\overset{CH_3}{\vert}}{C}HCH_3$	DDPA
	Alkyl pyrophosphoric acid  $RO{-}\overset{\overset{O}{\parallel}}{\underset{\underset{HO}{\vert}}{P}}{-}O{-}\overset{\overset{O}{\parallel}}{\underset{\underset{OH}{\vert}}{P}}{-}OR$	Octyl pyrophosphoric acid R is $C_8H_{17}{-}$	OPPA
	Dialkyl phosphinic acid  $R{-}\overset{\overset{O}{\parallel}}{\underset{\underset{R}{\vert}}{P}}{-}OH$	Bis (2,4,4-trimethyl pentyl) phosphinic acid  R is $H_3C{-}\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}{-}CH_2{-}\overset{\overset{CH_3}{\vert}}{C}H{-}CH_2{-}$	Cyanex 272
	Monoalkyl phosphonic acid  $R{-}\overset{\overset{O}{\parallel}}{\underset{\underset{OH}{\vert}}{P}}{-}OH$		

	Group	Example	Abbreviation
Neutral	Trialkyl phosphate  $RO-\overset{\overset{O}{\|}}{\underset{\underset{OR}{\|}}{P}}-OR$	Tributyl phosphate R is C_4H_9-	TBP
	Trialkyl phosphine oxide  $R-\overset{\overset{O}{\|}}{\underset{\underset{R}{\|}}{P}}-R$	Trioctyl phosphine oxide R is $H_3C(CH_2)_7-$	TOPO Cyanex 921
	Alkyl dialkyl phosphinate  $R-\overset{\overset{O}{\|}}{\underset{\underset{R}{\|}}{P}}-OR$		
	Dialkyl alkyl phosphinate  $R-\overset{\overset{O}{\|}}{\underset{\underset{OR}{\|}}{P}}-OR$		

Acid esters. The molar ratio of the reactants determines the type of ester. Thus, when an alcohol to P_2O_5 ratio is 2, an alkyl pyrophosphoric acid is obtained:



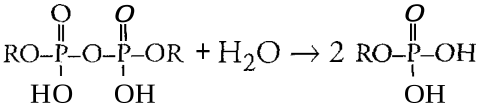
$$2ROH + P_2O_5 \rightarrow RO-\overset{\overset{O}{\|}}{\underset{\underset{HO}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OR$$

When a ratio of $3:1$ is used, a mixture of mono and dialkyl ortho phosphoric acid is obtained:

$$3ROH + P_2O_5 \rightarrow (RO)(HO)_2PO + (RO)_2(HO)PO$$

Data on D2EHPA and Cyanex 272 are given in Table 21.12 and Figures 21.23 and 21.24.

To prepare a monoalkyl phosphoric acid, P_2O_5 is slurried in a diluent such as kerosene, and the alcohol is then added while temperature is kept at about 15 °C. The reaction product is hydrolyzed at elevated temperature by refluxing with 1 M HCI:



$$RO-\overset{\overset{O}{\|}}{\underset{\underset{HO}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OR + H_2O \rightarrow 2\ RO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$$

In general, the following rules apply:

- Solubility of the phosphoric acid ester in the aqueous phase decreases with increasing chain length.
- Extracting power increases with increasing chain length, but for economic reasons chain lengths C_8–C_{12} are used.
- Low emulsifying tendency is achieved by branching in the chain.

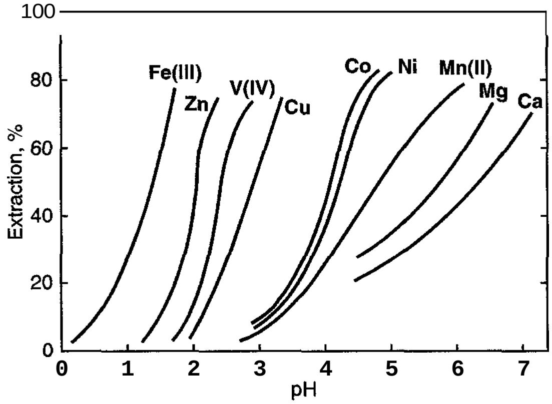


Figure 21.23: Extraction of metals by D2EHPA from sulfate solutions (Henkel Corporation).

Table 21.12: Physical properties of some phosphoric acid esters used as solvents.

	D2EHPA	Cyanex 272	TBP	TOPO
Molecular weight	322		266	386
Specific gravity	0.9770	0.92	0.973	0.88
Freezing point ("C)	−60		−80	47–52
Viscosity at 20 °C (cps)	53	142	3.4	
Solubility at 20 °C (%)				
in water	< 0.01	< 0.01	0.6	< 0.01
water in	2.4		7	
Flash point ("C)	196	108	145	

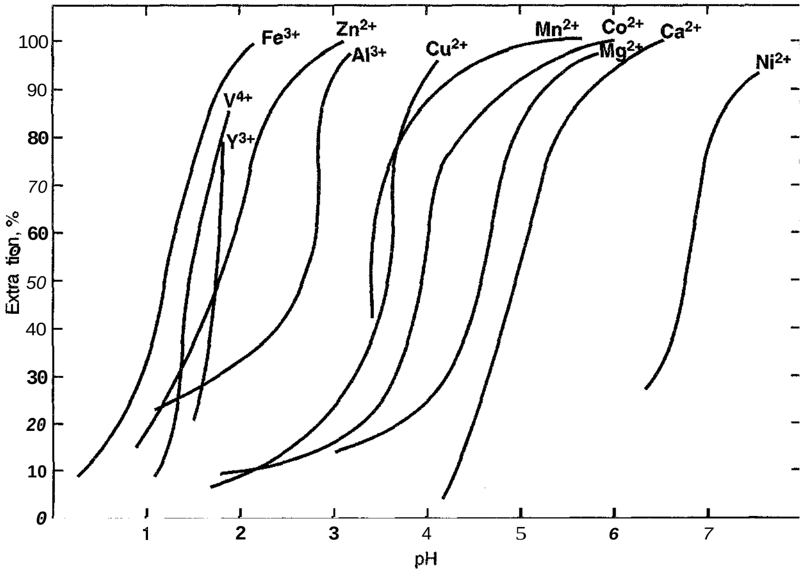


Figure 21.24: Extraction of metals by Cyanex 272 from sulfate solutions (Cyanamid).

Neutral esters. When a ratio 6:1 is used, a trialkyl phosphate is obtained:

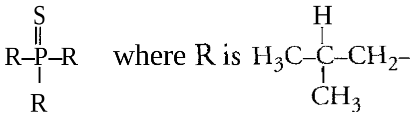
$$6ROH + P_2O_5 \rightarrow 2(RO)_3PO$$

Trialkyl phosphates can also be prepared by the interaction of $POCl_3$ with alcohols:

$$3ROH + POCl_3 \rightarrow (RO)_3PO + 3HCl$$

Commonly used extractants belonging to this group are tributyl phosphate, TBP, and trioctyl phosphine oxide, known as TOPO (Table 21.12). Extraction data are given in Figures 21.25 and 21.26.

Phosphine sulfides. Trialkyl phosphine sulfides are related to the phosphine oxides: The oxygen atom is replaced by sulfur. For example, Cyanex 471X is tri-isobutylphosphine sulfide:



$$\underset{\displaystyle R}{\overset{\displaystyle S}{\overset{\|}{\text{R–}\underset{|}{P}\text{–R}}}} \quad \text{where R is } H_3C\text{–}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}\text{–}CH_2\text{–}$$

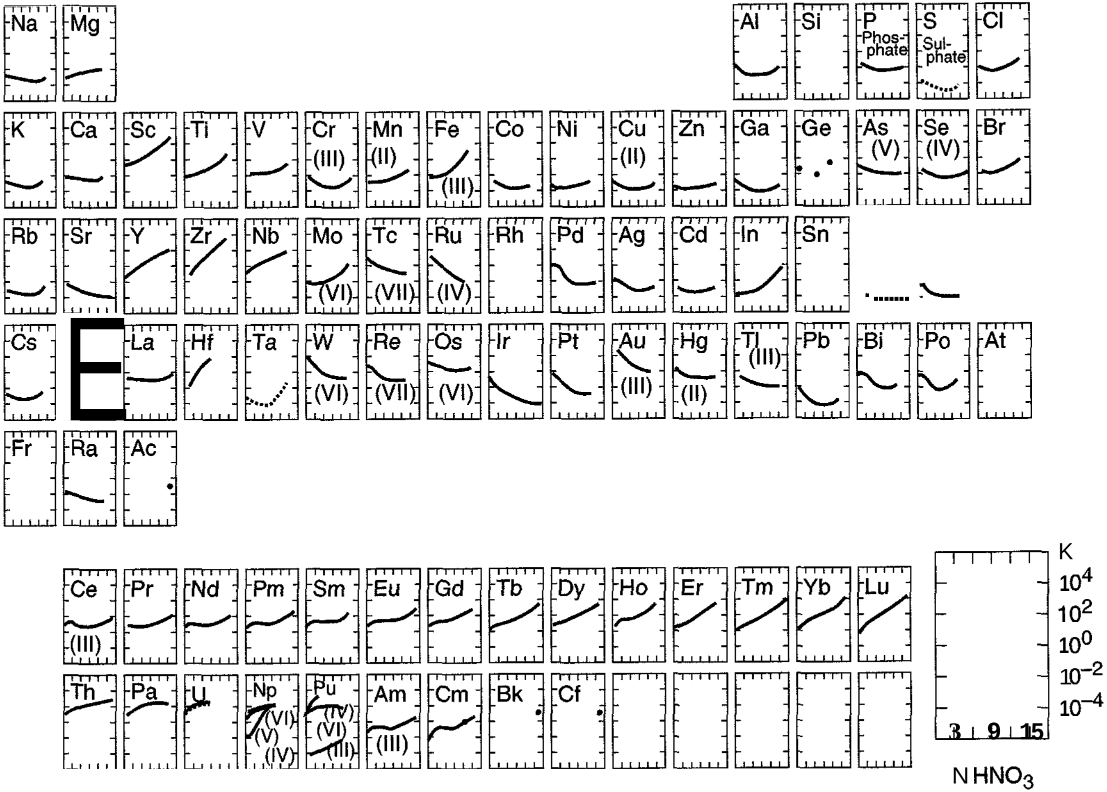


Figure 21.25: Extraction of metal ions from HNO_3 by TBP (Japan Atomic Energy Research Institute, 1963).

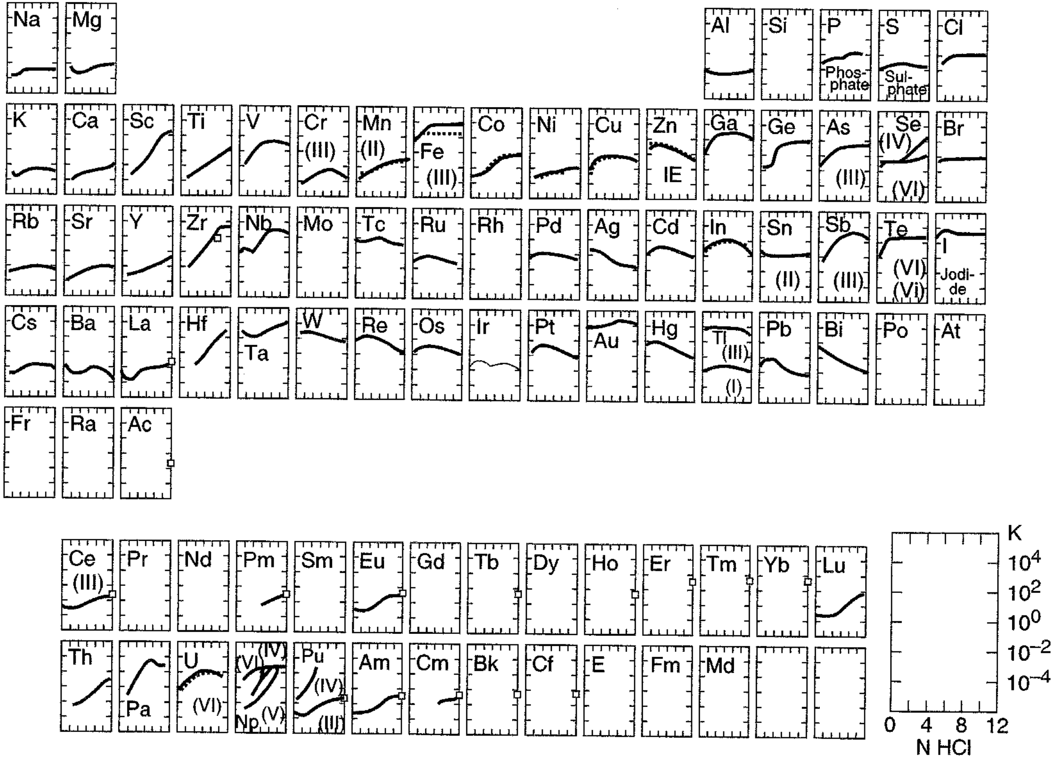


Figure 21.26: Extraction of metal ions from HCl by TBP (Japan Atomic Energy Research Institute, 1963).

It is used in the extraction of gold and silver, and in the separation of palladium from platinum.

Amines and amine oxides

The use of simple amines is limited to those of molecular weight between 250 and 600. Amines of molecular weight lower than 250 are appreciably soluble in water, and those of molecular weight higher than 600 are either not easily available or have low solubility in the organic phase. Table 21.13 gives some of the widely used amines as metal extractants. Most of these are commercial products which are mixtures of compounds in isomeric or homologous series. The predominating structure in each mixture is given. Alamine 336, for example, is 97% tertiary, 1% secondary, and 0.2% primary amine. Solubility of the amines in aqueous and organic solutions, as well as phase-separation properties, depends on the structure of the amine and the nature of the solvent. Water immiscibility decreases with increasing length of the aliphatic chain. Table 21.14 gives data on Alamine 336 and Figure 21.27 gives extraction data. Other extraction data are given in Figures 21.28 and 21.29.

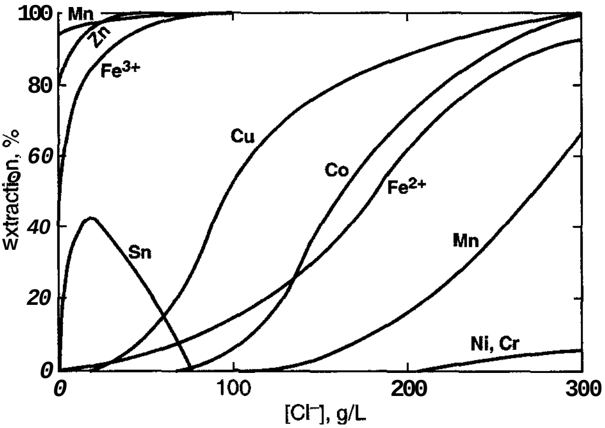
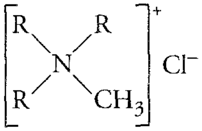


Figure 21.27: Extraction of metal ions by Alamine 336 from chloride solution at pH 2 and at 40 °C (Henkel Corporation).

Quaternary ammonium compounds. These are closely related to amines, but they are significantly different in behavior. While the simple amines are ineffective at high pH, the strong-base quaternary ammonium compounds are effective over a wide pH range. Aliquate 336 is a quaternary amine made by Henkel Corporation; it is tricapryl methyl ammonium chloride:



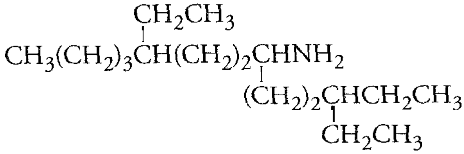
where R is a mixture of C_8 and C_{10} carbon chains with the C_8 predominating. Table 21.14 gives data on this solvent.

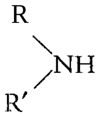
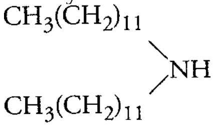
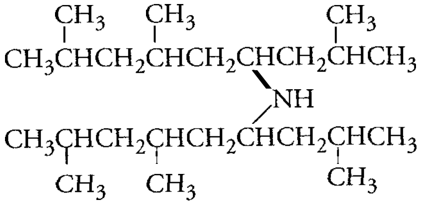
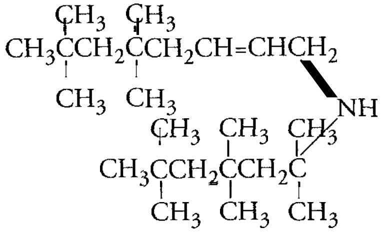
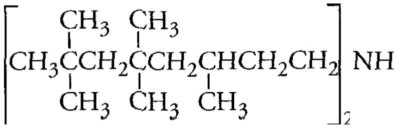
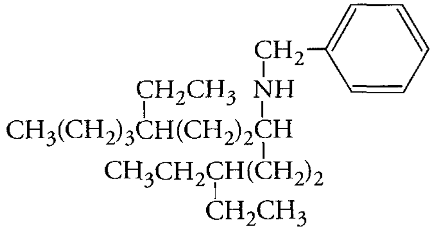
Amine oxides. These are formed by the oxidation of tertiary amines with H_2O_2:

$$R_3N + H_2O_2 \rightarrow R_3NO + H_2O$$

They are strong bases; they extract acids and many metal ions from acid solutions, e.g., uranium, plutonium, tungsten, molybdenum, rhenium, cobalt, thorium, zirconium, and cerium. Typical members of this group are trioctylamine oxide and tri-n-laurylamine oxide.

Table 21.13: Typical amines used for extracting metal ions.

Group	Example	Abbreviation or synonym
Primary RNH_2	Trialkyl methylamine $CH_3C(CH_3)_2CH_2C(CH_3)_2C(CH_3)_2CH_2\text{–}C(CH_3)_2CH_2C(CH_3)_2NH_2$ 1-(3-Ethylpentyl)-4-ethyloctylamine  $\mathrm{CH_3(CH_2)_3\overset{CH_2CH_3}{\overset{\mid}{C}}H(CH_2)_2\underset{(CH_2)_2\underset{CH_2CH_3}{\underset{\mid}{C}}HCH_2CH_3}{\underset{\mid}{C}}HNH_2}$ Octadecylamine $CH_3(CH_2)_{17}NH_2$	Primene JM

Group	Example	Abbreviation or synonym
Secondary 	Dilaurylamine 	Armeen **212** Amine **S-24**
	Bis (1-isobutyl-3,5-dimethyl hexyl) amine 	
	Dodecenyltrialkylmethylamine 	Amine 9D-178
	Di (tridecyl) amine  $[CH_3C(CH_3)_2CH_2C(CH_3)_2CH_2CH(CH_3)CH_2CH_2]_2NH$	
	N-Benzyl-1-(3-ethylpentyl)-4-ethyloctylamine 	Primene JM

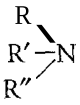
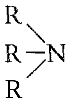
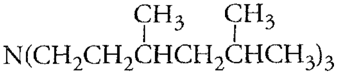
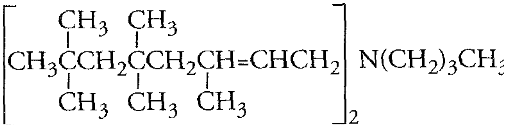
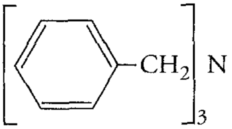
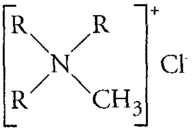
Group	Example	Abbreviation or synonym
Tertiary 	Tri-n-octylamine  where R is $CH_3(CH_2)_7$–	TOA Alamine 300
	Triisooctylamine  $N(CH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_3)_3$	TIOA Alamine 308
	A mixture of tri-n-octylamine and tri-n-decylamine	Alamine 336
	Butyldilaurylamine  $[CH_3C(CH_3)_2CH_2C(CH_3)_2CH_2CH(CH_3){=}CHCH_2]_2N(CH_2)_3CH_3$	
	Tribenzylamine 	
Quaternary ammonium salt	Tricapryl methyl ammonium chloride R is a mixture of C_8 and C_{10} carbon chains. 	Aliquate 336

Table 21.14: Physical properties of some amines (Henkel Corporation).

	Alamine 336	Aliquate 336
Appearance	Pale yellow liquid	Amber
Specific gravity	0.81	0.884
Average molecular weight	392	442
Viscosity at 30 °C (centipoise)	11	1,460
Solubility in water	< 5 ppm	0.1%

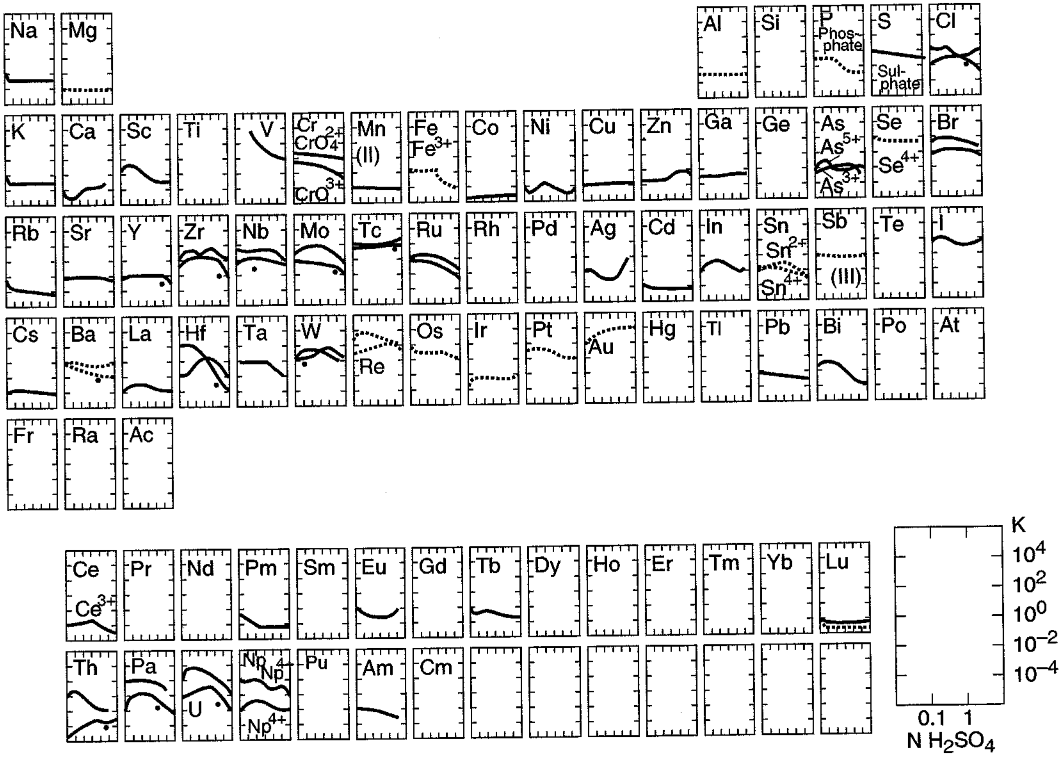


Figure 21.28: Extraction of metal ions from H_2SO_4 by 5% triisooctylamine in xylene. Those marked * are for 0.1% (Japan Atomic Energy Research Institute, 1964).

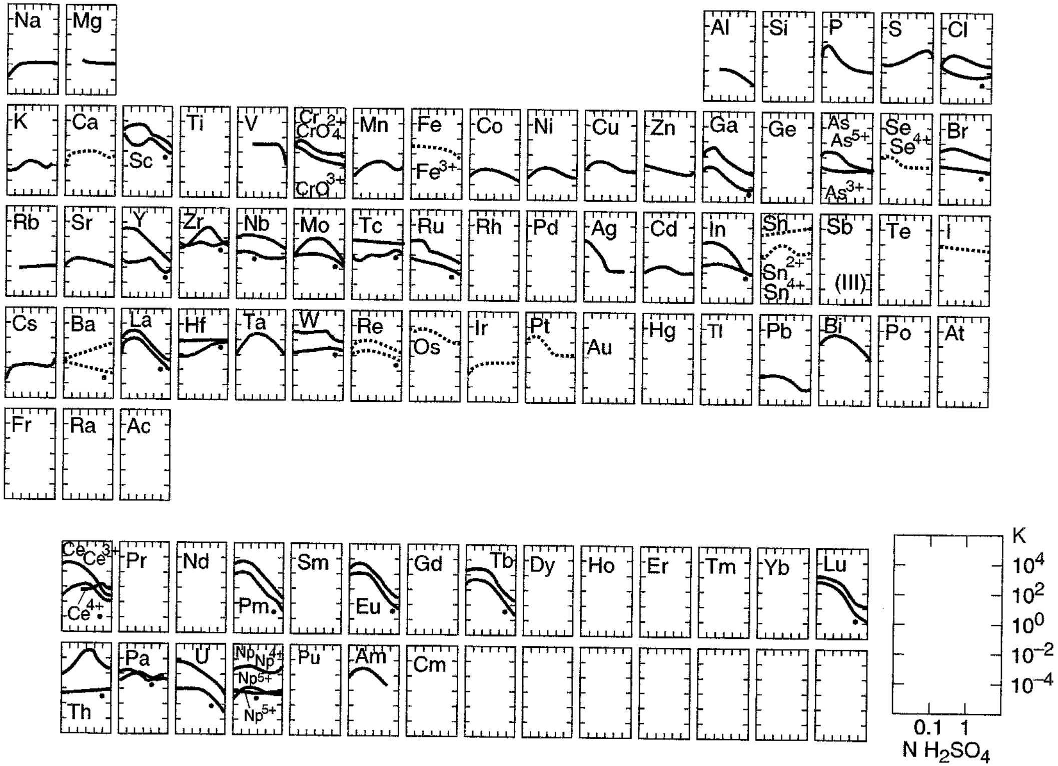
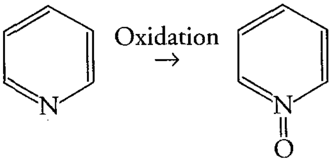


Figure 21.29: Extraction of metal ions from H_2SO_4 by 10% Primene JM-T in xylene. Those marked * are for 0.1% (Japan Atomic Energy Research Institute, 1964).

Pyridine oxides. Pyridine and its derivatives are tertiary amines from which pyridine oxides are prepared by oxidation with peracetic acid:



They are weak bases; typical members are 2-nonyl pyridine oxide and 4-(5-nonyl) pyridine oxide.

Organic sulfides and sulfoxides

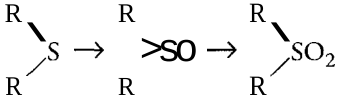
Organic sulfides are similar in structure to ethers whereby the oxygen in the ether is replaced by sulfur. Alkyl sulfides are prepared from alkyl halides and sodium sulfide:

$$2RX + Na_2S \rightarrow R_2S + 2NaX$$

They are important extractants for many metal ions. On the other hand, heterocyclic sulfur compounds found in petroleum distillation fractions are also valuable extractants. They are obtained during the purification of petroleum fraction by H_2SO_4.

Alkyl sulfides. Also known as thioethers, they have the structure R–S–R′, for example di-n-octyl sulfide is a selective extractant for palladium and gold. Extraction is slow taking several hours to reach equilibrium, so it must be operated as a batch process in stirred vessels.

Sulfoxides. These are derived from thioethers by controlled oxidation, otherwise sulfones are formed:



$$R_2S \rightarrow R_2SO \rightarrow R_2SO_2$$

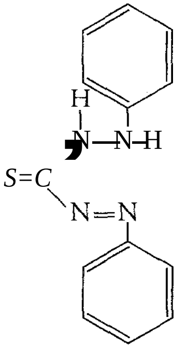
Dialkyl sulfides **Dialkyl sulfoxides** **Dialkyl** sulfones

Sulfoxides are extractants for a variety of metal ions; they are comparable to tributyl phosphate.

Other extractants

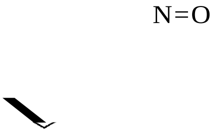
A few of the chelating agents that are used extensively in analytical chemistry and may be of potential metallurgical importance are the following:

- Dithizone

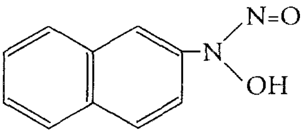


A violet black solid, insoluble in water and in dilute acids, slightly soluble in hydrocarbons, but readily soluble in chlorinated hydrocarbons.

- Cupferrons

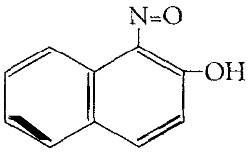


Phenylnitrosohydroxylamine
(Cupferron)

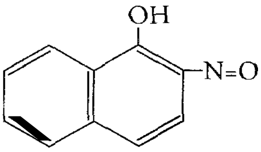


Naphthylnitrosohydroxylamine
(Neocupferron)

- Nitrosonaphthols



α-Nitroso-β-naphthol



β-Nitroso-α-naphthol

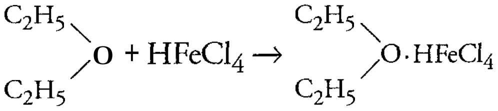
- Dyestuffs: alizarin, morin, etc.

MECHANISM OF EXTRACTION

The chemical process in which metal ions, or uncharged species in the aqueous phase, interact with the extractant forming an organometallic complex soluble in the organic phase takes place in one of the following ways:

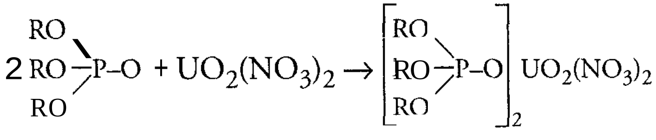
Ion pair transfer

In this case, electrically neutral molecules interact with the extractant to form an addition compound. The most suitable extractants for such interaction are those having an oxygen atom with a lone pair of electrons, e.g., ethers, alcohols, and the neutral phosphoric acid esters. For example, diethyl ether extracts iron from hydrochloric acid solution as follows:



$$(C_2H_5)_2O + HFeCl_4 \rightarrow (C_2H_5)_2O\cdot HFeCl_4$$

Tributyl phosphate extracts uranium from nitric acid solutions as follows:



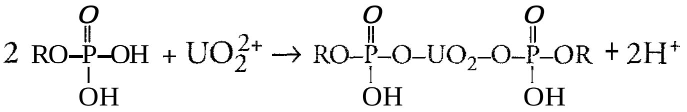
$$2\,(RO)_3P{-}O + UO_2(NO_3)_2 \rightarrow \left[(RO)_3P{-}O\right]_2\,UO_2(NO_3)_2$$

where R = C_4H_9. Because of the weak bonding between the metal species and the extractant, stripping is usually done with water.

Ion exchange

In this type, the metal is transferred from the aqueous phase as a simple ion, and at the same time an ion from the extractant is transferred stoichiometrically to the aqueous phase.

- *Cation exchange.* The extracted species is a positively charged ion and the extractant is an acid, e.g., monoalkylphosphoric acid, dialkylphosphoric acid, alkylpyrophosphoric acid, carboxylic acids, naphthenic acids, etc. For example, the extraction of uranium by a monoalkyl phosphoric acid takes place as follows:



$$2\ \mathrm{RO{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}OH} + \mathrm{UO_2^{2+}} \rightarrow \mathrm{RO{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}O{-}UO_2{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}OR} + 2\mathrm{H^+}$$

It can be seen that one uranyl ion is exchanged for two hydrogen ions. In stripping, the reaction is reversed by adding concentrated acid.

- *Anion exchange.* The extracted species is a negatively charged ion and the extractant is a base, e.g., an amine:

$$\mathrm{RNH_2 + HCl \rightarrow RNH_3^+Cl^-}$$

$$\mathrm{RNH_3^+Cl^- + A^- \rightarrow RNH_3^+A^- + Cl^-}$$

It can be seen that an anion A^- is stoichiometrically exchanged for another anion. Stripping of amines can be represented as follows:

– Displacement:

$$\mathrm{(R_3NH)_2UO_2(SO_4)_{2(o)} + 2NO_{3(a)}^- \rightleftharpoons 2R_3NHNO_{3(o)} + UO_{2(a)}^{2+} + 2SO_{4(a)}^{2-}}$$

– Hydrolysis and complexing whereby the free amine is liberated:

$$\mathrm{(R_3NH)_2UO_2(SO_4)_{2(o)} + 4CO_3^{2-} \rightleftharpoons 2R_3N_{(o)} + [UO_2(CO_3)_3]_{(a)}^{4-} + 2SO_4^{2-} + H_2O + CO_2}$$

– Precipitation:

$$\mathrm{2(R_3NH)_2UO_2(SO_4)_{2(o)}^{+} + 5MgO \rightleftharpoons 4R_3N_{(o)} + MgU_2O_{7(s)} + 4MgSO_4 + H_2O}$$

Chelation

In this type, an electrically neutral metal chelate[1] is formed which is insoluble in the aqueous phase but readily soluble in the diluent. For example, acetyl acetone in the enol form reacts with beryllium ion to give a chelate in which the beryllium replaces the enolic hydrogen

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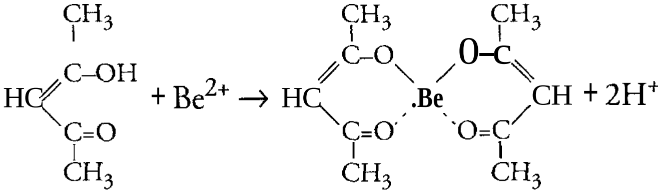
[1] When an organic molecule containing both acidic and basic functions combines with a metallic ion, and if in the combination both functional groups are operative, a so-called inner-complex or chelate salt is formed.

atom and is coordinately bound to the keto oxygen, forming a ring as follows:



Belonging to this group are the diketones, oximes, oxine, nitrosonaphthols, cupferrons, and dithizone. In stripping, the reaction is reversed by adding concentrated acid.

Extraction by mixed solvents

The extracting power of a mixture of solvents exceeds the sum of the extracting powers of the components. This phenomenon is called *synergism*[1], and was observed for a variety of solvent mixtures. For example:

- Dialkyl phosphoric acid, $(RO)_2POOH$, with neutral organophosphorus esters, such as $(RO)_3PO$, $(RO)_2HPO$, $(RO)H_2PO$, and R_3PO (R = n-butyl) (Figure 21.30).
- Alkyl phosphoric acids with alkyl amines.
- Tributyl phosphate and thenoyl trifluoro acetone (Figure 21.31)
- Mixtures of ethers (Figure 21.32).
- Mixtures of ketones, e.g., methyl isobutyl ketone and diisobutyl ketone.

In some cases, the individual solvents have no extracting power for a metal ion but the mixture does. Thus, neither thenoyl trifluoro acetone nor triisooctylamine in benzene can extract thorium from 2 M HCl, but a mixture of the two does. This effect is also dependent on the diluent.

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[1] Synergism is derived from Greek, συν = together, and εργο = to work, hence synergism means to work together.

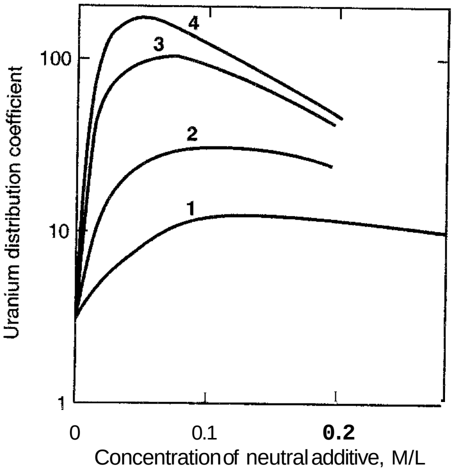


Figure 21.30: Effect of adding neutral organic phosphorus compounds to D2EHPA on the extraction of uranium from H_2SO_4 (Blake et al., 1958). (1) Tributyl phosphate, (2) Dibutyl butyl phosphonate, *(3)* Butyl dibutyl phosphinate, *(4)* Tributyl phosphine oxide.

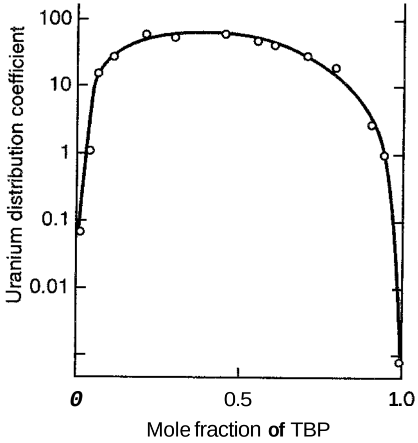


Figure 21.31: Extraction of uranium by mixed solvents TTA + TBP (Irving and Eddington, 1960).

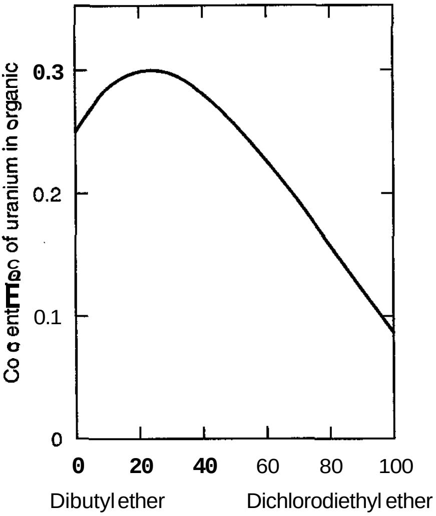


Figure 21.32: Extraction of uranyl nitrate by a mixture of dibutyl ether and ββ′-dichlorodiethyl ether in benzene (Vdovenko and Kirovkhatskii, 1960).

In extraction by mixed ketones, there is interaction between the ketones themselves, showing positive deviation from Raoult's law. Thus, the maximum observed on the vapor pressure curves due to molecular interaction coindices with the synergic behavior during extraction with the mixed solvent. In extraction with a mixture of an acidic (or a chelating) and a non-acidic solvent, the situation is more complicated. It was shown, by means of infrared measurements, that there was no interaction between thenoyltrifluoroacetone and the neutral phosphate ester tributylphosphate when mixed together in the absence of metal ions, but that there was a definite interaction in the mixed metal complexes.

If the acidic solvent is denoted by HX, where H is an acidic group, and the neutral solvent by B, then three mechanisms are possible for explaining this effect, e.g., for the extraction of uranyl nitrate.

- *Addition mechanism.* The acidic solvent forms uncharged chelate with the metal ion which is more easily extracted by the neutral solvent than other uncharged complexes of the metal ion. This can be represented as follows:

  $$UO_2^{2+} + 4HX \rightarrow UO_2X_2(HX)_2 + 2H^+$$

$$UO_2X_2(HX)_2 + B \rightarrow UO_2X_2(HX)_2 \cdot B$$

The complex $UO_2X_2(HX)_2$ is more easily extracted by B than the neutral species, $UO_2(NO_3)_2$. The above equation takes in consideration the fact that the solvent HA exists as dimer in the organic phase.

- *Substitution mechanism.* In this mechanism, it is assumed that the neutral solvent liberates free molecules of the other solvent from the extracted species, thus:

  $$UO_2^{2+} + 4HX \rightarrow UO_2X_2(HX)_2 + 2H^+$$

  $$UO_2X_2(HX)_2 + 2B \rightarrow UO_2X_2B_2 + 2HX$$

  This liberated solvent now can extract more ions from solution.

- *Solvation mechanism.* This mechanism takes into account the water molecules transported to the organic phase during extraction with the acidic solvent. It is assumed that the neutral solvent has the capacity to displace this water, thus rendering the extracted species less hydrated, i.e., more readily extracted:

  $$[UO_2^{2+}(H_2O)_x] + 4HX \rightarrow UO_2(H_2O)_xX_2(HX)_2 + 2H^+$$

  $$UO_2(H_2O)_xX_2(HX)_2 + yB \rightarrow UO_2X_2(HX)_2 \cdot yB + xH_2O$$

The reverse of synergism, i.e., *antisynergism,* or *antagonistic effect,* takes place under certain conditions. For example, the distribution ratio of uranium between tributyl phosphate and nitric acid decreased with the addition of benzoic, lauric, oleic, or stearic acids to the organic phase. This was attributed to the formation of a strong hydrogen bond between tributyl phosphate and the carboxylic acid as confirmed by infrared spectrometry. An antisynergic effect takes place in the extraction of inorganic salts when an amine such as tri-*n*-octylamine is mixed with a phosphoric acid ester such as di-n-butyl phosphoric acid.

Effect of temperature

Extraction by organic solvents is usually fast at room temperature, equilibrium being achieved within a few seconds. Few cases are known in which such process is slow, i.e., in the extraction of beryllium ion from H_2SO_4. Extraction of metal ions from aqueous solutions is a sllightly exothermic process. Consequently, the distribution ratio decreases with increasing temperature, but the rate of extraction increases with increasing temperature.

THE ORGANIC PHASE

As mentioned before, a certain weight of an extractant has a limited capacity for extracting a certain metal ion from solution. When this limit is reached, the extractant is then saturated with the metal ion and is said to have reached its maximum loading. Maximum loading varies widely from one extractant to the other. The organic phase increases in viscosity with increasing metal ion loading and sometimes it is necessary to operate at a solvent loading substantially below the maximum loading of the extractant. Saturation concentration can be determined by contacting the organic phase several times with fresh aliquots of the aqueous phase until the amount of metal in the organic phase becomes constant. For example, Table 21.15 shows saturation data for the extraction of thorium from sulfuric acid solution by di-(2-ethylhexyl) phosphoric acid at different pH values.

Table 21.15: Saturation of the organic phase in the extraction of thorium. Organic phase: *10* mL of di (2-ethylhexyl) phosphoric acid in kerosene; Aqueous phase: 10 mL of *0.1* M H_2SO_4 containing *2* g/L Th (Tedesco et al., *1966*).

pH	D2EHPA, M	Weight of D2EHPA in 10 ml, mM	Weight of Th extracted, mM	Molar ratio D2EHPA/Th
1.5	0.407	4.07	1.07	3.80
	0.207	2.07	0.54	3.83
	0.120	1.20	0.31	3.87
2.0	0.407	4.07	1.20	3.39
	0.207	2.07	0.64	3.23
	0.120	1.20	0.36	3.33
2.6	0.407	4.07	1.20	3.39
	0.207	2.07	0.65	3.18
	0.120	1.20	0.37	3.24
3.0	0.407	4.07	1.25	3.25
	0.207	2.07	0.59	3.57
	0.120	1.20	0.36	3.33

Nature of the extracted species

Usually, at the saturation concentration, the molecular ratio extractant: metal ion extracted is a whole number, as can be expected from a reaction of the type:

$$M^{n+} + nHX \rightleftharpoons MX_n + nH^+$$

where n is an integer. However, the simultaneous extraction of other species may cause deviation from a whole number. For example, data in Table 21.15 show that the ratio extractant: metal ion extracted at saturation is about 3.8 at pH 1.5 and about 3.3 at pH 2–3. This is due to the reactions:

$$Th^{4+} + 4HX \rightleftharpoons ThX_4 + 4H^+$$

$$ThO^{2+} + 2HX \rightleftharpoons ThOX_2 + 2H^+$$

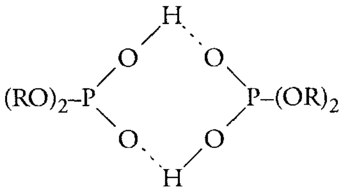
which occur simultaneously and are pH-dependent. According to the first reaction, the ratio is 4 and according to the second, it is only 2. Therefore, the value of the saturation concentration helps to throw light on the stoichiometry of the reaction and the nature of the extracted species.

The saturated organic phase so obtained can be studied in a variety of ways. The simplest way is by heating it at low temperature and under vacuum to evaporate both the diluent and the uncombined extractant. The residue obtained, which may be a liquid or a crystalline solid, is the extracted species, i.e., the compound between the metal and the extractant, which usually has a definite boiling or melting point. Table 21.16 shows some examples of compounds isolated during extraction processes. It can be seen that some of these compounds contain water of crystallization.

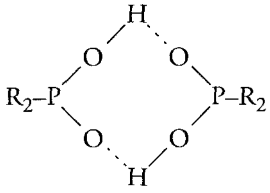
It should be pointed out that when micro amounts are extracted (trace concentrations), the extracted species may be different from those when macro amounts are extracted. For example, when trace concentrations of thorium were extracted from H_2SO_4 solutions by primary octylamine, the extracted species was $2(RNH_3)_2SO_4 \cdot Th(SO_4)_2$. When, however, macro amounts (0.0086–0.029 M) were extracted by the same solvent, the extracted compound, when separated from the organic phase, analyzed as $(RNH_3)_2 \cdot Th(SO_4)_2$. Infrared and nuclear magnetic resonance measurements are used extensively to identify the nature of the extracted species in the organic phase.

Polymerization of extractant

Some amines tend to associate in polar hydrocarbon diluents and remain in stable colloidal dispersion. Dialkylphosphoric acids and the dialkylphosphinic acids are often dimeric in the organic diluent, presumably by hydrogen bonding:



Dialkylphosphoric acid dimer



Dialkylphosphinic acid dimer

In the case of the monoalkylphosphoric acids, $ROPO_3H_2$, and the monoalkylphosphinic acids, RPO_3H_2, larger polymers have been found. Such polymerization directly affects cation exchange, since the hydrogen atoms are not free to react.

Role of diluents

The diluents themselves are unable to extract metal ions from the aqueous phase, but they greatly affect the extraction behavior of the solvent (Tables 21.17 and 21.18). The reason is the interaction that may take place between the diluent and the extractant. Further, some diluents favor the polymerization of the extractants while others do not. Calorimetric measurements usually give a good indication about such interaction. For example, it was found that mixing tributyl phosphate with heptane, nonane, and decane was accompanied by absorption of heat, while mixing with chloroform and carbon tetrachloride was accompanied by liberation of heat. The endothermic effect in the first case is due to the dissociation of TBP dimers in the hydrocarbon diluent, while the exothermic effect in the second case is due to the association of TBP with the chlorinated hydrocarbons to form

$CHCl_3 \cdot TBP$ and $CCl_4 \cdot 2TBP$. Such a bond considerably reduces the effective concentration of TBP in the organic phase, which is the cause for the low extraction capability of TBP solutions in chloroform and carbon tetrachloride.

Table 21.16: Examples of extracted species (Habashi, 1970).

System	Extracted species
Th^{4+}–H_2SO_4–octyl amine	$Th(SO_4)_2(RNH_3)_2$
Fe^{3+}–H_2SO_4–di(3,5,5-trimethylhexyl) amine	$FeOH(SO_4)_2(R_2NH_2)_2$
UO_2^{2+}–H_2SO_4–dioctylamine	$UO_2SO_4 \cdot 2(R_2NH_2)_2SO_4$
H_2PtCl_6–H_2SO_4–trioctylamine	$PtCl_6(R_3NH)_2$
UO_2^{2+}–H_2SO_4–trioctylamine	$UO_2SO_4 \cdot 2(R_3NH)_2SO_4$ $UO_2SO_4 \cdot 2(R_3NH)_2SO_4 \cdot 3H_2O$ $UO_2SO_4 \cdot 2(R_3NH)_2SO_4 \cdot nH_2O$
UO_2^{2+}–HNO_3–trioctylamine	$UO_2(NO_3)_3 \cdot R_3NH$ $UO_2(NO_3)_4 \cdot (R_3NH)_2$
UO_2^{2+}–HCl–trioctylamine	$UO_2Cl_4 \cdot (R_3NH)_2$
UO_2^{2+}–HNO_3–diethylether	$UO_2(NO_3)_2 \cdot 3H_2O \cdot (C_2H_5)_2O$ $UO_2(NO_3)_2 \cdot 2H_2O \cdot 2(C_2H_5)_2O$ $UO_2(NO_3)_2 \cdot 2H_2O \cdot 4(C_2H_5)_2O$
Cr(CI)–HCl–tributyl phosphate	$HCrO_3Cl \cdot 2TBP$
$La(NO_3)_3$–tributyl phosphate	$La(NO_3)_3 \cdot 3TBP$
Mo(IV)–HCl–tributyl phosphate	$MoO_2Cl_2 \cdot 2TBP$
Niobium fluoride–tributyl phosphate	$HNbF_6 \cdot 3TBP$
$NbCl_5$–HCl–tributyl phosphate	$HNbOCl_4 \cdot 3TBP$
Pt(IV)–HCl–tributyl phosphate	$HPtCl_5 \cdot 3TBP$ $HPtCl_5 \cdot 2TBP$
Tantalum fluoride–tributyl phosphate	$H_2TaF_7 \cdot 2TBP$
Uranous nitrate–tributylphosphate	$U(NO_3)_4 \cdot 2TBP$
Uranyl nitrate–tributylphosphate	$UO_2(NO_3)_2 \cdot 2TBP$
UCl_4–tributyl phosphate	$UCl_4 \cdot 2TBP$ $UCl_4 \cdot 3TBP$
V(V)–HCl–tributyl phosphate	$HVO_2Cl_2 \cdot 2TBP$
W(VI)–HCl–tributyl phosphate	$WO_2Cl_2 \cdot 2TBP$

Correlation between the effect of a diluent and its dielectric constant is sometimes feasible. In extraction by cation exchange mechanism, the diluents having the least dielectric constant, e.g., kerosene and CCl_4, lead to the best extractions (Table 21.17). This is because such diluents do not favor polymerization of the extractant in the organic phase through hydrogen bridges. The effect of diluent on amines is complex (Table 21.18) since some amines tend to polymerize, while others do not polymerize in the same organic phase, depending on the structure of the amine.

Table **21.17:** Effect of diluent on the extraction of uranium from sulfate system by D2EHPA (Blake et al., 1958).

	Dielectric constant	Distribution ratio
Kerosene	2.0	135
Carbon tetrachloride	2.2	17
Benzene	2.3	13
Chloroform	4.8	3
2-Ethvlhexanol	≈ 10	0.1

Table 21.18: Effect of diluents on the extraction of uranium from sulfate system by different amines (Coleman et al., 1958).

	Dielectric constant	Distribution ratio		
		Primene JM-T	Amine *S-24*	Tri-n-octylamine
Kerosene	2.0	3	110	30
Benzene	***2.3***	10	***20***	**150**
Chlofororm	4.8	90	***2***	***5***

Effect of extractant concentration

The distribution coefficient increases with increasing concentration of the extractant in the organic phase. When $\log D$ is plotted against the logarithm of extractant concentration, a straight line is obtained (Figures 21.33 to 21.35). This linearity can be interpreted **as** :follows:

$$MY_{(a)} + nX_{(o)} \rightleftharpoons MY \cdot nX_{(o)}$$

$$K = \frac{[MY \cdot nX]}{[MY][X]^n} = \frac{D}{[X]^n}$$

$$D = K[X]^n$$

$$\log D = n \log[X] + \text{constant}$$

This is an equation of a straight line with slope *n*.

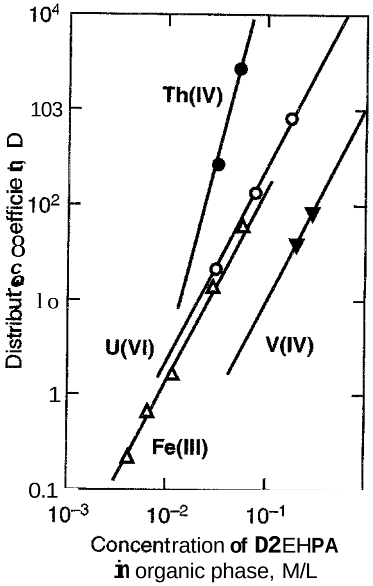


Figure 21.33: Metal extraction from 0.5 M sulfate solutions with D2EHP in kerosene; aqueous pH = 1 (Blake et al., 1958).

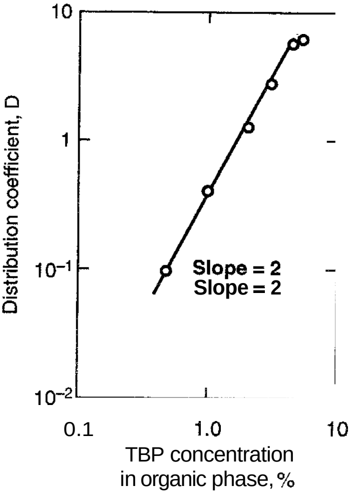


Figure 21.34: Extraction of uranyl nitrate by TBP in kerosene (McKay, 1956).

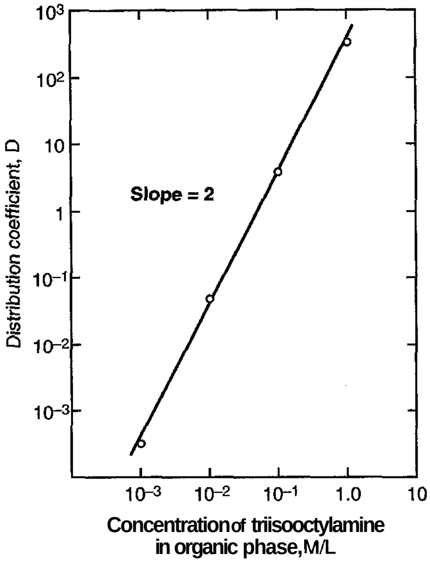


Figure 21.35: Distribution of ^{60}Co between triisooctylamine chloride and aqueous phase as a function of amine concentration (Brooks and Rosenbaum, 1963).

Third-phase formation

Some amines, particularly the tertiary, when in contact with mineral acids, form salts which are insoluble in the organic phase, thus a third-phase — liquid or solid — is formed during extraction. Third-phase formation also depends on the diluent. For example, in the extraction of HNO_3 by methyl dioctylamine, a third phase was formed when the amine was diluted with hexane, pentane, isopentane, and cyclohexane, and no third phase was formed when the amine was (dilutedwith benzene, nitrobenzene, $CHCl_3$, and CCl_4. The addition of a long-chain alcohol such as n-decanol overcomes this difficulty.

The amount of decanol required to prevent the third-phase formation can be determined in the following way: After equilibrating the organic phase with the aqueous phase and allowing it to settle, the two organic phases are separated and titrated with the alcohol till a single phase is formed. Usually, about 3% alcohol is sufficient to prevent third-phase formation.

THE AQUEOUS PHASE

Effect of metal ion concentration

For the process:

$$MY_{(a)} + nX_{(o)} \rightleftharpoons MY \cdot nX_{(o)}$$

it was shown that:

$$D = K[X]^n$$

where [X] is the concentration of free extractant at equilibrium. But:

$$[X] = [S] - [MY \cdot nX]$$

where [S] is the total concentration of extractant, and $[MY \cdot nX]$ is the concentration of the extractant bound to the metal species. This latter concentration increases with increasing metal ion concentration in the aqueous phase. Therefore, [X] and consequently D should decrease with increasing metal ion concentration in the aqueous phase. This has been verified experimentally [Table 21.19).

Table 21.19: Distribution of uranyl nitrate between 2 M HNO_3 and 40% vol. TBP in kerosene (Goldschmidt et al., 1956).

$[UO_2(NO_3)_2]$, mol/L	D
0.04	5.7
0.21	2.6
1.68	0.4

Effect of foreign ions

In ion-pair transfer, the addition of non-extractable electrolytes to the aqueous phase greatly enhances the extraction of the metal ion in question. For example, the addition of ammonium, aluminum, or calcium nitrates to nitric acid solutions containing uranium greatly enhances the extraction of uranium by ether, as shown in Figure 21.36. These electrolytes are called *salting-out agents,* and they act mainly in suppressing the dissociation of the extractable species.

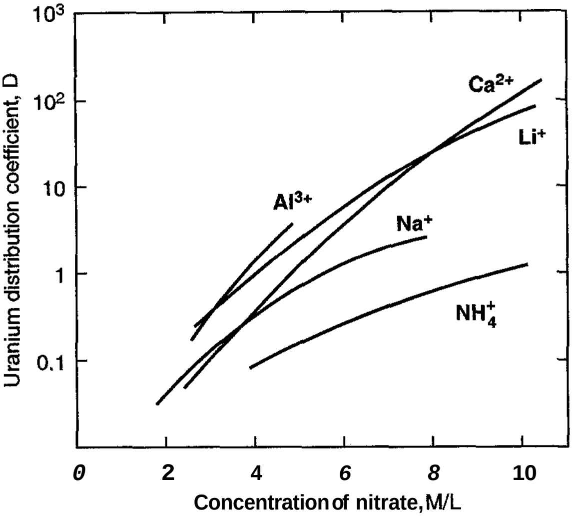


Figure 21.36: Extraction of uranyl nitrate by ethyl ether using various salting-out agents (Furman et al., 1950).

In extraction by an ion exchange mechanism, the addition of electrolytes has an opposite effect. Foreign ions in solution will compete with the exchangeable ions of the extractant and therefore reduce the distribution ratio. For example, in the extraction of uranium from sulfate medium by tri-n-octylamine, D decreases with increasing concentration of foreign anions, as shown in Figure 21.37 (anion exchange). In the extraction of uranium from sulfate medium by octylphosphoric acid, D decreases with increasing concentration of foreign cations, e.g., Fe^{3+}, as shown in Figure 21.38 (cation exchange).

Complex formation in the aqueous phase

Highly charged metal ions are usually complexed in the aqueous 'phase:

Metal ion + Complexing agent ⇄ Metal complex

'The complex may be electrically neutral, anionic, or cationic. If it is 'electrically neutral, then extraction by ion-pair transfer is favored. If it is electrically charged (positive or negative), then extraction by ion exchange mechanism (cationic or anionic, respectively) is favored. Complexing agents such as ethylene diamine tetraacetic acid, EDTA, or ammonium thiocyanate are often added to the aqueous phase to facilitate extraction or separation of metal ions. For example, hafnium is extracted selectively by hexone from a hydrochloric acid solution containing both zirconium and hafnium to which ammonium thiocyanate has been added. On the other hand, the presence of PO_4^{3-} ions in the aqueous phase hinders the extraction of uranium by tributyl phosphate, due to the strong complexing action of phosphate ion. Both processes are ion-pair transfer. In the first case, hafnium forms a stable, uncharged complex with ammonium thiocyanate, and is therefore easily extracted, while in the second case, phosphate ion forms a charged complex which cannot be extracted by TBP.

Figure 21.39 shows the effect of HNO_3 concentration on the extraction of uranium by TBP. It is seen that below 5 M HNO_3, the extraction is favored due to the salting-out effect, but above 5 M HNO_3, the value of D decreases for two reasons:

- HNO_3 itself is also extracted, thus competing with metal ion transfer to the organic phase.
- Great excess of nitrate concentrations promotes the formation of unextractable anions such as $[UO_2(NO_3)_3]^-$.

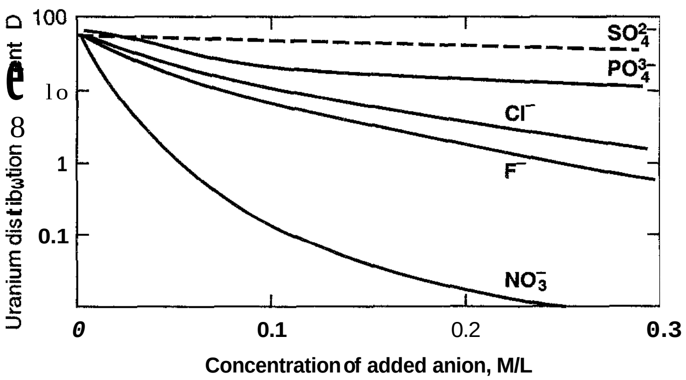


Figure 21.37: Effect of added anions on uranium extraction from sulfate solution by 0.1M tri-n-octylamine-Amsco D-95; aqueous phase 1 M SO_4, pH 1 (Coleman et al., 1958).

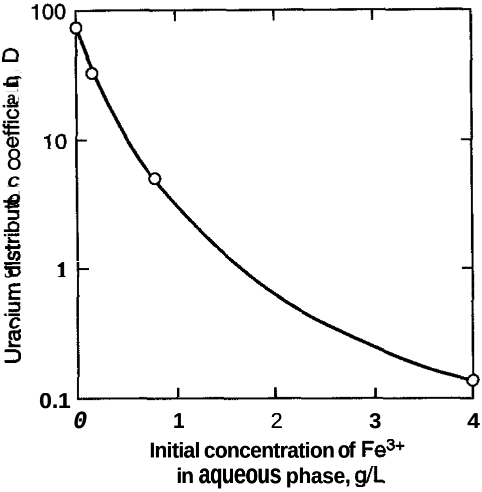


Figure 21.38: Effect of Fe^{3+} on the extraction of uranium from sulfate solution by OPA (Ellis et al., 1955).

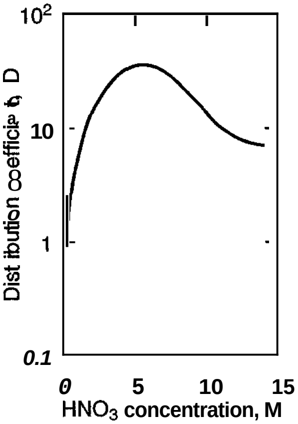


Figure 21.39: Extraction of uranium from HNO_3 solution by 19% TBP in kerosene (Alcock et al., 1958).

In the extraction of uranium from H_3PO_4 solutions by OPPA, the value of D decreases with increasing H_3PO_4: the reason is that the process involves cation exchange and, at high H_3PO_4 concentrations, uranium is complexed in the aqueous phase as uncharged species which cannot be extracted by a cationic reagent. An example of extraction by anion exchange mechanism showing the effect of various acids is given in Figure 21.40. Numerous data are now available in form of periodic tables showing the extraction of metal ions by different extractants.

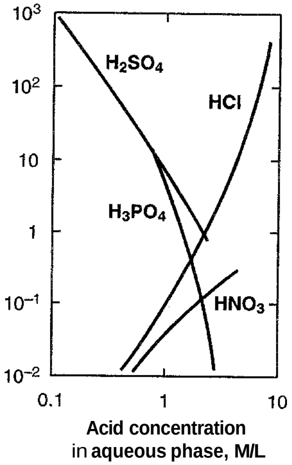


Figure 21.40: Uranium extraction by 0.1M tri-n-octylamine in Amsco D-95 (Coleman et al., 1958).

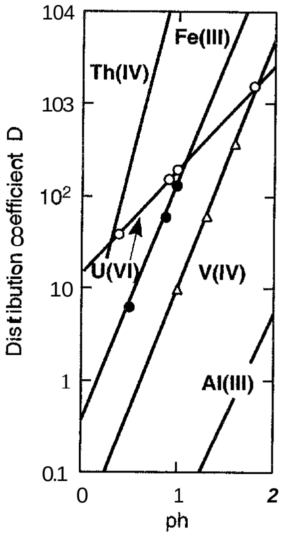


Figure 21.41: Metal extractions from 0.5M sulfate solutions with 0.1M D2EHPA in kerosene (Blake et al., 1958).

Effect of pH

Extraction by cationic solvents is greatly affected by the pH of the aqueous phase (Figure 21.41) since H^+ ions are taking part in the process:

$$M^{2+} + H_2X \rightleftharpoons MX + 2H^+$$

Decreasing the hydrogen ion concentration, i.e., increasing the pH, shifts the equilibrium from left to right thus favoring the extraction. In many other cases, the variation of distribution coefficient with pH may be due to the effect of the latter on the stability of the complexes in the aqueous phase, as previously mentioned — for example, the extraction of uranyl ion from sulfate solutions by amines (Figure 21.42).

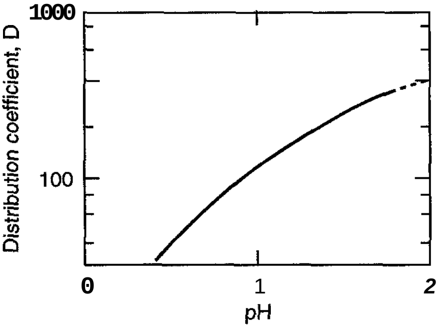


Figure *21.42:* Effect of the pH on the extraction of uranium(VI) from sulfate solution by tri-n-octylamine (Coleman et al., 1958).

:Effect of ion hydration

It is reasonable to expect that strong hydration of an ion reduces its extractability into an organic phase. This has been verified in a number of cases. For example, Figure 21.43 shows the extraction of the alkali metals with 4-*sec*-butyl-2(α-methyl benzyl) phenol. The distribution coefficient decreases in the order Na c K < Rb < cs, which is the reverse order of increasing ion hydration. Sodium, ion, being the highest hydrated ion in this series, has the lowest distribution coefficient. Also, in the extraction of lanthanides by tributyl phosphate and by ketones from nitric acid solution, the distribution coefficient was found to increase with increasing atomic numbers.

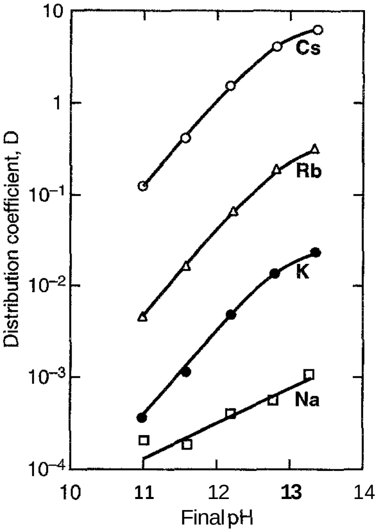


Figure 21.43: Effect of ion hydration; extraction of the alkali metals by 4-*sec*-butyl-2(α-menthylbenzyl) phenol (Arnold et al., 1965).

However, this assumption does not appear to be valid in all cases. Thus, it was found that the distribution coefficient for the extraction of the alkaline earth nitrates by di-(2-ethylhexyl) phosphate decreases in the order Ba < Sr < Ca < Be. Beryllium, being the most hydrated ion in this series, has, nevertheless, the highest distribution coefficient. The reason is that the factors which determine selectivity in extraction are many and they may interact in a very complex way. The characteristics that lead to a strong hydration may also lead to strong coordination with an organic phase extractant, so that the net effect is difficult to predict. Thus, for example, it was found that the distribution coefficient in the extraction of the alkali metals by carboxylic acids goes through a maximum at potassium.

Extraction of inorganic acids

During the extraction of metal ions by organic solvents, it is found that most inorganic acids are extracted as well. Since metal ion extraction is usually carried our from acid solution, it is important to consider in some detail the extraction of acids. Not only so, but there is interest at present to utilize this property to purifying acids by extraction with organic solvents. For example, phosphoric acid obtained from phosphate rock by leaching with acid can be extracted by an organic solvent to get pure H_3PO_4, suitable for purposes other than for making fertilizers. Also, extraction of acids by organic solvents finds wide application in the recovery of acids from plating electrolytes and pickle solutions.

Sulfuric acid is not extracted by ketones, ethers, or esters, but is extracted by alcohols. Hydrochloric acid is poorly extracted by ethers and only slightly extracted by alcohols, while nitric acid is extracted. Amines and organic phosphorus compounds also have the capacity to extract acids.

Extraction of acids depends also on the nature of the diluent, as shown in Table *21.20.* It is influenced too by the presence of extractable metal ions in the aqueous phase. Thus, the distribution of nitric acid between an aqueous phase containing uranyl ion and tributyl phosphate decreases with increasing uranyl ion concentration, which is also extracted by TBP, as shown in Figure *21.44.* Synergic effect was also observed when extracting an acid by mixed solvents, as shown in Figure *21.45.*

'**Table 21.20:** Effect of diluents on the extraction of inorganic acids by 0.1 M Alamine 336 (Ager et al., 1965).

Acid	% extraction into:		
	Kerosene	Benzene	Chloroform
HNO_3	90.0	97.6	99.0
HBr	82.8	95.2	98.5
HCI	66.0	85.2	84.8
H_2SO_4	51.1	86.8	92.3
H_3PO_4	0.7	25.3	64.4

Complexes are also formed between the extractant and the acid in the extraction process. For example, the extraction of nitric acid by tributyl phosphate can be represented by:

$$HNO_{3(a)} + TBP_{(o)} \rightleftharpoons HNO_3 \cdot TBP_{(o)}$$

$$K = \frac{[HNO_3 \cdot TBP]_{(o)}}{[HNO_3]_{(a)} \cdot [TBP]_{(o)}} = D \cdot \frac{1}{[TBP]_{(o)}}$$

$$D = K \times [TBP]_{(o)}$$

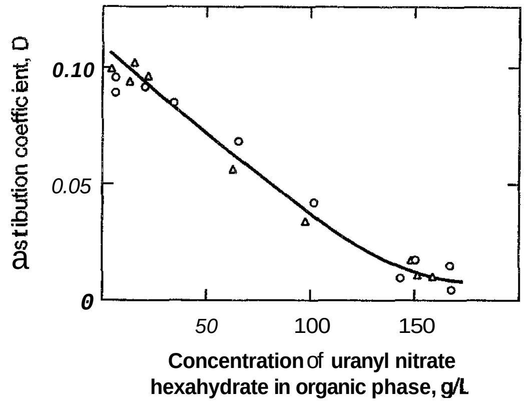


Figure 21.44: Effect of uranyl ion on the extraction of nitric acid by TBP; ○ 2.5M HNO_3; △ 5.0M HNO_3.

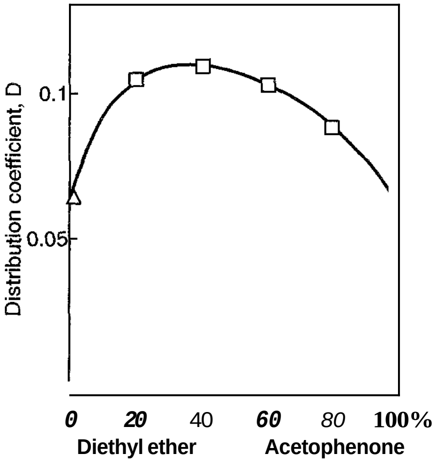


Figure 21.45: Extraction of nitric acid by diethylether acetophenone mixtures (Vdovenko and Krivokhatchii, 1960).

Plotting D against $[\text{TBP}]_{(o)}$ gives a straight line, as shown in Figure 21.46, thus supporting the above mechanism. Table 21.21 gives selected data on the type of extracted species.

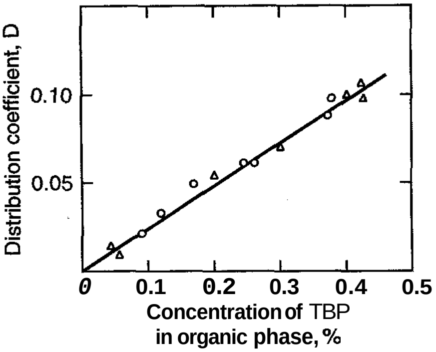


Figure 21.46: Effect of TBP concentration on the extraction of HNO_3 from the aqueous phase (Moore, 1951); **O** 2.5 M HNO_3; **A** 5.0 M HNO_3.

Table 21.21: Species extracted by organic phase (Habashi, 1970).

System	Species
HCl–TBP	HCl·TBP
HNO_3–TBP	HNO_3·TBP
H_2SO_4–TBP	H_2SO_4·TBP
$HClO_4$–TBP	$HClO_4$·TBP
HF–TBP	HF·TBP
H_3BO_3–TBP	H_3BO_3·TBP
H_3PO_4–TOA	H_2PO_4·TOAH
	HPO_4·$(TOAH)_2$
HNO_3–EHPA	HNO_3·EHPA
HCl–EHPA	HCl·2EHPA
$HClO_4$–EHPA	$HClO_4$·2EHPA

:Extraction of water

During extraction processes, water is usually coextracted. Figure 21.47 shows the water content of tributyl phosphate when contacted with different mineral acids. Water content in the organic phase is usually determined by titration with the Karl-Fischer reagent. There appear to be no rules to predict the extractability of water (Figures 21.48 and 21.49). While water is coextracted with uranyl perchlorate by tributyl phosphate, this is not the case with uranyl nitrate (Figure 21.48). Extraction of water results in changes in volumes of the organic and aqueous phases.

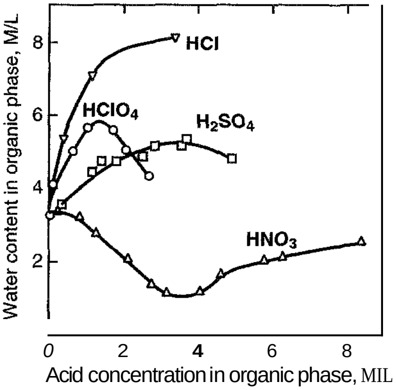


Figure 21.47: Coextraction of water by TBP from acid medium (Hesford and McKay, 1960).

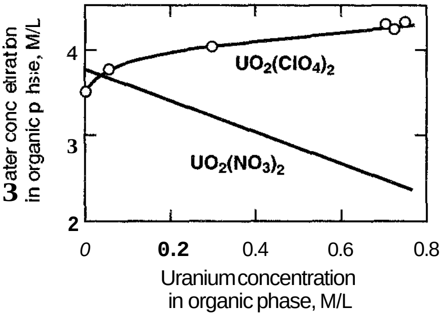


Figure *21.48:* Water content of organic phase after extraction of uranyl nitrate and uranyl perchlorate solutions with tributyl phosphate (Hesford and McKay, 1960).

APPLICATIONS

Solvent extraction is used extensively in the following fields:

- Recovery of a metal from a leach solution.
- Separation of two or more closely related metals.
- Purification of a leach solution, i.e., removal of unwanted impurity such as iron.
- Production of pure acids, e.g., H_3PO_4.
- Treatment of electroplating effluents, e.g., chromium electroplating bath.
- Regeneration of pickle solutions.

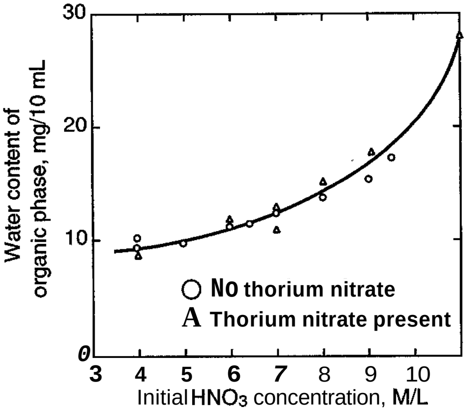


Figure 21.49: Extraction of water during the equilibrium of HNO_3 solutions with tri-n-octylamine (Verstegen, 1964).

- Reprocessing of nuclear fuel element.

Recovery

Numerous metals are extracted on industrial scale by organic solvents; some details are given below.

Beryllium

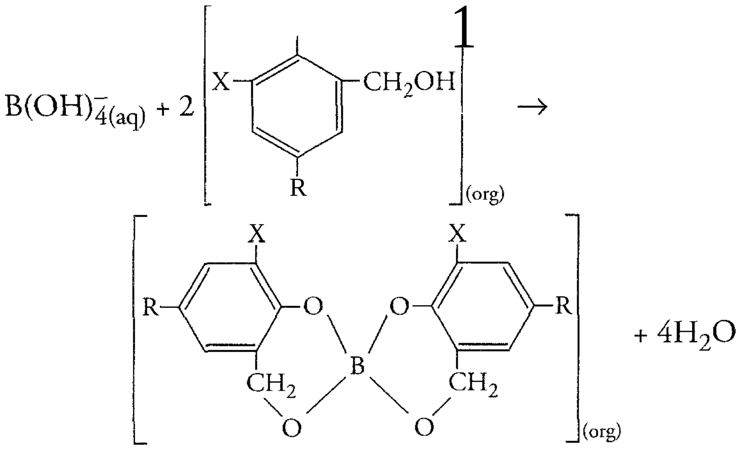
The extraction of beryllium with amines and organophosphorus compounds from sulfuric acid solutions has been studied by a number of investigators. A characteristic of the phosphoric acid extractant is its low beryllium extraction rate, necessitating long contact times. Tri-iso-octylamine, as well as other tertiary, secondary, and quaternary ones, are unable to extract beryllium from sulfuric acid leach solutions. However, primary amines, especially 1-(3-ethylpentyl)-4-ethyloctylamine, can extract beryllium rapidly from sulfate solutions.

With both amines and organophosphorus compounds, fluoride ion greatly decreases the extractability of beryllium. Iron is coextracted when present as Fe(III) ion, but not as Fe(II). Aluminum, the major impurity in leach solutions, is also coextracted to a lesser degree. To minimize the contamination of aluminum, several suggestions have been made:

- Fluoride ion interferes with beryllium extraction from pure solutions by primary amines, but its presence in solutions containing aluminum is desirable, since it complexes the aluminum in the aqueous phase and thereby reduces aluminum competition for the amine extractant. To improve the purity of beryllium, the addition of fluoride in amounts equivalent to the aluminum was therefore suggested.
- Prior to the extraction of beryllium from sulfuric acid leach solution by organophosphorus compounds, it was suggested to add ethylenediamine tetraacetic acid to complex all the impurities.
- In the extraction of beryllium from sulfuric acid solutions by organophosphorus compounds, it was suggested to strip the organic phase with 9 M H_2SO_4. Under these conditions, beryllium is precipitated as $BeSO_4 \cdot 2H_2O$ while aluminum remains in solution.

Boron

A process was developed for the recovery of borax from Searles Lake, California, by solvent extraction. The brine contains about 1% borate and 35% other dissolved salts (sodium, potassium, chloride, and sulfate). Extraction is carried out from the alkaline brines by polyols dissolved in kerosene:



Boron is stripped from the organic phase by dilute sulfuric acid. The strip solution is passed over activated charcoal to remove traces of entrained organic phase. On evaporation of the purified strip solution, boric acid crystallizes out and can be separated by centrifugation and then dried to yield a product containing 99.9% H_3BO_3, 0.05% SO_4, and 0.1% Na. The mother liquor from the crystallization step is evaporated further to crystallize and recover mixed sulfates of sodium and potassium.

Cesium

A process based on the use of a substituted phenol was developed for the extraction of cesium from pollucite ore. The extractant is 4-*sec*-butyl-2-(α-methyl benzyl) phenol, highly selective for cesium. Since the phenol can be used only in alkaline medium, the pollucite ore is opened by roasting with sodium carbonate, and it is then leached with water. The process was originally developed for extracting radioactive cesium from reactor waste solutions.

Copper

The recovery of copper from dump leaching solutions containing around 1 g/L Cu is usually achieved by displacing the copper ion by scrap iron — the cementation process. The cost of precipitation by this method is still high despite increased mechanization and better control techniques. Also, the process suffers from the introduction of ferrous ion in the solutions which are to be recycled in the dumps. Precipitated copper still has to be processed further to yield a marketable product. It is not a particularly attractive material for handling because of its fineness and the difficulty of washing it free from acid. Solvent extraction with subsequent hydrogen reduction under pressure or electrodeposition of a marketable product offers a convenient method of recovery. There is the added advantage that acid is liberated in the recovery step and can therefore be used as a stripping solution in the extraction process. The extractant commonly used is LIX-64 (see page 465). Figure 21.50 shows a scheme of copper recovery by dump leaching, solvent extraction, and electrowinning.

Indium

Indium is extracted on industrial scale from zinc sulfate leach solutions by di (2-ethylhexyl) phosphoric acid.

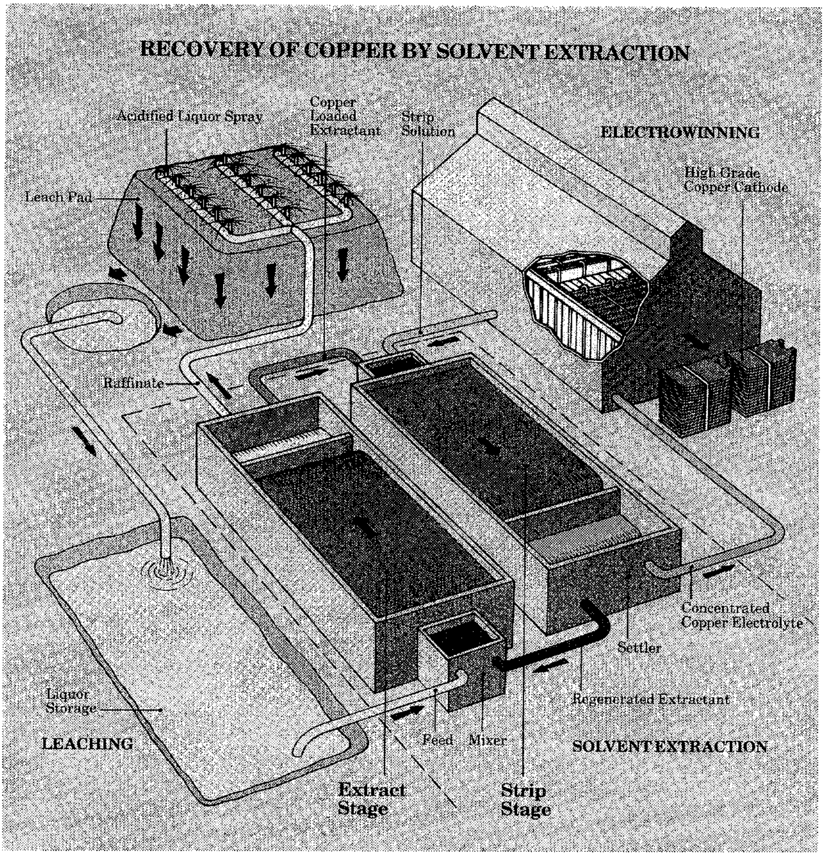


Figure 21.50: The recovery of copper from low-grade ores by leaching–solvent extraction–electrowinning; a widely used **pro**-cess.

Rhenium

Rhenium is recovered by VEB Mansfeld Kombinat in Germany from dusts collected in the copper smelter. The dust is dissolved in dilute acid at pH 3; it has the analysis shown in Table 21.22. Rhenium is extracted by an organic phase containing 1% secondary aliphatic amine, 30% aliphatic alcohol, and 65% aliphatic hydrocarbon. Organic/aqueous phase 1/10. The organic phase is washed with 0.01 M NH_4OH solution, then stripped by 2–4 M NH_4OH, organic/aqueous 10/1 to get a solution containing *4–8* g/L Re from which ammonium perrhenate 95–97% obtained.

Table 21.22: Analysis of rhenium-containing solution.

	g/L
Re	0.03–0.08
Zn	8–12
Cd	1–2
Tl	0.05–0.15
As	0.02–0.05
Cl	8–12
Sulfur as SO_4^{2-}	4–6

Thorium

Thorium is recovered on a commercial scale as a by-product of uranium ore processing by extraction with an organic phosphorus compound. The effluent from the ion exchange columns is processed for thorium recovery. Thorium is also recovered by dissolving the thorium-rich precipitate, obtained from monazite sand leach solution, in nitric acid and then extracting the thorium with tributyl phosphate, the rare earths are left behind since their distribution coefficient is very low as compared to that of thorium.

Tungsten

The recovery of tungsten from wolframite concentrate by extraction with amines is applied on a commercial scale. The concentrate is digested with NaOH solution, and filtered to remove the gangue; the leach solution is acidified with H_2SO_4 to the proper pH; then tungsten is extracted with the amine. Stripping is affected by NH_4Cl + NH_4OH solution to yield a solution of ammonium tungstate. The main impurity in the leach solution is usually molybdenum and it is coextracted with tungsten by amines and is also co-stripped. Removal of most of the molybdenum is affected by evaporating the strip solution to crystallize relatively pure ammonium tungstate.

Uranium

The application of solvent extraction to the uranium industry is one of the most important fields in this technology. Uranium is generally extracted industrially from the following solutions:

Sulfuric acid. These are the leach solutions of uranium ores. The most commonly used processes are the following:

- *Dapex Process.* 3–5% D2EHP in kerosene and about the same concentration TBP (synergic effect). Stripping by 10% Na_2CO_3. Uranium is recovered from strip solution by precipitation with NaOH to obtain the yellow cake.
- *DDPA Process.* 0.1 M solution of DDPA in kerosene. Stripping by 10 M HCl. Strip solution is evaporated to recover HCl, then uranium is precipitated by NH_4OH to obtain the yellow cake.
- *Amex Process.* Secondary or tertiary lauryl amines are used as extractants. Stripping by dilute NaCl solution. Molybdenum is coextracted with uranium but is not stripped from the amine during uranium stripping. Sodium carbonate or ammonia strips molybdenum and prevents its buildup in the organic phase.

Nitric acid. This acid is mainly used to get a high-purity uranium suitable for nuclear reactors:

- Sodium or ammonium uranate (yellow cake) obtained by processing the strip solutions of the above processes are dissolved in HNO_3, then extracted by TBP.
- When uranium is recovered by ion exchange and the resin is eluted by nitrate–nitric acid solution, the eluate is treated with lime to pH 3.5 to remove sulfate as gypsum and precipitate iron and thorium. Uranium can then be recovered from the solution by TBP. In these process, uranium is stripped by water: Pure uranyl nitrate solution is obtained, which on evaporation and decomposition yields a high-grade UO_3 (orange cake).

Phosphoric acid. Wet process H_3PO_4 obtained by dissolving sedimentary phosphate rock in H_2SO_4 contains about 1 g/L uranium which is recovered as a by-product of the fertilizer industry (see page 347). At least three extraction processes are used commercially:

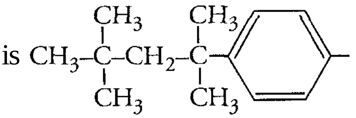
- *OPPA Process.* The extractant octyl pyrophosphoric acid extracts uranium in the tetravalent state; therefore, a reducing agent, usually metallic iron, is added to the acid to reduce its uranium content. Uranium is stripped from the solvent by concentrated hydrofluoric acid, yielding UF_4.
- *D2EHPA Process.* The extractant di(2-ethylhexyl) phosphoric acid is used in conjunction with trioctyl phosphine oxide (TOPO) because the mixture exhibits a synergic effect. The mixture has also the advantage that it is stable and extracts uranium in the

hexavalent state. Uranium is stripped from the solvent by ammonium carbonate solution under conditions that result in the precipitation of ammonium uranyl tricarbonate.

- *OPhPO Process.* The extractant is a mixture of mono and dioctylphenyl phosphoric acids:

$$\mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}{-}OR} \qquad \mathrm{HO{-}\overset{\overset{O}{\|}}{\underset{\underset{OR}{|}}{P}}{-}OR}$$

where R is



The extractant is used in conjunction with tributyl phosphate (TBP) because of the synergic action of the mixture. It is cheap, stable, available commercially, and has a high extraction coefficient than the previous mixture. It is, however, effective for extracting uranium in the tetravalent state. Uranium is stripped from this solvent by ammonium carbonate solution.

Vanadium

The association of vanadium with uranium in many ores, and the ease with which a separation by solvent extraction could be accomplished, led to commercial application. Vanadium is extracted together with uranium by DDPA or HDPA. The addition of tri-alkylamine increases the extraction due to synergic effect. Vanadium is stripped first by 2 M HCl, and then uranium by 10 M HCl. The loaded extractant can also be stripped with Na_2CO_3 solution to give a concentrated solution of uranium and vanadium, from which uranium can be precipitated by NaOH, leaving a solution containing sodium vanadate.

During the treatment of bauxite by the Bayer Process, any vanadium in the ore goes into solution together with aluminum. However, it does not coprecipitate with $Al(OH)_3$. When the alkaline solution is concentrated by evaporation, vanadium fluorocomplexes are precipitated. These are filtered, dissolved in dilute acid, and processed for vanadium recovery. The process is used in Lauta, Germany. The solution has a pH 5 and has the analysis shown in Table 21.23. The organic phase is composed of a mixture of 10% secondary aliphatic amine, 30% alcohol, and 60% aliphatic hydrocarbon as a diluent. Organic aqueous phase 1/4. After washing the organic phase with 0.02 M NH_4OH at organic/aqueous phase 1/1, vanadium solution containing 30–35 g/L V_2O_5 from which ammonium metavanadate 97–98% is obtained.

Table 21.23: Analysis of vanadium-containing solution

	g/L
V_2O_5	5
P_2O_5	6–7
As	0.5
F	1.5–2
Na	12–15

Separation

An important application of solvent extraction is its use in separating a number of metals occuring together. This can usually be achieved by selecting the proper pH, adding a complexing agent in the aqueous phase, and above all choosing a solvent that shows more selectivity for one metal than for the other. For example, sulfuric acid leach solutions of monazite sand contain rare earths, thorium, and uranium. On examining the data shown in Table 21.24, it would be seen as possible to devise a method for separation based on extraction by amines. Other examples of metal separation are given below.

Cobalt–nickel

Numerous schemes have been worked out to separate cobalt from nickel and an extensive literature is available. Figure 21.11 shows the use of octyl alcohol in separating the two metals from HCl solution. Separation can also be achieved by using tertiary amines, i.e., tri-*iso*-octyl amine. This separation is based on the fact that cobalt forms an anionic complex, $[CoCl_4]^{4-}$, while nickel does not. Carboxylic acids are used, at the Nickel Refinery in Norilsk, Russia.

Table 21.24: Extraction of thorium, uranium, and lanthanides by amines.

	Thorium	Uranium	Rare earths
Primary amines	Very strong	Moderate	Moderate
Secondary amines			
Straight chain or			
branching far from N-atom	Strong	Moderate	Nil to weak
branching near N-atom	Weak	Strong	Nil
Tertiary amines	Nil	Strong	Nil

Hafnium–zirconium

The advantages of hafnium-free zirconium for nuclear reactors have resulted in the development and application of solvent extraction for the separation of the two metals on a commercial scale. Hexone is used to extract hafnium and some zirconium from a hydrochloric acid solution containing both metals, to which thiocyanic acid has been added. The organic phase is then stripped with HCI to remove zirconium, and then with H_2SO_4 to remove hafnium. Both metals are next recovered from their respective aqueous solutions by precipitation as hydroxides by ammonium hydroxide. The hydroxides are filtered, washed, and then ignited to the oxides.

Niobium-tantalum

Columbite ore containing 58% Nb_2O_5 and 17% Ta_2O_5 is digested with 70% hydrofluoric acid, and the leach solution is then diluted and mixed with H_2SO_4. Both metals are extracted simultaneously by hexone leaving the impurities behind. The organic phase is then stripped with water whereby all the niobium and only a small amount of tantalum is transferred to the aqueous phase. Removal of this tantalum is achieved by further contacting the strip solution with fresh hexone. The organic phase, containing pure tantalum, is then stripped with water. Niobium and tantalum hydroxides are precipitated from the respective raffinates by NH_4OH. Both hydroxides are filtered, washed, and calcined to the respective oxides. Niobium oxide so obtained contains less than 0.03% Ta_2O_5, and the tantalum oxide also contains a similar amount of Nb_2O_5.

Plutonium–uranium fission products

Reprocessing of spent nuclear fuel element has the following purposes:

- Recovery of plutonium which is produced in small amounts during uranium fission.
- Removal of fission products which are produced during the fission process and tend to absorb the neutrons thus hindering the chain reaction.
- Recovery of high-purity uranium suitable for recycle in a nuclear reactor.

Reprocessing by solvent extraction is based on dissolving the spent fuel element in nitric acid to get a solution containing about 1 part uranium, 0.003 parts plutonium, and 0.01 parts fission products. The following processes are used:

Purex Process. In this process, nitrous acid is added to the feed solution to reduce Pu(VI) to Pu(IV), which then together U(VI) is extracted by TBP. The bulk of the fission products remain in the aqueous phase. The organic phase is then stripped in the following sequence:

- HNO_3 to remove any fission products extracted.
- HNO_3 + Fe^{2+} to remove plutonium. Ferrous ion is added to reduce Pu(IV) to Pu(III), which has a very low affinity for the organic phase.
- Water to remove uranium.

Redox Process. In this process, U(VI) and Pu(VI) are extracted by hexone, while the bulk of the fission products remain in the aqueous phase. The organic phase is then stripped in the following sequence:

- Aluminum nitrate solution to remove any fission products extracted.
- HNO_3 + Fe^{2+} to remove plutonium.
- Dilute HNO_3 to remove uranium.

TTA Process. In this process, sodium nitrite is added to the feed solution to reduce plutonium to Pu(IV) which is then extracted by thenoyltrifluoroacetone in benzene. Zirconium is coextracted, but separation is readily achieved by selective stripping. Plutonium is stripped by an acid solution containing ferrous ion to reduce Pu(IV) to less extractable Pu(III), while zirconium is stripped by an oxalic acid–HNO_3 mixture. The raffinate containing uranium and the rare earths is then contacted with a TTA–hexone mixture to extract uranium selectively, leaving the rare earths behind.

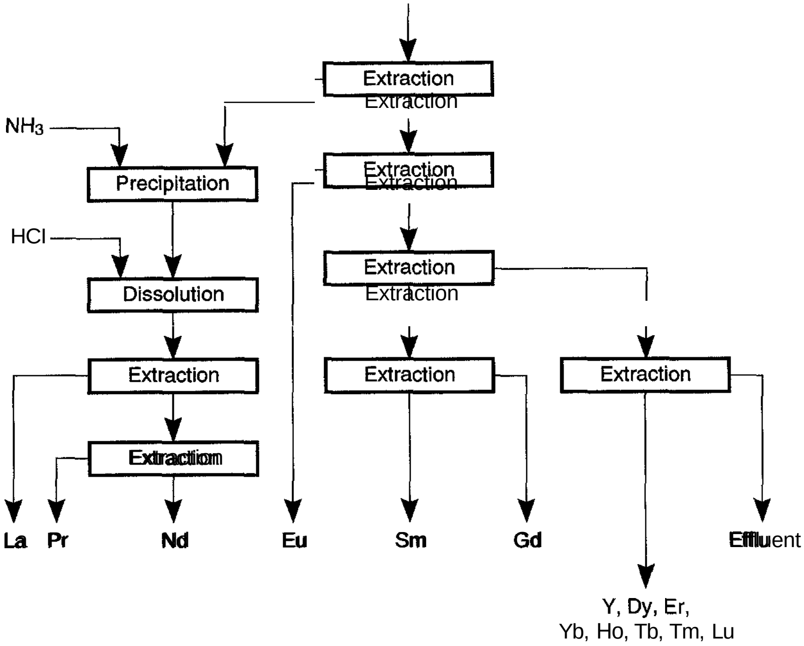


Figure 21.51: Separation of the lanthanides from bastnasite by extraction with D2EHPA (Molycorp Process).

Lanthanides

The scheme of separation of the lanthanides from leach solution of bastnasite concentrates by extraction with D2EHPA is shown in Figure 21.51. Cerium is already separated in the leaching step since it is transformed into soluble cerium(IV) compound and is recovered from the residue. Each extraction step in Figure 21.51 includes numerous stages of contact with the extractant and the stripping agent under certain conditions of organic/aqueous ratio, and extractant and stripping agent concentrations. The plant is computerized and is fully automated (Figure 21.52).

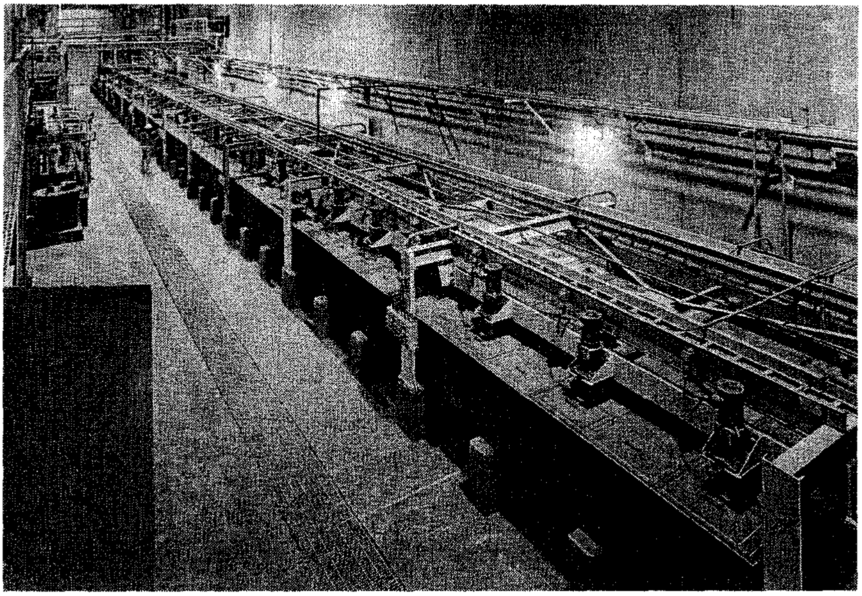


Figure 21.52: Inside of Molycorp's rare earths extraction plant at Mountain Pass, California.

Scandium–uranium

Small amounts of scandium are usually present in uranium ores and are dissolved during acid leaching, yielding up to 0.001 g/L Sc_2O_3. Scandium was found to follow uranium in an organic phase composed of dodecyl phosphoric acid and kerosene. However, it is not stripped with uranium in 10 M HCl. After several contacts of the extractant, scandium builds up into the organic phase and can be stripped with HF. A fluoride precipitate analyzing approximately 10% Sc_2O_3 and 20% ThO_2 is obtained. This is then purified by digestion in 15% NaOH to convert it into hydroxides, and then digested with hydrochloric acid, the pH being adjusted to 4 to remove Ti, Zr, Fe, and SiO_2. Scandium is recovered from the solution by precipitation with oxalic acid. The oxalate is calcined and the oxide is further purified by dissolution in HCl and solvent extraction.

In Australia, uranium is recovered from the leach solution by ion exchange. Scandium, yttrium, thorium, and the rare earths are not sorbed on the column and are therefore found in the effluent. A process using di-(2-ethylhexyl) phosphoric acid to extract scandium was developed.

Purification

Di-isopropyl ether and secondary aliphatic amines are used to remove iron impurity from aluminum chloride solution obtained by leaching clays with HCl.

Production of pure phosphoric acid

Phosphoric acid and its salts needed for the food and detergent industries is usually prepared from elemental phosphorus produced by the reduction of phosphate rock with carbon in an electric furnace: Phosphate rock $\rightarrow P \rightarrow P_2O_5 \rightarrow H_3PO_4$. Wet process H_3PO_4 produced by leaching phosphate rock with H_2SO_4 (page *343)* is not suitable for these purposes because of the impurities it contains. Since the production of elemental phosphorus is becoming more and more costly, attention was directed to the purification of wet process acid. Production of pure H_3PO_4 from this source that is competitive with the thermal route acid is now achieved on a commercial scale using butyl alcohol as a solvent. Phosphoric acid is transferred to the organic phase leacing the impurities behind. Pure H_3PO_4 is then recovered from the organic phase by stripping with a limited amount of water or by distillation of the alcohol under vacuum.

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[1] *See* also **chapter** 2.

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1976: The Aqueous/Organic Interface and Its Role in Solvent Extraction, London, England.

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Conference	Year	Location	Publication
1	1962	Oak Ridge, Tennessee	Journal of Inorganic & Nuclear Chemistry, Volume 17, 1963.
2	1963	Brussels, Belgium	Proceedings: Aqueous Reprocessing Chemistry.
3	1965	Harwell, England	Solvent Extraction Chemistry of Metals. Proc. Intern. Conf. Harwell, edited by H.A.C. McKay et al., Chemical Rubber Co., Cleveland, Ohio.
4	1966	Gorhenburg, Sweden	Solvent Extraction Chemistry. Proc. Intern. Conf., Interscience, New York, 1967. Editors J. Rydberg, D. Dyrssen, J.O.L. Liljelzin.
5	1968	Jerusalem, Israel	Solvent Extraction Research, edited by A.S. Kertes and Y. Marcus, Wiley–Interscience, New York, 1969.
6	1971	LeHague, Netherlands	Proceedings (2 volumes). Society of Chemical Industry, London, 1971. Editors J.G. Gregory, B. Evans, P.C. Weston.
7	1972	Antwerp, Belgium	International Symposium of Solvent Extraction in Metallurgical Processes.
8	1974	Lyon, France	Proceedings of International Solvent Extraction Conference (3 volumes), Society of Chemical Industry, London, 1974. Editor G.V. Jeffreys.
9	1977	Toronto, Canada	Proceedings of the International Solvent Extraction Conference (ISEC), 2 volumes, Canadian Institute of Mining & Metallurgy, Montreal, 1977.
10	1980	Liège, Belgium	Proceedings of the International Conference on Solvent Extraction.
11	1983	Denver, Colorado	Proceedings ISEC'83, American Institute of Chemical Engineers, 1983.
12	1986	Frankfurt, Germany	
13	1988	Moscow, USSR	

Conference	Year	Location	Publication
14	1990	Kyoto, Japan	Solvent Extraction 1990, 2 parts, editors: T Sekine and S. Kusakabe, Elsevier, Amsterdam, 1992.
15	1993	York, England	Solvent Extraction in the Process Industries.
16	1996	Melbourne, Australia	Value Adding Through Solvent Extraction

Part Five

Treatment of Leach Solutions: Precipitution

Chapter Twenty-Two

General Aspects

Precipitation Methods.................................... 531
Physical.................................... 531
Chemical.................................... 532
Basic Principles.................................... 535
The precipitate.................................... 535
Precipitation.................................... 537
Coprecipitation.................................... 537
The precipitant.................................... 538
The role of complexing ion.................................... 538
The role of oxidizing and reducing agents.................................... 539
Disproportionation.................................... 539
Summary.................................... 542

PRECIPITATION METHODS

Precipitation is the final step in any hydrometallurgical process[1]; it can be physical or chemical (Figure 22.1).

Physical

In this method. no reagents are added. but the concentration and temperature are ***so*** adjusted that crystallization should take place. It can be represented by the equation:

$$yM^{x+} + xA^{y-} + nH_2O \rightarrow M_yA_x \cdot nH_2O_{(s)}$$

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[1] It is also used as a purification step **to** separate impurities.

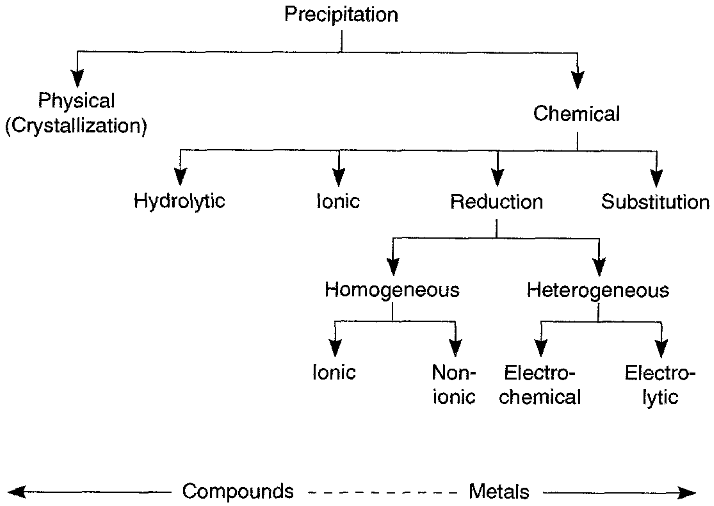

Figure 22.1: Methods of precipitation from an aqueous solution.

It is usually a slow process and the crystals obtained have a high solubility in water and usually contain water of crystallization. Crystallization is a common procedure for obtaining pure salts, e.g., sodium chloride, borax, etc. It is used occasionally for recovering some metals from solutions, e.g., $CuSO_4 \cdot nH_2O$ and $NiSO_4 \cdot 4H_2O$. Also, all methods for recovering alumina from non-bauxite sources are based on a crystallization step.

Chemical

In this method, reagents are added to precipitate a specific compound.

Hydrolysis

When water is the only reagent added, the process is called hydrolysis and this usually leads to the precipitation of oxides, hydrated oxides, hydroxides, or hydrated salts. For example, the precipitation of hydroxides can be represented by:

$$M^{x+} + xH_2O \rightarrow M(OH)_x + xH^+$$

Ionic

It is evident that hydrolytic reactions can be enhanced if the H^+ ions formed in the above reaction are neutralized by a base, i.e.:

$$M^{x+} + xOH^- \rightarrow M(OH)_x$$

Reactions between ions like the above are ionic precipitation and have the general equation:

$$yM^{x+} + xA^{y-} \rightarrow M_yA_{x(s)}$$

where A^{y-} is an anion. Precipitation usually takes place rapidly because the compound formed has low solubility and is attached together by electrostatic forces.

Reduction

When precipitation involves electron transfer from different ions or from a solid, i.e., oxidation–reduction couples, the process is precipitation by reduction. It can be homogeneous or heterogeneous.

Homogeneous reduction. This process may be ionic or non-ionic. In both cases, a reducing agent is added which results in the precipitation of a metal and itself is oxidized:

$$M^{n+} + \text{Reduced species} \rightarrow M + \text{Oxidized species}$$

- *Ionic reducing agents.* For example, ferrous ion, sulfite ion, hypophosphite ion, etc. The precipitation of silver from $AgNO_3$ by ferrous ion is typical:

$$Ag^+ + \underset{\substack{\text{reduced}\\\text{species}}}{Fe^{2+}} \rightarrow \mathbf{Ag} + \underset{\substack{\text{oxidized}\\\text{species}}}{Fe^{3+}}$$

  This is an oxidation–reduction process as follows:

$$Fe^{2+} \rightarrow Fe^{3+} + e-$$

$$Ag^+ + e^- + Ag$$

- *Non-ionic reducing agents.* For example, hydrogen, carbon monoxide, formaldehyde, or hydrazine; the oxidation process being:

$$H_2 \rightarrow 2H^+ + 2e^-$$

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^-$$

$$H_2N{-}NH_2 \rightarrow N_2 + 4H^+ + 4e^-$$

Reduction of metal ions takes place as follows:

$$M^{n+} + ne^- \rightarrow M$$

Oxides may also be precipitated in this way.

Heterogeneous reduction. In these processes, the transfer of electrons takes place at a solid surface which may be itself the reducing agent (electrochemical process), or the cathode in an electrolytic cell (electrolytic process).

- *Electrochemical processes.* In this case, the reducing agent is activated charcoal or a less noble metal than the metal ion in solution. In the first case, charcoal is oxidized to CO or CO_2:

  $$C + H_2O \rightarrow CO + 2H^+ + 2e^-$$

  $$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

  These reactions are specific for the precipitation of gold from chloride solutions. In the second case, the less noble metal, X, goes into solution displacing the more noble metal as follows:

  $$X \rightarrow X^{n+} + ne^-$$

  $$M^{n+} + ne^- \rightarrow M$$

  For example, the precipitation of copper from copper sulfate solution by metallic iron:

  $$Fe \rightarrow Fe^{2+} + 2e^-$$

  $$Cu^{2+} + 2e^- \rightarrow Cu$$

  These reactions are considered electrochemical because the transfer of electrons takes place at localized areas on the surface of the solid far from the area where the metal goes into solution.

- ***Electrolytic processes.*** In this case, precipitation of a metal from its aqueous solution is affected by imposing an outside electromotive force from a direct current source. This can be represented by:

  $$M^{n+} + ne^- \rightarrow M$$

For example, copper, zinc, cadmium, and nickel are recovered industrially from leach solutions by electrolytic methods — a process called "electrowinning". The aqueous solutions are electrolyzed using inert electrodes; the pure metal is deposited on the cathode.

Substitution

Precipitation by substitution takes place in connection with the extraction of metal ions from aqueous solution by organic solvents. The organic phase loaded with metal by coordination is then subjected to stripping by hydrogen at high temperature and pressure in a pressure reactor whereby metal powders precipitate. The reactions can be represented by:

$$H_{2(g)} \rightleftharpoons H_{2(org)}$$

$$R_2M_{(org)} + H_{2(org)} \rightarrow 2RH_{(org)} + M_{(s)}$$

where RM is the organic solvent and M is a divalent metal. For convenience, this method of precipitation will be discussed under *Reduction by Non-ionic Reducing Agents* (non-aqueous medium) (see page 647).

BASIC PRINCIPLES

The precipitate

The particle size and form of a precipitate depend upon the conditions under which it has been formed.

Particle size. A freshly formed precipitate is sometimes described as amorphous or gelatinous because of the difficulty of separating it by filtration. The particle size of such precipitate may be small and imperfect crystals due to the fast rate of precipitation. Precipitates usually undergoes continuous recrystallizations when left in contact with the mother liquor; the process is calles "aging". Ions continuously go into solution and redeposit on the surface of the solid and a state of equilibrium is achieved. The process is accelerated by heating. For example, a freshly precipitated hydroxide is difficult to filter and wash. On heating before filtration, it is converted into a non-gelatinous form rendering it easy to handle. Freshly prepared $Fe(OH)_3$ undergoes a process of condensation, whereby H_2O molecules are split, until finally water-free Fe_2O_3 is formed:

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

Crystal form. The crystal form of a precipitate may depend on the medium of precipitation. For example, β-FeOOH is formed when ferric ion is precipitated from chloride or fluoride medium while α- and γ-FeOOH are precipitated from sulfate, nitrate, and bromide medium. Aluminum hydroxide precipitated by neutralizing aluminum ion from acid medium is gelatinous, difficult to filter and wash free from impurities, while that precipitated from alkaline medium, e.g., sodium aluminate solution, is crystalline and readily filtered and washed.

There are three forms of beryllium hydroxide depending on the method of precipitation:

- Amorphous $Be(OH)_2 \cdot nH_2O$. This is precipitated when the stoichiometric quantity of alkali is added to cold beryllium salt solution. It is gelatinous, has a high capacity to adsorb other ions from solution, is difficult to filter and wash free of the adsorbed foreign ions, and is soluble in ammonium carbonate solution, in dilute NaOH, and in acids.
- Crystalline α-$Be(OH)_2$. A metastable hydroxide forms during the aging of the amorphous hydroxide. Aging takes place slowly in water or in air, and is facilitated by boiling. It is easily filtered, does not adsorb ions, is insoluble in ammonium carbonate and in dilute NaOH, and slowly soluble in acids.
- Crystalline β-$Be(OH)_2$. Formed when precipitation is carried out from alkaline solutions, e.g., by boiling a beryllate solution. It can be easily filtered and washed free from impurities.

Calcium carbonate in form of calcite (rhombohedral) precipitates from cold solutions containing Ca^{2+} ions on addition of CO_3^{2-} ions, and in form of aragonite (rhombic) if precipitation is conducted at the boiling point. The existence of a compound in more than a crystal foam is called polymorphism (see p. 551).

Precipitation

Precipitation involves two steps: Nucleation and crystal growth. Factors favoring increased rate of nucleation are: concentrated solution, high speed of agitation, and the presence of finely divided solid in the solution which act as nucleating agent. If the rate of nucleation is high, the precipitate will be finely divided. On the other hand, if the rate of nucleation is slow, the precipitate will have large particle size. As a result, finely divided precipitates are obtained from concentrated solutions and coarse precipitates are obtained from dilute solutions. Rate of precipitation may also decrease as a result of the presence of certain metal ions or organic compounds in solution.

Usually, precipitation is carried out under strict conditions to achieve the necessary separation from the other constituents. In general, the following factors control a precipitation process:

- Precipitation should be conducted within a certain pH range, since most precipitates are redissolved outside this range. For example, $Al(OH)_3$ precipitates from dilute solution at pH *4* but redissolves at pH 8.
- Precipitation should be conducted at an optimum temperature since most precipitates are more soluble in hot than in cold solutions.

Coprecipitation

Coprecipitation is the contamination of a precipitate by substances that are normally soluble under the conditions of the precipitation. It can be used to advantage to precipitate an ion that is difficult to precipitate due to its very low concentration, e.g., radioactive trace amounts in leach solution, but it can be an inconvenience due to the difficulty of obtaining a desired pure precipitate. In the first case, a coprecipitant is added deliberately and is called a collector or carrier. Coprecipitation may result because of the following reasons:

- *Occlusion.* This results when trace impurities at the surface of a crystal become mechanically trapped as the crystal layers are deposited. This type of precipitate may be purified by repulping in water, filtration, and washing.

- *Adsorption.* This is especially important when a gelatinous precipitate with a large surface area is formed. Trace impurities are adsorbed on the surface. In some cases, the forces of adsorption are weak and the impurities may be desorbed by hot water. In others, surface reactions may take place and removing by washing is not possible. For example, when ferric hydroxide is precipitated, is usually adsorbs a number of other ions. This principle is sometimes utilized in purifying leach solutions before electrolysis, e.g., $ZnSO_4$ leach solution.
- *Formation of solid solution.* This takes place when the ionic radii are nearly the same thus an impurity ion can substitute an ion of the macrocomponent in the crystal lattice. Substitution takes place at random and therefore the impurity ion forms a solid solution with the macrocomponent. In this type, it is not possible to remove the impurity by washing. Use is made of this phenomenon to separate radium during the sulfuric acid leaching of uranium ores. This is achieved by adding barium chloride to the solution to form $BaSO_4$, which acts as a carrier for $RaSO_4$. The precipitate can be represented by $(Ba,Ra)SO_4$.

The precipitant

The choice of a precipitant for a certain metal ion depends, beside the economic factor, on the following factors:

- It should be specific as far as possible so that pure precipitates can be obtained.
- It should form a precipitate consisting of crystals easy to filter and to wash.
- It should form a very insoluble precipitate so that quantitative recoveries are possible.

It is comparatively rare to find a precipitant having all these requirements, and it is often that the precipitate obtained is only a crude concentrate which has to be redissolved and purified.

The role of complexing ion

The presence of a complexing ion in solution may prohibit the precipitation of an ion. For example, AgCl precipitates readily from silver nitrate solution on adding a chloride ion but not from a cyanide solution since silver in such solution is complexed as $[Ag(CN)_2]^-$. This principle is often utilized to make separations. For example, by adjusting the pH of a solution to 10, using sodium carbonate, uranium remains in solution as a complex sodium uranyl carbonate, while aluminum and manganese are precipitated as hydroxides. If NaOH were added, then uranium together with other impurities would precipitate.

The role of oxidizing and reducing agents

Change in valency by adding an oxidizing or a reducing agent to the solution is sometimes exploited to effect selective precipitations. For example, both Co^{2+} and Ni^{2+} ions precipitate as hydroxides at pH 6.7, but Co^{3+} precipitates at pH **3.** Therefore, to precipitate cobalt selectively from a mixture with nickel, oxidation of Co^{2+} to Co^{3+} prior to precipitation is conducted.

The presence of a reducing agent may also be necessary for the formation of a precipitate. For example, most of the tetravalent uranium salts are insoluble in water while the hexavalent salts are soluble. Therefore, uranium(VI) in leach solutions may be reduced to uranium(IV):

$$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$$

so that in the presence of a precipitant, e.g., fluoride ion, an insoluble salt is formed. Similarly, cuprous salts are less soluble than cupric and therefore can be precipitated by adding a reducing agent:

$$Cu^{2+} + e^- \rightarrow Cu^+$$

Cuprous ion may undergo hydrolysis to precipitate as an oxide, undergo disproportionation to produce a metal, or in presence of certain ions, e.g., Cl^- or CN^-, precipitate to form an insoluble salt.

Disproportionation

This involves the simultaneous oxidation and reduction of an ion; application in hydrometallurgy is limited to cuprous ion which can lose an electron to become cupric, and gain an electron to become elemental copper simultaneously:

Table 22.1: Summary of precipitation methods.

Method	Characteristics	Reactions	Examples
Crystallization	Slow, high solubility of salt	$yM^{x+} + xA^{y-} + nH_2O \rightarrow M_yA_x \cdot nH_2O_{(s)}$	$Cu^{2+} + SO_4^{2-} + 5H_2O \rightarrow CuSO_4 \cdot 5H_2O$
Hydrolysis	Slow, accelerated by nucleation	$M^{x+} + xH_2O \rightarrow M(OH)_x + xH^+$	$TiO^{2+} + H_2O \rightarrow TiO_2 + 2H'$ $AlO(OH)_2^- + H_2O \rightarrow Al(OH)_3 + OH-$
Ionic precipitation	Fast, low solubility of precipitate	$yM^{x+} + xA^{y-} \rightarrow MA_{(s)}$	$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$ $Cu^{2+} + S^{2-} \rightarrow$ c u s $Cu^+ + Cl^- \rightarrow CuCl$
Ionic reduction	Homogeneous, involves oxidation–reduction, reagent in ionic form	M'" + Reduced species $\rightarrow$ M + Oxidized species	$Au^+ + e^- \rightarrow Au$ $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $Au' + Fe^{2+} \rightarrow Au + Fe^{3+}$ $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e-$ $SeO_3^{2-} + 6H^+ + 4e^- \rightarrow Se + 3H_2O$ $SeO_3^{2-} + 2H^+ + 2SO_3^{2-} \rightarrow Se + 2SO_4^{2-} + H_2O$
Non-ionic reduction	Homogeneous, involves oxidation–reduction, reducing agent is non-ionic	$M' + {}^{x}/_{2}H_2 \rightarrow M + xH^+$	$Ni^{2+} + 2e- \rightarrow Ni$ $H_2 \rightarrow 2H^+ + 2e^-$ $Ni^{2+} + H_2 \rightarrow Ni + 2H^+$
	Substitution in organic medium, 200°C, 100 kPa	$RM_{(org)} + H_{2(org)} \rightarrow RH_{2(org)} + M_{(s)}$	

Method–	Characteristics	Reactions	Examples
Electrochemical reduction	Heterogeneous, involves oxidation–reduction	$4M' + \underset{\text{activated charcoal}}{xC} + 2xH_2O \rightarrow$ $4M + xCO_2 + 4xH^+$	$Au^{3+} + 3e- \rightarrow Au$ $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e-$ $4Au^{3+} + 3C + 6H_2O \rightarrow 4Au + 3CO_2 + 12H^+$
		$M^{n+} + \underset{\substack{\textbf{less noble} \\ \text{metal}}}{X} \rightarrow M + X^{n+}$	$Cu^{2+} + 2e^- \rightarrow Cu$ $Fe \rightarrow Fe^{2+} + 2e^-$ $Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$
Electrolytic reduction	Imposed EMF	$M^{x+} + xe^- \rightarrow M$	$Cu^{2+} + 2e^- \rightarrow Cu$

Oxidation: $Cu^+ \rightarrow Cu^{2+} + e^-$

Reduction: $Cu^+ + e^- \rightarrow Cu$

Overall reaction: $2Cu^+ \rightarrow Cu + Cu^{2+}$

It can be seen from the overall equation that half the cuprous ion is precipitated as a metal and the other half remains in solution but at a higher valency state. In acid medium, this reaction is usually slow at ambient conditions; a temperature of 150 to 180 °C is needed to have appreciable transformation. However, in basic medium, when the cuprous ion is complexed, e.g., by ammonia, the reaction may be rapid at ambient conditions. Thus, on acidification of a cuprous ammine complex to $pH < 3$, disproportionation is instantaneous (see **p.** 626):

$$[Cu(NH_3)_4]^+ + 4H^+ \rightleftharpoons Cu^+ + 4NH_4^+$$

$$2Cu^+ \rightarrow Cu + Cu^{2+}$$

SUMMARY

Table 22.1 gives a summary of precipitation processes.

Chapter Twenty-Three

Physical Precipitation: Crystallization

Introduction 544
crystals 544
  Formation 546
  Water of crystallization 548
  Acids in crystals 549
  Hygroscopy, deliquescence. and efflorescence. 549
  Dehydration. pyrohydrolysis. and oxyhydrolysis 550
  Isomorphism 551
  Polymorphism 551
  Isomerism 552
Solubility Diagrams 554
  Pure salts 554
  Transition temperature 556
Crystallization of a Single Salt 557
  Effect of temperature 557
  Effect of common ion 559
  Effect of organic solvents 560
Crystallization of a Binary Mixture 560
  Solubility diagrams 560
  Products of crystallization. 564
Crystallization of a Quaternary Mixture 566
  Conversion reactions 567
Fractional Crystallization 570
Engineering Aspects 570
  Solar crystallizers 570
  Vacuum crystallizers 571
  Spray drying 573
  Submerged combustion 574
Applications 574
  Surface and subterranean waters 575
  Leach solutions of salt deposits 583
  Hydrometallurgical solutions 587

INTRODUCTION

Crystallization from aqueous solution is a simple and old method for the recovery of metal values from purified leach solution or natural brines. It is a physical process[1] in which no reagents are added but the concentration and temperature of the solution are so adjusted to lead to the formation of an ionic solid crystalline phase which may contain water of crystallization. The process can be represented by:

$$yM^{x+} + xA^{y-} + nH_2O \rightarrow M_yA_x \cdot nH_2O_{(s)}$$

In contrast to precipitation, the process is usually slow and the solid obtained is soluble in water. However, the basic principles of formation of crystals or precipitates are essentially the same: Nucleation and growth, formation of saturated solutions, the possible formation of solid solutions, perfect geometrical form, and lattice defects. It is only the speed with which crystals form and their high solubility in water that make the distinction with precipitation. That is why the engineering aspects in both processes are different.

From production point of view, crystallization involves a much larger tonnage than precipitation. It is applied mainly in the recovery of:

- Salts from surface waters
- Salts from leach solutions of saline deposits
- Metal values from ores or secondary leach solutions.

CRYSTALS

A crystal has definite geometrical form and is bounded by plane faces. The size and the external shape of the crystal of a given substance may vary, but the angle between two corresponding faces is the same. The geometrical form of a crystal depends on the arrangement of the atoms or group of atoms throughout the crystal. The positions of the atoms in the crystal which determine the framework is known as the crystal lattice. The smallest unit of this lattice representing the relative positions of all the atoms or group of atoms is known as unit

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[1] An exception **is** crystallization from a quaterny mixture whereby conversion may take place — a physicochemical process (page 566).

cell. There are only six crystal systems based on the position of the faces in relation to definite axes (Figure 23.1):

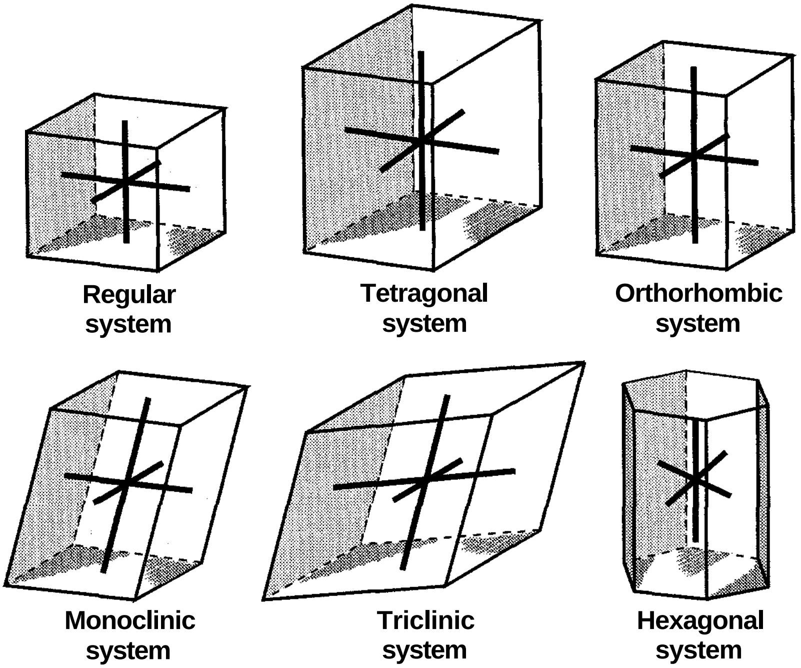

Figure 23.1: Crystal systems.

- *Isometric or regular.* Three axes of equal length intersecting each other at right angles. There are three different space lattices in this system:
  - Simple cubic. One structural unit is at each corner of the cube.
  - Face-centered cubic. One unit at each corner and one in the center of each face of the cube.
  - Body-centered cubic. One unit is at each corner and one in the center of the cube.
- *Tetragonal.* Two axes of equal length intersecting each other and third axis, either shorter or longer, at right angle.
- *Orthorhombic.* Three axes of unequal length intersecting each other at right angles.
- *Monoclinic.* Three axes of unequal length, two intersecting each other at right angles, with the third axis perpendicular to only one of the two.

- *Triclinic.* Three axes of unequal length intersecting each other at oblique angles.
- *Hexagonal.* Three axes of equal length in the same plane, intersecting each other at an angle of 60°, and a fourth axis of different length perpendicular to this plane.

Formation

Crystallization like precipitation involves two steps: Nucleation and growth (page 537). The size of the deposited crystals depends on the rate of evaporation. Slow evaporation produces large crystals and vice versa, rapid evaporation produces small crystals. The crystal form depends on the manner in which the crystal is maintained in solution. When it is uniformly surrounded by solution as in an agitated tank, the crystal can grow in all directions. When the crystal is adhering to a solid surface or when certain organic compounds are added to inhibit surface nucleation, its growth will be limited to certain directions. For example, sodium chloride usually crystallizes in form of cubes but in presence of a small amount of urea, it takes the shape of regular octahedron. Although the two shapes look different, actually they are geometrically related as shown in Figure 23.2; the angle between the faces of the octahedron is always the same. Hence, on crystallization, sodium chloride does not change its form due to inhibited surface nucleation, it simply changes its habit. The external shape and appearance of a crystal is called *habit.* Figure 23.2 shows also the relation of the tetrahedron to the cube.

Surface nucleation causes twinned or multicrystal growth (Figure 23.3). Both are undesirable because:

- They entrap mother liquor and become difficult to wash thus affecting purity
- They lead to breakage during handling thus producing fines.

That is why it is undesirable to have single crystals during crystallization, and these are obtained when all surface nucleation has been suppressed.

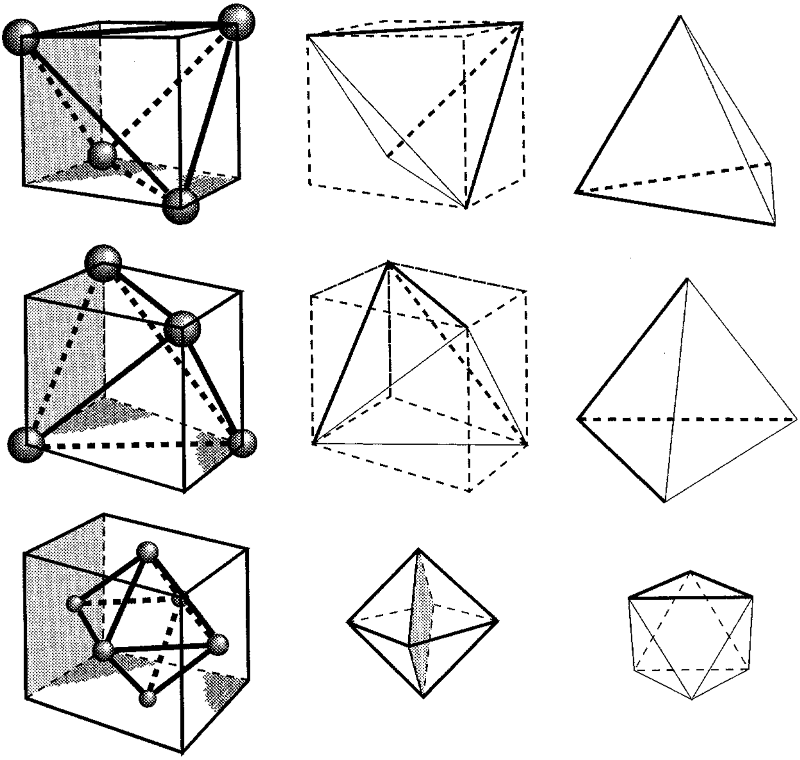

Figure *23.2:* The relation of the tetrahedron and the octahedron (bottom) to the cube.

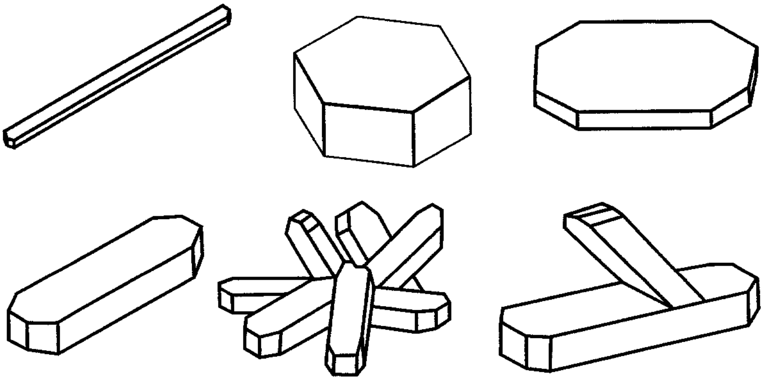

Figure *23.3:* Top: Needle, chanky, and platelet single crystal forms. Bottom: Single, multi-, and twinned crystal habits.

Water of crystallization

Ions in solution are hydrated, i.e., they are surrounded by water molecules. A cation is surrounded by water molecules whose oxygen atoms, which have a slight negative charge, are directed at the positive ion while an anion is surrounded by water molecules whose positively charged ends point toward the anions. Cations are much smaller than anions and therefore the charge is more concentrated on their surfaces. **As** a result, cations attract much more water molecules than anions. This is especially the case for highly charged cations. The number of water molecules held by an ion is called the *coordination number* of the ion. Thus, the coordination number of Be^{2+} is *4* because it is associated with $4H_2O$ and for Mg^{2+}, which is larger than Be^{2+} ion, it is 6 because it is associated with $6H_2O$ as shown in Figure *23.4.*

In many cases, cations hold water so tightly that the water molecules accompany the cations when ionic solids crystallize from aqueous solution. This water is called *water of crystallization*. Many crystalline salts, especially those of dipositive and tripositive cations, have stoichiometric quantities of water of crystallization. Three types may be identified:

- The cation retains all its water of hydration when the salt crystallizes. For example, $BeSO_4 \cdot 4H_2O$, $MgCl_2 \cdot 6H_2O$, $Fe(NO_3)_2 \cdot 6H_2O$.

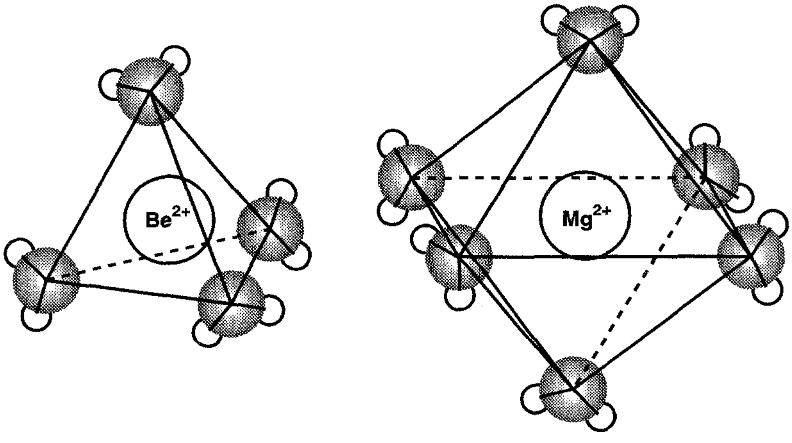

Figure *23.4:* Hydrated metal ions in aqueous solutions: Be^{2+} and Mg^{2+}

- The cation retains all its water of hydration with an additional water molecule retained by the anion. For example, in $FeSO_4 \cdot 7H_2O$, six H_2O are retained by Fe^{2+} ion and one H_2O retained by SO_4^{2-} ion.
- The cation retains only a part of its water of hydration. For example, $MgSO_4 \cdot H_2O$.

Acids in crystals

Hydrated crystals formed from acidic solutions usually contain acids that cannot be washed away by water, i.e., it is not a superficial layer of the mother liquor.

Hygroscopy, deliquescence, and efflorescence

The absorption of water from the air by a crystal is called hygroscopy (from Greek, to become wet). This is usually the case of highly soluble crystals, e.g., NaOH or salts capable of forming crystals containing water of crystallization, e.g., anhydrous $CuSO_4$. When crystals continue to absorb water until the hydrate dissolves, the process is called deliquescence (from Latin, to become liquid). For example, the anhydrous salt $CaCl_2$ absorbs enough water from the air to form first the hydrate $CaCl_2 \cdot 6H_2O$, and then continue to absorb water to form a solution.

The reverse process, i.e., the loss of water from a crystalline solid, is called efflorescence (from Latin, to blossom, because of the appearance of the crystal after losing water that look like a flower). This is usually the case of crystals containing a large number of molecules of water of crystallization, e.g., $Na_2CO_3 \cdot 10H_2O$, $Na_2SO_4 \cdot 10H_2O$, or $Na_2HPO_4 \cdot 12H_2O$. These phenomena are related to the actual water pressure in the atmosphere with respect to that of a saturated solution of the crystal. If the vapor pressure in the atmosphere is higher than the vapor pressure of the saturated solution of the salt, then the crystal deliquesces, and vice versa. These phenomena are important in handling and storage of crystals.

Dehydration, pyrohydrolysis, and oxyhydrolysis

Crystalline solids lose their water of hydration when heated, and the loss usually takes place in stages. For example, $CuSO_4 \cdot 5H_2O$ loses two moles H_2O at about 90 °C, another two at 110 "C, and the last mole at 250 °C (Figure 23.5):

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O \rightarrow CuSO_4$$

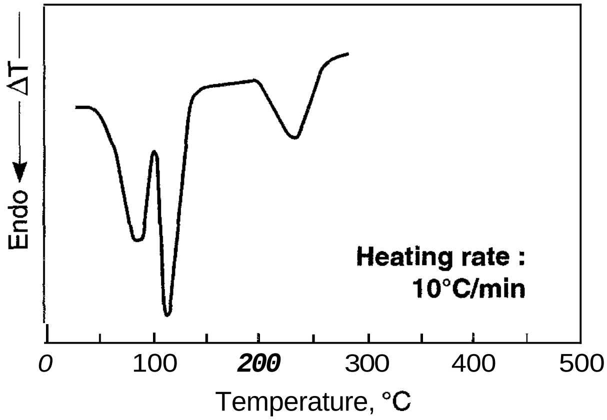

Figure 23.5: Dehydration of $CuSO_4 \cdot 5H_2O$ thermograms showing the stepwise loss of water.

This shows that the water of hydration is not equally bound in the crystal. Some hydrates, however, hydrolyse during dehydratation and the process is known as pyrohydrolysis, for example, $AlCl_3 \cdot 6H_2O$:

$$AlCl_3 .6H_2O \rightarrow AlCl_3 .{}^3/_2H_2O + {}^9/_2H_2O$$

$$2AlCl_3 \cdot {}^3/_2H_2O \rightarrow Al_2O_3 + 6HCl$$

To obtain an anhydrous material in this case, it is necessary to conduct the dehydration in presence of a gas flow of HCl.

If the metal ion in the crystalline salt is susceptible to react with air, then oxidation takes place during pyrohydrolysis and the process is called oxyhydrolysis, e.g., on dehydration of ferrous chloride:

$$FeCl_2 \cdot 4H_2O \rightarrow FeCl_2 \cdot H_2O + 3H_2O$$

$$2FeCl_2 \cdot H_2O + {}^1/_2O_2 \rightarrow Fe_2O_3 + 4HCl$$

Other reactions may take place during dehydration, e.g., oxidation–reduction (**see** page 565).

Isomorphism

Crystals of different composition but having the same form are called isomorphs and the phenomenon is called isomorphism. For example, crystals of $MnCO_3$ and $CaCO_3$, or $MnSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$ are isomorphs. The similarity in crystal form is due to the similarity in the way the crystals are built. Isomorphous crystals usually have similar formulas and when allowed to crystallize together from a mixed solution, they form solid solution, i.e., single crystals containing both substances provided that the different ions are of nearly equal size. For example, $MnCO_3$ and $CaCO_3$ form solid solutions in which the Mn^{2+} and Ca^{2+} ions are arranged at random in the positions occupied by one kind of ion alone in a pure substance.

Substitution of an ion by another in a crystal is a general phenomenon that takes place from an aqueous solution provided the radii of both ions are near to each other, and regardless of similarity in chemical properties, valency, or even crystal structure. For example, Ag^+ ion substitutes Pb^{2+} ion in lead sulfide although PbS and Ag_2S have different crystalline forms and $Ag+$ and Pb^{2+} ions have different valency. They only have similar ionic radii, 1.26Å and 1.20Å respectively. The excess charge due to Pb^{2+} results in a cation vacancy, i.e., $Ag+$ + cation vacancy = Pb^{2+}. Because such limited substitution does not change the crystal form of the macrocomponent, it is called isomorphous substitution, and is in effect another form of coprecipitation (**see** page 537).

Polymorphism

A compound may crystallize in one form under certain conditions and in a different form under other sets of conditions. For example, the blue tetragonal $NiSO_4 \cdot 6H_2O$ changes to the green monoclinic form at 53.5 °C. It is similar to the formation of precipitates in different polymorphic forms.

Isomerism

Crystals having the same number and kind of atoms (formula) but different structures may form on crystallization; these are called isomers and the phenomenon is called isomerism. Few inorganic compounds exhibit this phenomenon as compared to organic compounds. Isomers differ in physical and chemical properties, e.g., water solubility, absorption spectra, and reaction with chelating ions. The following types are common:

Structural isomerism

This results from the different ways in which the atoms can be attached to each other. For example, when ammonium cyanate is dissolved in water and the solution is evaporated, crystal of urea (also known as carbonic acid diamide or carbamide) are formed:

$$NH_4^+ + CNO^- \rightarrow (NH_2)_2CO$$

Geometrical isomerism

In this case, the isomers have the same structural formula but the atoms have a different distribution in space. When the **like** groups are close together, they are called the cis form, and when far apart, they are called the *trans* form (from Latin *cis* = on the same side, and *trans* = across). Geometrical isomerism is possible in square planer and octahedral complexes but not in tetrahedral arrangement because in the latter case all four coordinating groups are equidistant from one another. For example:

- *Square planer complexes.* When NH_3 is added to a solution containing $PtCl_4^{2-}$ ions and the solution is evaporated, the crystals obtained differ in physical properties from those obtained when HCl is added to a solution containing $[Pt(NH_3)_4]^{2+}$ ions and the solution similarly evaporated:

  $$PtCl_4^{2-} + 2NH_3 \rightarrow [Pt(NH_3)_2Cl_2] + 2Cl^-$$

  $$[Pt(NH_3)_4]^{2+} + 4HCl \rightarrow [Pt(NH_3)_2Cl_2] + 2NH_4Cl + 2H^+$$

  Both crystals obtained have the same chemical composition, the difference is attributed to different geometrical orientation. In the first case, the cis-isomer is formed while in the second, it is the *trans* as shown in Figure 23.6. It can be ssen that the four coordinating groups are equidistant from the central atom, but they are not equidistant from one another.

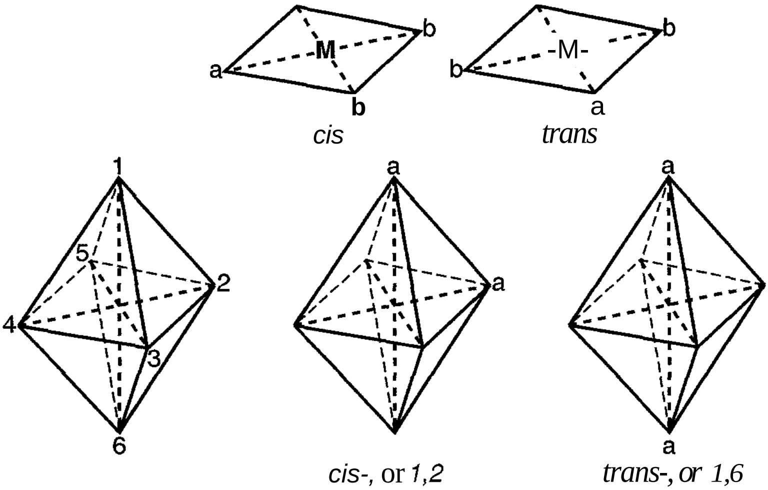

Figure 23.6: Cis- and trans-isomers. Top: Square planar complexes. Bottom: Octahedral complexes.

- *Octahedral complexes.* Cobalt(III) chloride forms two different crystalline ammine complexes. Green crystals are obtained when NH_3 is added to a $CoCl_2^+$ solution and the solution is evaporated, while violet crystals are obtained when HCl is added to a solution of $[Co(NH_3)_4]^{3+}$ and the solution similarly evaporated. The difference is attributed to different geometrical orientation. The green crystals are the cis-isomers while the violet are the trans (Figure 23.6). When the crystals are dissolved in water, only one third of the chloride ion can be precipitated by Ag^+, thus indicating the coordination of the other two chloride ions with the Co^{3+} ion.

Chromium(III) chloride, $CrCl_3 \cdot 6H_2O$, and chromium(III) sulfate also from different octahedrally coordinated isomers which vary in color from violet to green as shown in Table 23.1. Only the Cl^- or SO_4^{2-} ions that are not coordinated to Cr^{3+} ion can be precipitated by Ag^+ or Ba^{2+} ions, respectively. The change in color from violet to green takes place by dissolving the crystals in water and warming. The reaction is reversed by cooling.

Table 23.1: Chromium (III) salts.

Salt	Structure	Color	Cl^- or SO_4^{2-} ions precipitated
$CrCl_3 \cdot 6H_2O$	$[Cr(H_2O)_6]Cl_3$	violet	all
	$[Cr(H_2O)_5Cl]Cl_2$	green	2/3
	$[Cr(H_2O)_4Cl_2]Cl$	green	1/3
$Cr_2(SO_4)_3 \cdot 12H_2O$	$[Cr(H_2O)_6]_2(SO_4)_3$	violet	all
	$[CrSO_4(H_2O)_4]_2SO_4 \cdot 4H_2O$	green	1/2
	$Cr[Cr(SO_4)_3] \cdot 6H_2O$	green	none

SOLUBILITY DIAGRAMS

Solubility diagrams are constructed to show the solubility of a pure salt or a mixture of salts as a function of temperature at equilibrium. Each point on the diagram represents a saturated solution, i.e., a solution which is in equilibrium with undissolved salt. Supersaturated solution are sometimes obtained; these represent unstable solutions which contain more than the equilibrium concentration of the solute. This commonly arises when a solid is dissolved in water and the solution is cooled without shaking or stirring. The solution remains supersaturated as long as there are no nuclei upon which crystallization can start.

Pure salts

A typical solubility diagram for a pure salt is shown in Figure 23.7, from which it can be seen that the solubility increases as the temperature of the solution rises. For example, at 60 "C, 108 g of solid KNO_3 will dissolve in 100 g of water to produce a saturated solution. Any point on the curve represents the concentration of an unsaturated solution. For example, the point marked X represents a saturated solution containing 68 g of KNO_3 dissolved in 100 g of water at 65 "C. If the temperature of this solution is gradually lowered, in accordance with the broken horizontal line leading left from point X, the solution will become saturated at 42 "C. If the temperature is lowered further to 30 "C, 46 g of KNO_3 will remain in solution and 22 g of crystals will come out of solution (68 – 46 = 22). Any point above the curve represents the concentration of a supersaturated solution. For example, at the point marked X', the solution would contain 55 g of KNO_3 dissolved in 100 g of water at 25 "C, whereas the saturation temperature for this concentration is 35 "C. If a crystal of solid KNO_3 is dropped into this supersaturated solution at 25 "C, the concentration will fall to that of a saturated solution at this temperature, i.e., 37 g of KNO_3 in 100 g of water. Consequently, 18 g of KNO_3 will crystallize out of solution (55 – 37 = 18).

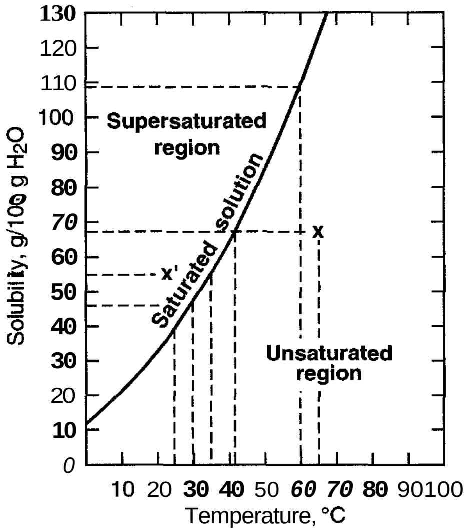

Figure *23.7:* Solubility curve of a salt in water.

Solubility diagrams may be plotted in form of a phase diagram as shown in Figure 23.8 for the system $MgCl_2$–H_2O. It can be seen that different hydrates form, and a mixture of ice and $MgCl_2 \cdot 12H_2O$ has a melting point of *–40* "C (hence the use of salts for the preparation of freezing mixtures). The marked fields in the diagram are as follows:

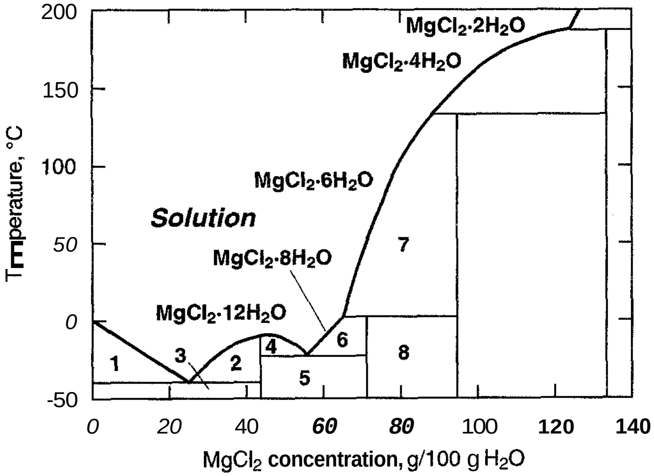

Figure 23.8: The system $MgCl_2$–H_2O.

1. Solution + ice
2. Solution + $MgCl_2.12H_2O$
3. Ice + $MgCl_2 \cdot 12H_2O$
4. $MgCl_2 \cdot 12H_2O$ + $MgCl_2.8H_2O$
5. Solution + $MgCl_2 \cdot 8H_2O$
6. Solution + $MgCl_2 \cdot 4H_2O$
7. $MgCl_2 \cdot 8H_2O$ + $MgCl_2 \cdot 4H_2O$

Transition temperature

While the solubility of most salts increases with temperature (Figure 23.9), there are few that are less soluble with increased temperature. For example, sodium sulfate shows a decreased solubility above 32.4 °C (Figure 23.10). The temperature at which a salt changes its solubility is called the transition temperature. Above 100 °C, when heating of solution is conducted in an autoclave, the solubility of most salts decreases and at about 250 °C, it becomes practically nil (Figure 23.11).

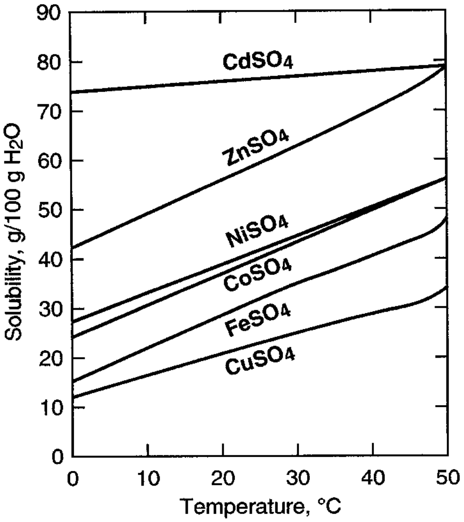

Figure 23.9: Increase in the solubility with increasing temperature.

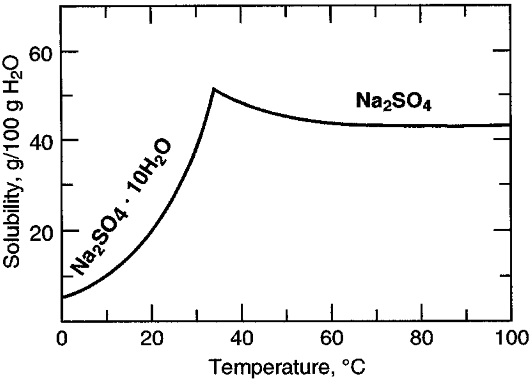

Figure 23.10: Solubility of sodium sulfate in water.

CRYSTALLIZATION OF A SINGLE SALT

Effect of temperature

Crystallization of a salt can be predicted from its solubility diagram:

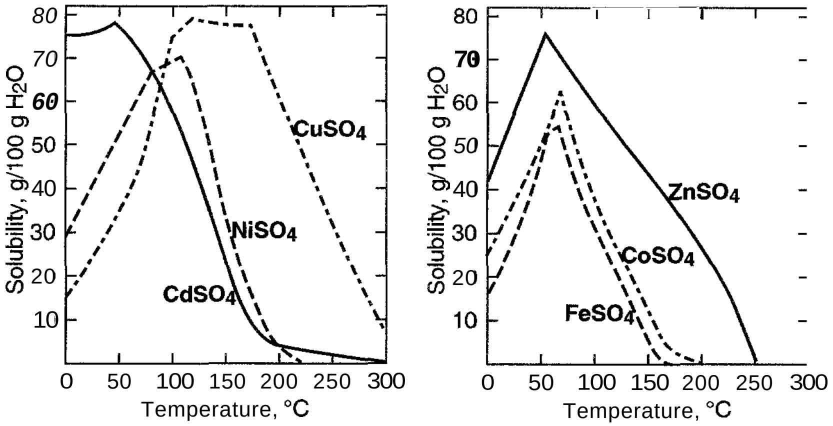

Figure 23.11: Crystallization of sulfates at high temperature.

- While cooling saturated solution of KNO_3 will effectively lead to the crystallization of the salt, cooling of saturated solution of NaCl will not be effective because the solubility of this salt is practically unchanged with temperature. Therefore:
  - When there is a large increase in solubility with temperature, crystallization can be effected by cooling a hot solution.
  - When there is a small increase in solubility with temperature, crystallization can best be effected by evaporation.
- Differences in solubilities may be used for separating salts by crystallization provided no interaction takes place during the process (see Binary Mixtures). For example, at 10 "C, $NaNO_3$ is about four times more soluble than KNO_3 (Figure 23.12). Therefore, KNO_3 containing $NaNO_3$ as an impurity can be purified by dissolution and cooling at 10 "C to crystallize pure KNO_3 leaving behind $NaNO_3$ in solution. For example, if 100 g KNO_3 containing 1% $NaNO_3$ is dissolved in 100 g hot water and the solution is cooled to 10 °C, 80 g of pure KNO_3 will crystallize. The mother liquor will contain 20 g KNO_3 and 1 g $NaNO_3$. If the crystals are removed and the solution concentrated by evaporation then cooled again to 10 "C, more KNO_3 will crystallize out substantially free of $NaNO_3$.

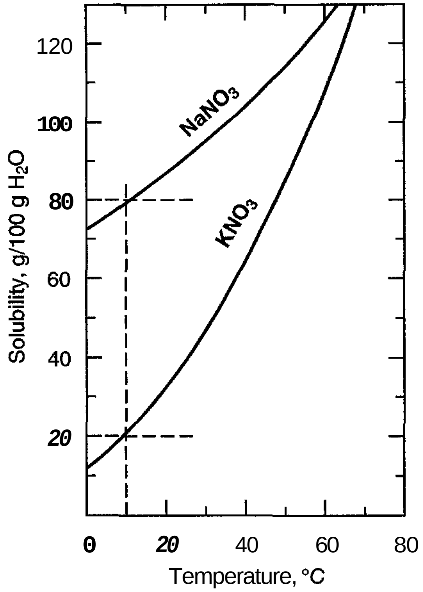

Figure 23.12: Purification by crystallization based on differences in solubility.

- A hot concentrated solution of sodium sulfate when cooled to 50 °C and held at this temperature for some time will form the anhydrous salt Na_2SO_4, but when cooled to **30** °C and held at this temperature will form the hexahydrate, $Na_2SO_4 \cdot 10H_2O$.

- Hydrolysis may take place during evaporating a salt solution to dryness which results in the formation of water-insoluble residues. For example, on evaporating a solution of magnesium chloride to dryness, it is not possible to get the anhydrous salts due to hydrolysis.

$$Mg^{2+} + 2H_2O \rightarrow Mg(OH)_2 + 2H^+$$

Effect of common ion

Solubility of most salts decreased in presence of acids with a common ion. For example, when concentrated H_2SO_4 is added to copper sulfate solution crystals of $CuSO_4 \cdot H_2O$ deposit because of decreased solubility of copper sulfate (Figure 23.13).

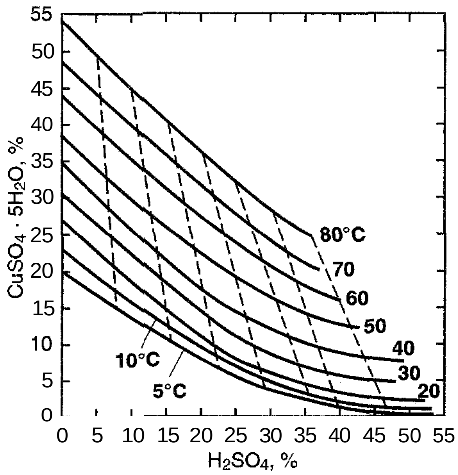

Figure **23.13:** Solubility of copper sulfate in sulfuric acid solutions.

Effect of organic solvents

Solubility of most salts decreases in presence of miscible organic solvents such as alcohol and acetone. These solvents have lower dielectric constant than water. Hence the electrostatic forces between the anions and cations decrease and precipitation takes place.

CRYSTALLIZATION OF A BINARY MIXTURE

Solubility diagrams

A binary mixture is a solution containing two salts with a common ion, e.g., two sulfates or two chlorides; or a sulfate and a chloride of a same metal.

In the rectangular cordinates, the concentration of one component is plotted on the horizontal axis and that of the other on the vertical axis at different temperatures. The following cases are considered:

- Each salt decreases the solubility of the other differently. This is the most common case. For example, in the system NaCl–KCl (Figure *23.14)*. The solubility diagram is represented by two curves AB and BC. It can be seen that the solubility of NaCl decreases with increased concentration of KCI (curve AB) and at the same time the solubility of KCl decreases with increased concentration of NaCl (curve BC).

- One salt decreases the solubility of the other while the solubility of the other is not influenced. For example, in Figure 23.15 which shows the system $FeSO_4$–$CuSO_4$, the solubility of $FeSO_4$ decreases with increasing $CuSO_4$ concentration (curve AB) while that of $CuSO_4$ is not influenced by $FeSO_4$ (curve BC).

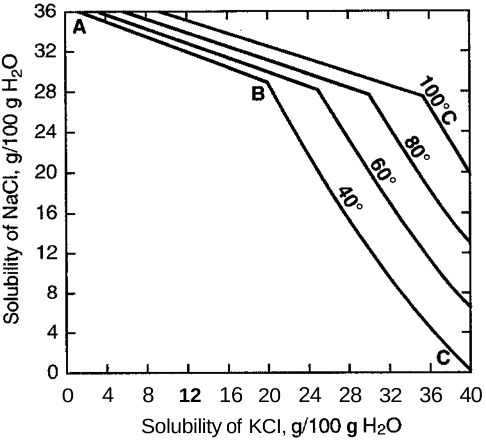

Figure 23.14: Solubilities in the system KCl–NaCl.

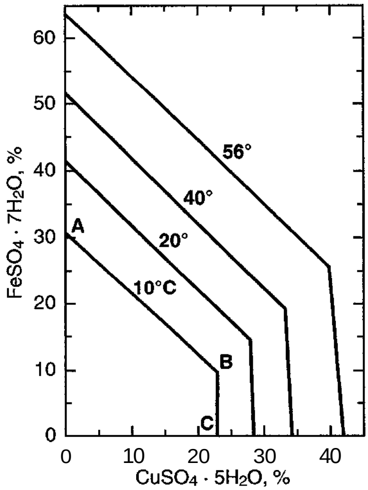

Figure 23.15: Solubility diagram of the binary system $FeSO_4$–$CuSO_4$ in rectangular coordinates (Agade and Barkholt, 1926).

- Each salt equally decreases the solubility of the other, for example, in the case of $FeCl_2$–$FeCl_3$, $NiSO_4$–$ZnSO_4$, and $Al_2(SO_4)_3$–$Fe_2(SO_4)_3$. In these cases, a single straight line is obtained as shown in Figure 23.16. The solubility of any mixture of the two components will fall on this straight line.

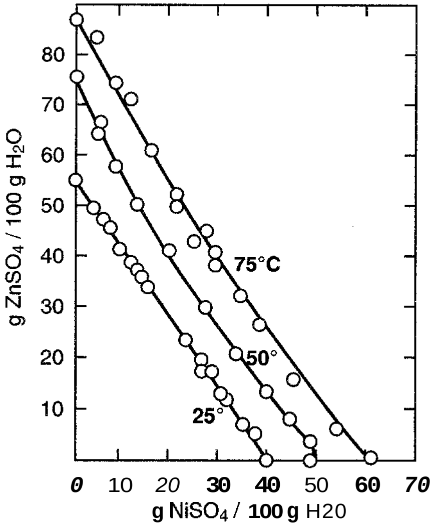

Figure 23.16: Solubilities in the system $NiSO_4$–$ZnSO_4$ (Jangg and Gregori, 1967).

The rectangular coordinate diagram for the first two cases have the following characteristics:

- The point B represents a solution saturated with respect to both salts and the area ABCO represents a homogeneous solution, while the area outside ABC can be divided into three regions *a*, *b*, and c. For example, in the case of NaCl–KCl:
  - Solid NaCl in equilibrium with its saturated solution.
  - A heterogeneous mixture of NaCl and KCl in equilibrium with a saturated solution of both salts of one composition.
  - Solid KCl in equilibrium with its saturated solution.
- When the solubility isotherms are represented at different temperatures, the breaking points at different temperatures on the diagram fall on the same curve.

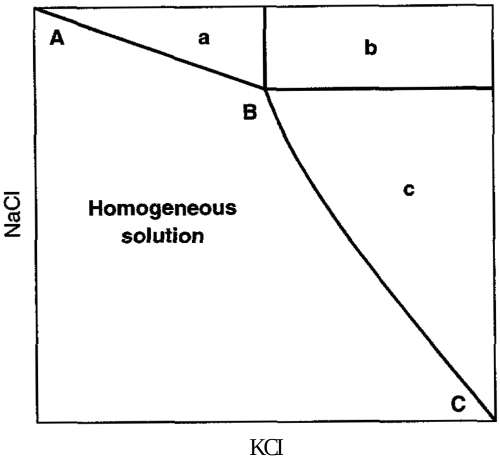

Figure **23.17:** The system NaCl–KCl. *(a)* Solid NaCl in equilibrium with its saturated solution. *(b)* **A** heterogeneous mixture of NaCl and KCl in equilibrium with saturated solution of both salts. (c) Solid KCl in equilibrium with its saturated solution.

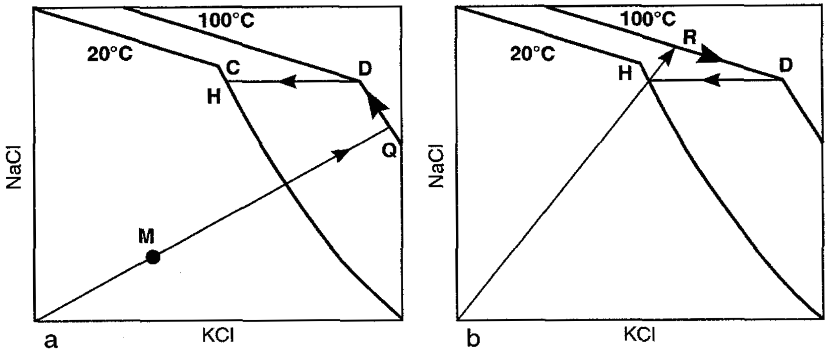

Figure **23.18:** Separation of KCl from NaCl.

- If a solution of composition M is evaporated (Figure 23.18a), the concentration of both salts increases in the same ratio until the composition Q is reached. Here, the solution is saturated with respect to KCl. Further evaporation precipitates KCl and the composition of the solution moves from Q to *D*. Cooling the solution crystallizes KCl, and the line segment DH represents the amount of KCl crystallized on cooling to 20 °C. No NaCl is crystallized because of the increased solubility of NaCl as KCI is removed from the solution, indicated by the line CD.

- If a solution of composition *H* is evaporated [Figure 23.18b), it begins to deposit NaCl at composition *R* and continues to the point *D*. If the deposited NaCl is filtered off and the solution cooled from *D* to *H*, another crop of KCl can be obtained. In this manner, the original solution can be separated into its components KCl, NaCl, and H_2O.

Products of crystallization

On crystallizing a binary mixture, three types of crystals may be obtained:

Heterogeneous crystals

In this case, a heterogeneous mixture of crystals composed of the two original salts is obtained; they can be either anhydrous or hydrated. For example, when a mixture of NaCl and KCl is dissolved in water and the solution allowed to crystallize, the solids obtained will be a mixture of NaCl and KCl as can be identified by the individual X-ray diffraction pattern of each salt, i.e., each salt has preserved its identity during dissolution and crystallization. This is because the ionic radii of Na+ and K^+ are different and therefore no chance of one ion taking place of the other in the crystal lattice. Other systems that form heterogeneous mixtures are $CuSO_4$–Li_2SO_4–H_2O, $CuSO_4$–$Al_2(SO_4)_3$–H_2O, and $CuSO_4$–$CdSO_4$–H_2O.

In these systems, it is usually possible to separate one salt from the other because of differences in solubilities with respect to temperature. Thus KCl can be separated from NaCl by cooling a hot solution saturated with both salts; KCl crystallizes out while NaCl remains in solution because the solubility of KCl decreases greatly with decreased temperature but that of NaCl remains practically the same. In some cases, however, it is not possibie. For example, in the system $ZnSO_4$–$NiSO_4$ where one salt equally decreases the solubility of the other (Figure 23.16). The composition of the aqueous phase is the same as that of the solid phase, i.e., when crystals separate from an aqueous solution of the two salts, it will be found that the ratio of one component to the other in the solid phase is the same as that in the aqueous phase. Thus, it will not be possible to separate the two components by crystallization.

Solid solution

In this case, homogeneous crystals are obtained in which the ratio of the components salts is variable. For example, when crystals of $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ are dissolved in water and the solution is allowed to crystallize, a homogeneous crystalline solid is obtained in which the copper and iron ions are irregularly distributed, i.e., there will be crystals of $CuSO_4 \cdot nH_2O$ incorporating iron in their structure and crystals of $FeSO_4 \cdot nH_2O$ incorporating copper in their structure. Such mixture may be represented by $(Cu, Fe)SO_4 \cdot nH_2O$ which indicates the isomorphous substitution of the two ions. The X-ray diffraction pattern of the mixed crystal will be similar to the original salts but the diffraction lines are slightly shifted. The color of the product is also different from that of the mechanical mixture of the individual hydrated components. Thus, while $CuSO_4 \cdot 5H_2O$ is dark blue and $FeSO_4 \cdot 7H_2O$ is pale green, the mixed crystals are pale blue. In this case, the two salts did not preserve completely their identity during dissolution and crystallization because the ionic radii of Cu^{2+} and Fe^{2+} are nearly similar. Other systems that form mixed crystals are: $CuSO_4$–$ZnSO_4$–H_2O, $CuSO_4$–$MnSO_4$–H_2O, and $CuSO_4$–$NiSO_4$–H_2O.

Hydrated mixed crystals may undergo interaction between the component metal ions on dehydration. For example, on dehydrating $(Cu, Fe)SO_4 \cdot nH_2O$ in an inert atmosphere at 300 °C, partial oxidation of ferrous to ferric and reduction of cupric to cuprous takes place:

$$Cu^{2+} + Fe^{2+} \rightarrow Cu^{+} + Fe^{3+}$$

The valency change is manifested by a color change: While the anhydrous individual crystals are colorless, the anhydrous mixed crystals in this case are violet.

Double salts

This is a compound formed from the two salts which has a distinct X-ray diffraction pattern and chemical properties. For example, when $FeSO_4 \cdot 7H_2O$ and $(NH_4)_2SO_4$ are dissolved in water and the solution allowed to crystallize, a compound having the formula $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and known as ferrous ammonium sulfate is obtained. While $FeSO_4$ oxidizes readily in the air, ferrous ammonium sulfate is quite stable, that is why it is usually used in analytical chemistry to prepare solutions of ferrous ion. Double sulfates are more exactly represented by the formula $M^I_2M^{II}(SO_4)_2\cdot nH_2O$ for a monovalent and a divalent metal or $M^IM^{III}(SO_4)_2\cdot nH_2O$ for a monovalent and a trivalent metal. A group of double sulfates having the formula $MIMIII(SO_4)_2\cdot 12H_2O$ is known as alums and are sometimes made use of in hydrometallurgy (Table 23.2).

Table 23.2: Alums of importance in hydrometallurgy.

	Formula	Application
Aluminum	$(NH_4)_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$ or $NH_4Al(SO_4)_2\cdot 12H_2O$	Separation of aluminum from beryllium in treatment of beryl
Chromium	$(NH_4)_2SO_4\cdot Cr_2(SO_4)_3\cdot 24H_2O$ or $NH_4Cr(SO_4)_2\cdot 12H_2O$	Separation of chromium in treatment of chromite

Formation of double salts may be a function of temperature. For example, in the system $NaSO_4$–$MgSO_4$–H_2O, the double salts astrakhanite, Na_2SO_4–$MgSO_4\cdot 4H_2O$ forms above 21.4 °C but not below this temperature (Figure 23.19). Other examples of systems that form double salts are: $CuSO_4$–Na_2SO_4, $CuSO_4$–K_2SO_4, $CuSO_4$–Rb_2SO_4, and $CuSO_4$–$(NH_4)_2SO_4$.

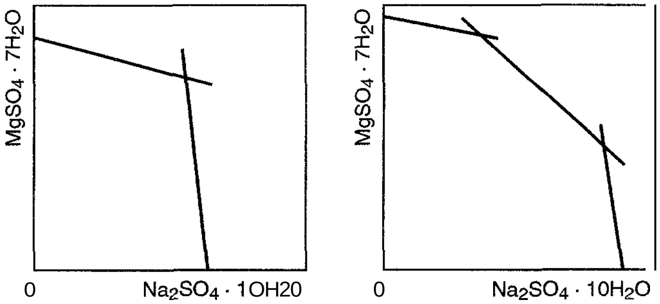

Figure 23.19: Solubility diagrams of the binary mixture $Na_2SO_4\cdot 10H_2O$ and $MgSO_4\cdot 7H_2O$ at 10 °C (left) and at 27 "C (right). The double salt astrakhanite $Na_2SO_4\cdot MgSO_4\cdot 4H_2O$ forms above 21.4 "C.

CRYSTALLIZATION OF A QUATERNARY MIXTURE

A quaternary mixture is a solution containing two salts without a common ion, e.g., a solution of KCl and $MgSO_4$, or KCl and

$NaNO_3$. On crystallizing such mixtures, complex products are usually obtained which may contain four or more different species. For example, on crystallizing a mixture of KCl and $MgSO_4$, the following equilibrium will be established:

$$2KCl + MgSO_4 \rightleftharpoons K_2SO_4 + MgCl_2$$

and therefore the crystals obtained will be composed of KCl, $MgSO_4$, K_2SO_4, and $MgCl_2$.

Conversion reactions

Under certain conditions, a conversion reaction takes place in a quaternary mixture resulting in two salts only. The reason is that in aqueous solutions, the salts are completely ionized and the less soluble salt will crystallize first. Three types of conversion reactions can be identified:

A system without a transition temperature

In the quaternary system NH_4HCO_3–NaCl, it is possible to crystallize $NaHCO_3$ by cooling because of its lowest solubility (Figure 23.20):

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl$$

This is the basis of Solvay Process for the manufacture of Na_2CO_3 which is then obtained by the decomposition of $NaHCO_3$.

A system with a single transition temperature

In the quaternary system NaCl–$MgSO_4$, it is possible to crystallize $Na_2SO_4 \cdot 10H_2O$ and keep $MgCl_2$ in solution (Figure 23.21):

$$MgSO_4 + 2NaCl + 10H_2O \rightleftharpoons Na_2SO_4 \cdot 10H_2O + MgCl_2$$

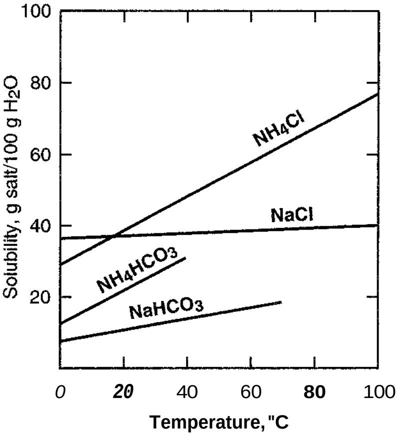

Figure 23.20: Solubility data for the system NH_4HCO_3 + NaCl $NaHCO_3$ + NH_4Cl

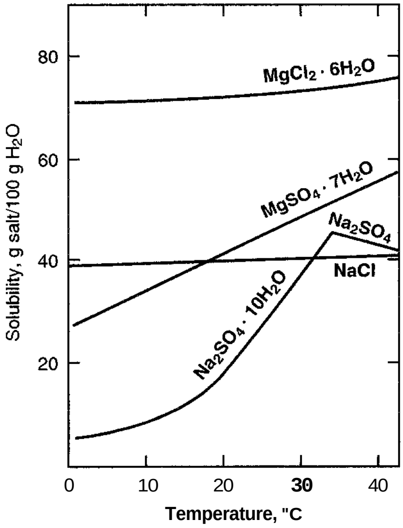

Figure 23.21: Solubility of salts in the quaternary system NaCl–$MgSO_4$.

This takes place only if crystallization is conducted below the transition temperature of sodium sulfate since under these conditions $Na_2SO_4 \cdot 10H_2O$ has the lowest solubility. Crystallization above the transition temperature results in the deposition of NaCl while $MgSO_4$ remains in solution because under these conditions, it is NaCl that has the lowest solubility. This method is used industrially to transform $MgSO_4$ into $MgCl_2$.

A system with two transition temperatures

In the quaternary system $NaNO_3$–KCl, it is possible to transform KCl into KNO_3 (Figure 23.22):

$$NaNO_3 + KCl \rightleftharpoons KNO_3 + NaCl$$

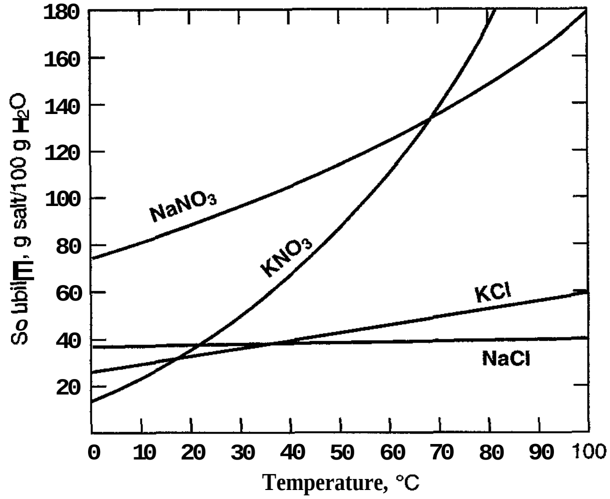

Figure 23.22: Solubility data for the system $NaNO_3$ + KCI KNO_3 + NaCl.

This takes place only if crystallization is conducted either below 20 "C or above 32 "C, the two transition temperatures that control the formation of KNO,. If crystallization is conducted below 20 "C, then under these conditions KNO_3 has the lowest solubility and therefore will be the first to crystallize. If crystallization is conducted above 32 "C, NaCl will have the lowest solubility and therefore will crystallize first. The first temperature represents the intersection of the KNO_3 and KCl solubility curves, while the second represents that of NaCl and KCl. It is evident, therefore, that either below 20 "C or above 32 "C the above equilibrium will be shifted to the right. This reaction is used industrially to convert the naturally occurring sodium nitrate into potassium nitrate using the naturally occurring potassium chloride (sylvite). It is conducted in the following way: **A** mixture of

$NaNO_3$ and KCl is dissolved in hot water. The solution is allowed to crystallize above 68 °C to deposit NaCl which is removed by centrifugation. The mother liquor is then cooled to below 32 °C to crystallize KNO_3.

FRACTIONAL CRYSTALLIZATION

This is one of the oldest methods for the separation of compounds of chemically similar metals. It depends on small differences which are magnified by repeated operations. Although in recent years it has been extensively replaced by ion exchange and solvent extraction which are faster and less tedious, nevertheless, the method still finds application particularly as a method of purification. Two conditions, however, must be satisfied for the salt to be purified:

- It must not interact with the impurity, i.e., it does not form a solid solution or a double salt.
- It must be more soluble at high than at low temperatures, otherwise much of it will remain in solution upon cooling, i.e., the yield will be low.

To obtain a pure sample by a single fractional crystallization, the amount of impurity must be relatively small. If this is not the case, then the process must be repeated many times, i.e., dissolution and recrystallization.

ENGINEERING ASPECTS

A selected method of crystallization depends on the nature of the solution available. For example, refrigeration is necessary to crystallize Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, while the following methods of crystallization by evaporation are widely used.

Solar crystallizers

This method is used for evaporating sea water or brines from wells for the large recovery of sodium chloride or other salts. For this purpose, large ponds are constructed adjacent to the source of the brine. The following points are worth noting:

- Ponds are prepared on compacted clay surface and may be lined with plastic layers to prevent leakage; then they are filled with brine.
- Evaporation of water from the brine takes place at a rate depending on the weather conditions. The climate in the region must show high yearly evaporation and low rainfall. A region where there is 1 cm evaporation per acre is equivalent to 550 000 liters or 550 tons of water.
- In hot regions, e.g., in Utah, it has been estimated that 5000 kilocalories of energy per day per square meter is available.
- Lake brine is fed into the ponds by gravity or by pumping depending on the elevation.
- When solids build up to a certain degree, the mother liquor in the pond is pumped into an adjacent pond, and the solids are collected.
- When the separation of certain impurities is possible, evaporation is conducted until a certain concentration is reached, the solution is then pumped forward to another pond to allow impurities to crystallize out. The saturated solution is then pumped again to crystallization ponds of much smaller size where continued evaporation drops the crystals to the bottom.
- Solids deposited are collected by special machines called “harvesters” (Figure *23.23)* and then stockpiled. These are usually crushed, mixed with a saturated brine then pumped as a slurry to storage tanks.

Vacuum crystallizers

Crystallization in this method takes place by vacuum evaporation. Equipment for this purpose may be a single-effect (Figure *23.24)* or a multiple-effect evaporator (see page *172).* Due to convection currents, the solution is continuously moving and as a result the crystal nuclei produced in these evaporators are uniformly surrounded with saturated solution and hence they grow in their normal form. Agitation keeps the crystals suspended in the solution where growth can occur.

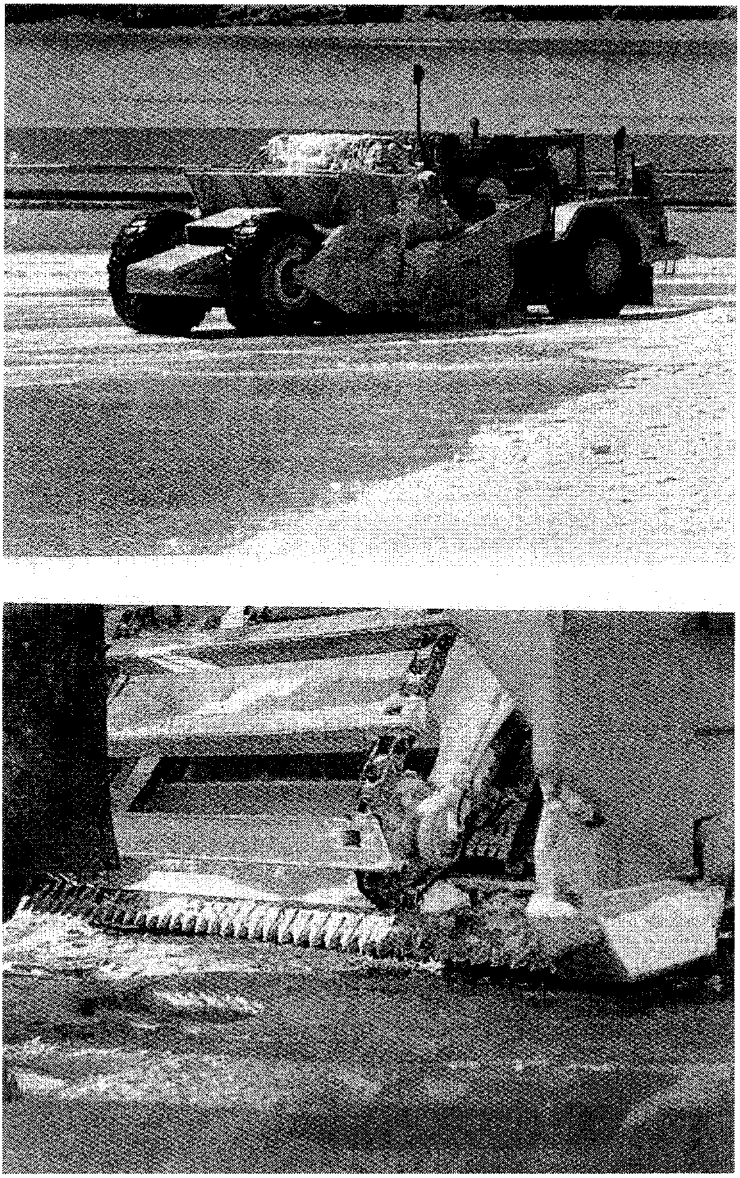

Figure 23.23: Equipment for harvesting deposited solids from solar ponds.

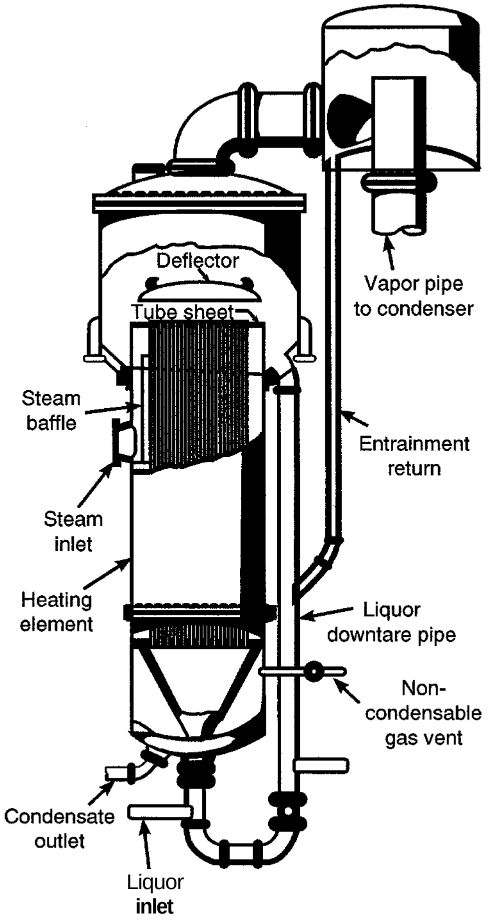

Figure *23.24:* Vacuum crystallizer.

Spray drying

In this method, the brine solution is sprayed in chambers heated with exhaust gases from gas-fired system. The crystals formed are collected at the bottom of the chamber while the exit gases are passed in a heat exchanger to recover their heat.

Submerged combustion

In this method of evaporation, a carbonaceous fuel is burned below the surface of the brine. The resultant water vapor and combustion gases leave the vessel together. These can be passed in a condensing tower–heat exchanger to condense the water vapor and recover the sensible heat in the combustion gases.

APPLICATIONS

Crystallization processes are conducted industrially on the following solutions:

- Surface and subterranean waters
- Leach solutions of salt deposits
- Hydrometallurgical solutions

The following points are worth noting:

- The first two processes are major operations and each usually produces a multiple of products. Crystallization of salts of non-ferrous metals is of minor importance and is largely displaced by solvent extraction.
- The production of sodium carbonate from these sources displaced the synthetic material made by the Solvay Process in USA.
- While lithium and magnesium are produced industrially from other terrestrial non-salt sources, such as spodumene (a silicate) and dolomite (a carbonate), respectively, boron, potassium, and sodium are only produced from surface waters and salt deposits. Another noted magnesium recovery operation is that by precipitation as a *hydroxide* from sea water.
- A salt deposit may contain brines on top or below. For example, Searles Lake in California is a dry lake, but about 40 meters below the surface there is a large body of complex brines from which many chemicals are extracted.
- The same product may be obtained either from surface and subterranean waters or from leach solutions of a salt deposit, e.g., Na_2CO_3, Na_2SO_4, and others.
- Brine from one edge of a large lake may be treated for one product while from another edge of the same lake another product is

obtained because of the irregular composition of the lake. For example, at Searles Lake or the Great Salt Lake, different products are obtained at different points.

- A deposit may be in form of a lake in the wet season and as a salt deposit during the dry hot season.
- Composition and salinity of a lake may vary with depth, for example, in the Dead Sea.
- Composition of a saline deposit in contact with brine changes with change of season because of changes in solubility and double salt formation as a function of temperature.

Surface and subterranean waters

A variety of salts are recovered from surface and subterranean waters. For example, sodium chloride, magnesium chloride, sodium borate (borax), and lithium chloride. Tables 23.3 to 23.5 give analysis of some natural brines. In addition, some subterranean brines and oil well brines are a source of iodine, for example, in USA. Seawater contains about 0.05 ppm of iodine which is too low for economic recovery. However, some seaweeds extract iodine from seawater and accumulate it in their cell structure. When they are burned properly, the resulting ash contains 1.4–1.8% iodine. Iodine also occurs in the caliche deposits in Chile in two crystalline forms: lautarite, CaI_2O_6, and dietzeite, $7CaI_2O \cdot 8CaCrO_4$. This was a major source of the element as a by-product of the sodium nitrate industry until the 1960s.

Sodium chloride from the sea

Typical analysis of sea water is given in Table 23.3. From this ionic composition, a large number of compounds can be obtained. In general, the insoluble carbonates precipitate first, then the sulfates gypsum and anhydrite. The halite, NaCI, precipitates only after 91.7% of the sea water has evaporated. Along with the halite crystallization, the other minerals such as sylvite, KCl, carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, and langbeinite, $K_2SO4 \cdot MgSO_4$, are formed. Table 23.6 shows analysis of salt from sea water.

Table **23.3:** Composition of some natural brines.

	Great Salt Lake, Utah %	Searles Lake, California %	Dead Sea %	Sea water %
Na^+	8.6	9.3	3.4	1.06
Mg^{2+}	0.9	—	4.1	0.13
K^+	0.5	2.1	0.7	0.04
Ca^{2+}	—	—	1.6	0.05
Br^-	—	0.1	0.6	0.01
Cl^-	14.8	10.3	20.5	1.90
SO_4^{2-}	2.2	3.9	0.1	0.26
CO_3^{2-}	—	2.2	—	—
$B_4O_7^{2-}$	—	1.0	—	0.002
PO_4^{3-}	—	0.1	—	—
Total dissolved solids, g/100 g			28.0	3.4

Table *23.4:* Typical analysis of Searles Lake brine, pH 9.8, density 1.305.

	%
NaCl	17.0
Na_2SO_4	7.6
KCl	4.3
Na_2CO_3	4.2
$Na_2B_4O_7$	1.2
Na_2S	0.2
$NaLi_2PO_4$	0.07
Na_3PO_4	0.07

Table **23.5:** Average brine composition in the nucleus of the Salar de Atacama, Chile; density 1.226.

	g/L
Na^+	93.18
K^+	21.95
Li^+	1.96
Mg^{2+}	12.26
Ca^{2+}	0.30
SO_4^{2-}	23.29
Cl^-	192.00
B	0.84

Table 23.6: Composition of salt from sea water.

	%
Na^+	30.61
Mg^{2+}	3.69
Ca^{2+}	1.16
K^+	1.10
Cl^-	55.04
SO_4^{2-}	7.64
HCO_3^-	0.41

Lithium from natural brines

Lithium in brines can be as low as 200 ppm and still the occurrence be a viable reserve (Table 23.7). The other elements that are present in brine restrict the ease of recovery. Lithium chloride is more soluble than many other chlorides. The concentrated LiCl solution obtained is then treated chemically to precipitate Li_2CO_3 (see page 616).

Table *23.7:* Lithium content in natural brines.

Origin and location	g/L
Brines associated with oil wells USA	0.1–0.5
Geothermal brines Imperial Valley, California	0.2
Subsurface brines Clayton Valley, Nevada	0.3
Salt lakes	
Salar de Atacama, Chile	1.3
Salar de Uyuni, Bolivia	0.3
Searles Lake, California	0.07
Great Salt Lake, Utah	0.04

Salar de Atacama, Chile. The brine contains about 2 g/L Li. **A** non-porous polyvinyl chloride liner is used in the solar pond (Figure 23.25). The brines are mixed from different locations to precipitate gypsum and produce essentially a chloride brine. During evaporation halite, sylvinite, carnallite, and bischofite precipitate and the lithium concentration increases to 20% LiCl *(43* g/L Li). The precipitated salts are removed and stockpiled.

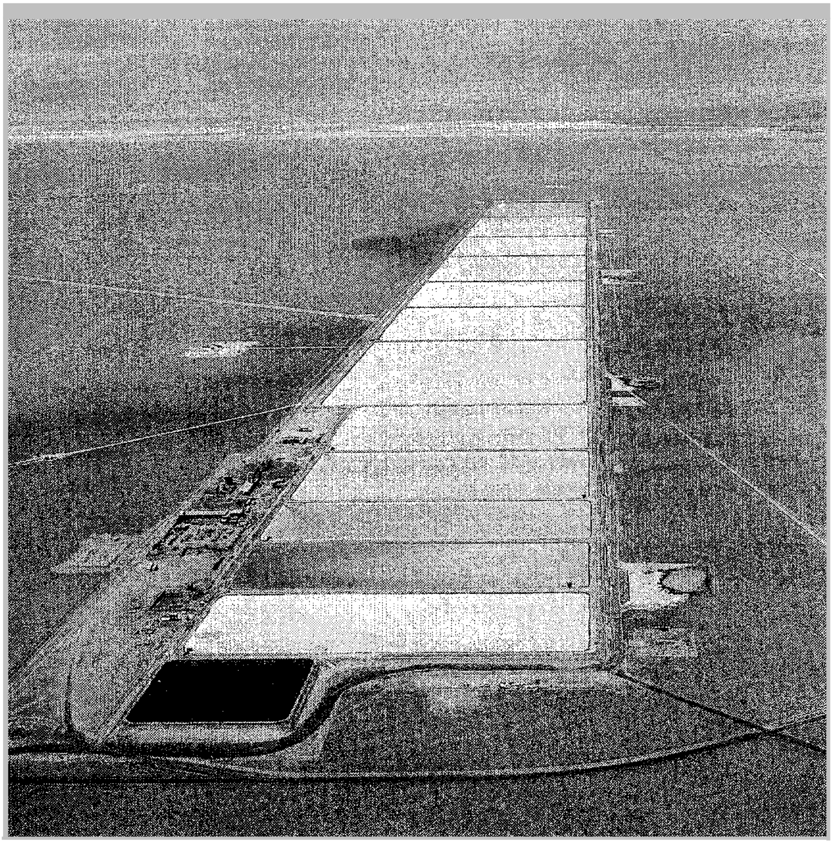

Figure *23.25:* Crystallization of lithium salts by solar evaporation at Salar de Atacama, Northern Chile; 252 acres lined with polyvinyl chloride (Foote Mineral Company).

Magnesium chloride

Magnesium chloride is found in many brines in association with KCl and NaCl. The basis of separating KCl from $MgCl_2$ can be understood from Figure 23.26 showing the system $KCl-MgCl_2-H_2O$ and Table **23.8.** All solutions are unsaturated within the boundary line AEFB, outside are heterogeneous mixtures of salts and solution. If a solution of composition X is evaporated isothermally at 25 °C, the concentration of the solution increases until line AE is reached. Further evaporation deposits KCl until the composition of the solution reaches E where carnallite forms. If the deposited KCl is not removed, it is dissolved and redeposited as carnallite. Carnallite is deposited until F is reached where $MgCl_2 \cdot 6H_2O$ also is deposited along with the carnallite. Potassium chloride can be separated from carnallite by adding sufficient water to dissolve all the $MgCl_2$ **and** form a solution of composition E. This dissolves only about 7.5% of the KCl present and the other 92.5% remains behind as a solid which can be separated.

Table 23.8: Composition of the solid phases in the system KCl–$MgCl_2$–H_2O.

Point	Solid phases	moles/1000 moles H_2O	
		K_2Cl_2	$MgCl_2$
A	KCl	44	0
B	$MgCl_2 \cdot 6H_2O$	0	108
E	KCl + carnallite	5.5	72.5
F	$MgCl_2 \cdot 6H_2O$ + carnallite	1	105

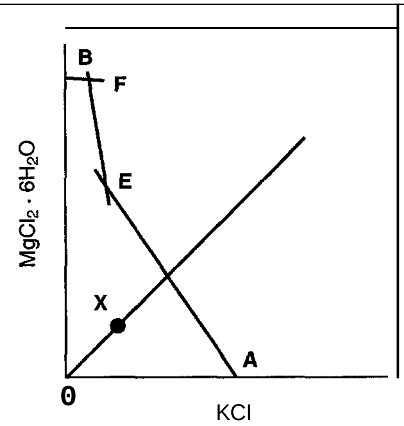

Figure *23.26:* Solubility diagram in the system $MgCl_2 \cdot 6H_2O$ and KCl; formation of the double salt carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ at E and F (see Table 23.8).

Dead Sea. A typical composition of Dead Sea brine is in g/L: 41 Mg^{2+}, 17 Ca^{2+}, 40 Na^+, 7.5 K^+, 215 Cl^-, 5 Br^-, and 0.65 SO_4^{2-}; Sp. gr. 1.220. A flowsheet for processing the sea water is shown in Figure 23.27. The water of the Sea is pumped into large evaporation basins which cover an area of about 130 km^2. When the total salt concentration reaches about 350 g/L, NaCl begins to crystallize and continues to do so during further evaporation until the volume of the water has diminished to about half of its original value. At this stage, about 90%

of the NaCl and more than 95% of the $CaSO_4$ are crystallized. The brine (mother liquor) is then transferred to other basins where evaporation is continued, and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) together with some NaCl begins to separate. A carnallite slurry containing 10–20% solids (crystals), is then pumped to thickeners and then vacuum filters. This filter cake forms the basis for recovering $MgCl_2$ and KCl.

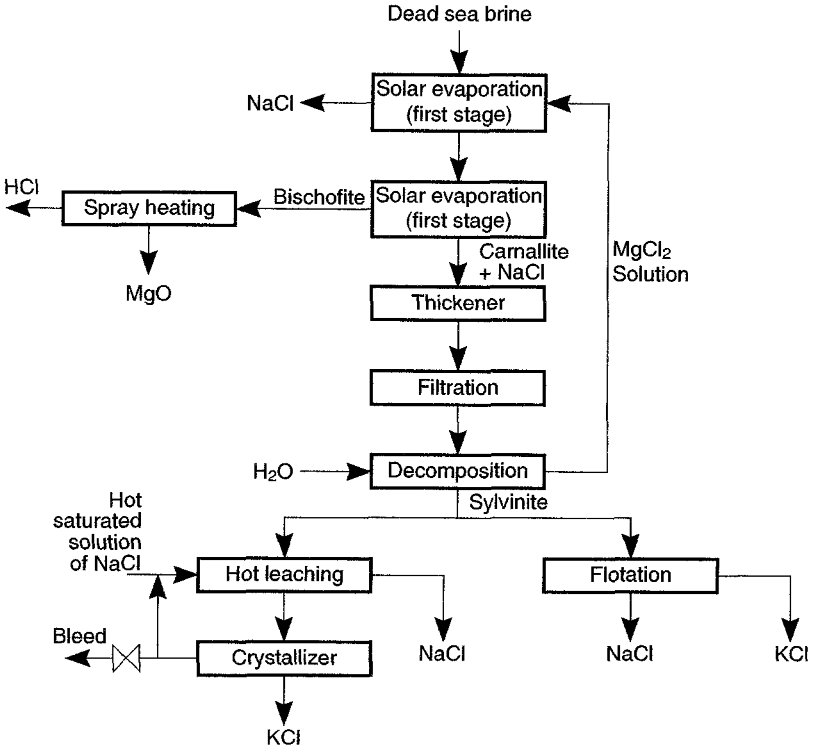

Figure 23.27: Processing of Dead Sea brine. Carnallite = $KCl \cdot MgCl_2 \cdot 6H_2O$, Bischofite = $MgCl_2 \cdot 6H_2O$, Sylvinite = KCl + NaCl. Flotation is an option for separating KCl and NaCl.

At first, $MgCl_2$ is removed by water leaving behind a solid phase of sylvinite (KCl + NaCl). Two methods are used for separating NaCl from KCl. In one method, the mixture is slurried and long-chain fatty amines are added to float KCl. In the other method, the salt mixture is leached by a hot saturated solution of NaCl. After thickening and centrifugeing, the hot brine, now saturated with respect to both salts, is allowed to cool; only KCl crystallizes out because its solubility in water rises steeply with temperature whereas that of NaCl is almost constant.

When the $MgCl_2$ brine is evaporated, bischofite ($MgCl_2 \cdot 6H_2O$) is formed. On heating the hexahydrate, the solid dissolves in its own water of crystallization. This brine is then thermally hydrolyzed in a spray reactor at 800 °C to form MgO and HCl. Other chlorides which include NaCl, KCl, and $CaCl_2$ are not decomposed. They are removed from the MgO by washing, which in turn is converted to $Mg(OH)_2$. It is then dried, calcined back to MgO, then sintered. Bromine is also recovered as a by-product of this process.

Great Salt Lake. The brine contains about 1% Mg; it is concentrated in a system of solar evaporating ponds to about 7.5% Mg^{2+}, 4% SO_4^{2-}, 0.5% Na^+, 0.7% K^+, 0.1% Li^+, and 20% Cl^-. The solution is then treated with $CaCl_2$ to precipitate $CaSO_4$, KCl, and NaCl which are removed in a thickener. Anhydrous magnesium chloride is then obtained from this solution by spray drying evaporation. The product is used directly for the electrolytic production of magnesium. In Utah, solar evaporation is possible only through the summer months. About 50% of the magnesium chloride is recovered in this way, the rest precipitates as other salts of magnesium. Figure 23.28 shows the Amax Magnesium operation on the shores of the Great Salt Lake.

Sodium sulfate

Natural sodium sulfate is extracted from brines in California, Texas, and Utah. In Saskatchewan and Alberta, sodium sulfate is recovered by solution mining. There are also some natural sodium sulfate processing in Russia, Spain, and Mexico. The usual method of recovering Na_2SO_4 in Canada has consisted of pumping strong brine from the surface of the deposit during the summer and storing it in large ponds. When the cold weather comes in late fall, the brine in the pond cools sufficiently to allow a crop of Glauber's salt crystal to form and sink to the bottom. The mother liquor, which contains some Na_2SO_4 as well as other salts, is either run back to the deposit or to a disposal area. During the winter, the salt in the pond is bulldozed in trenches to allow some liquor drainage and then trucked to storage.

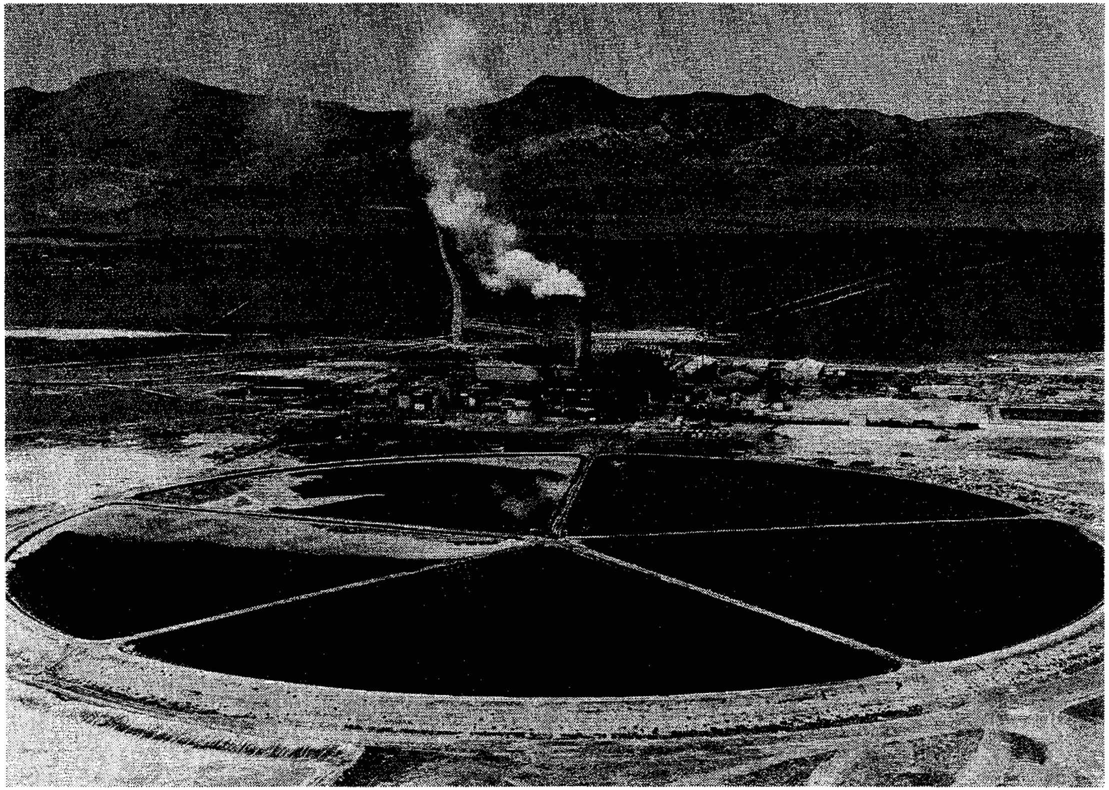

Figure 23.28: Crystallization of magnesium chloride on the shores of the Great Salt Lake, Utah (Amax).

In-situ leaching with hot water at about 38 °C is conducted in some mines in Canada to get a solution rich in Na_2SO_4. Water for leaching is heated by the hot gases produced from the submerged combustion evaporators used to crystallize sodium sulfate. Dehydration of Glauber's salt is usually achieved in fluidized bed, rotary kilns, or other equipment.

Leach solutions of salt deposits

Surface salt deposits are generally mined, dissolved in water, then filtered to separate insoluble gangue minerals. The clear solution is then evaporated to crystallize the desired salt. Underground deposits may be mined, brought to the surface, and treated similarly, or directly leached in situ and the solution then allowed to crystallize. Typical operations are the recovery of potash, trona, borax, sodium chloride, sodium sulfate, and carnallite.

Potash

Potash is the commercial name for potassium salts and is usually expressed as K_2O. Almost all commercial sources of potash contain sodium chloride as the major impurity, together with varying amounts of calcium and sodium sulfates, and magnesium chloride. In potash recovery, the slurry is pumped to hydrocyclones to separate calcium :sulfate as an overflow. The underflow is then floated using amines and oil. The concentrate obtained is leached with a minimum amount of water to remove sodium chloride, then dried, and transported to storage silos. Figure 23.29 shows a view of a potash recovery plant in Canada.

Potassium sulfate is produced from kainite, $KCl \cdot MgSO_4 \cdot 3H_2O$, by first treatment with a solution of $MgSO_4$ to transform it to schonite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. Schoenite is then decomposed with water to get solid K_2SO_4 and a solution of $MgSO_4$ for recycle.

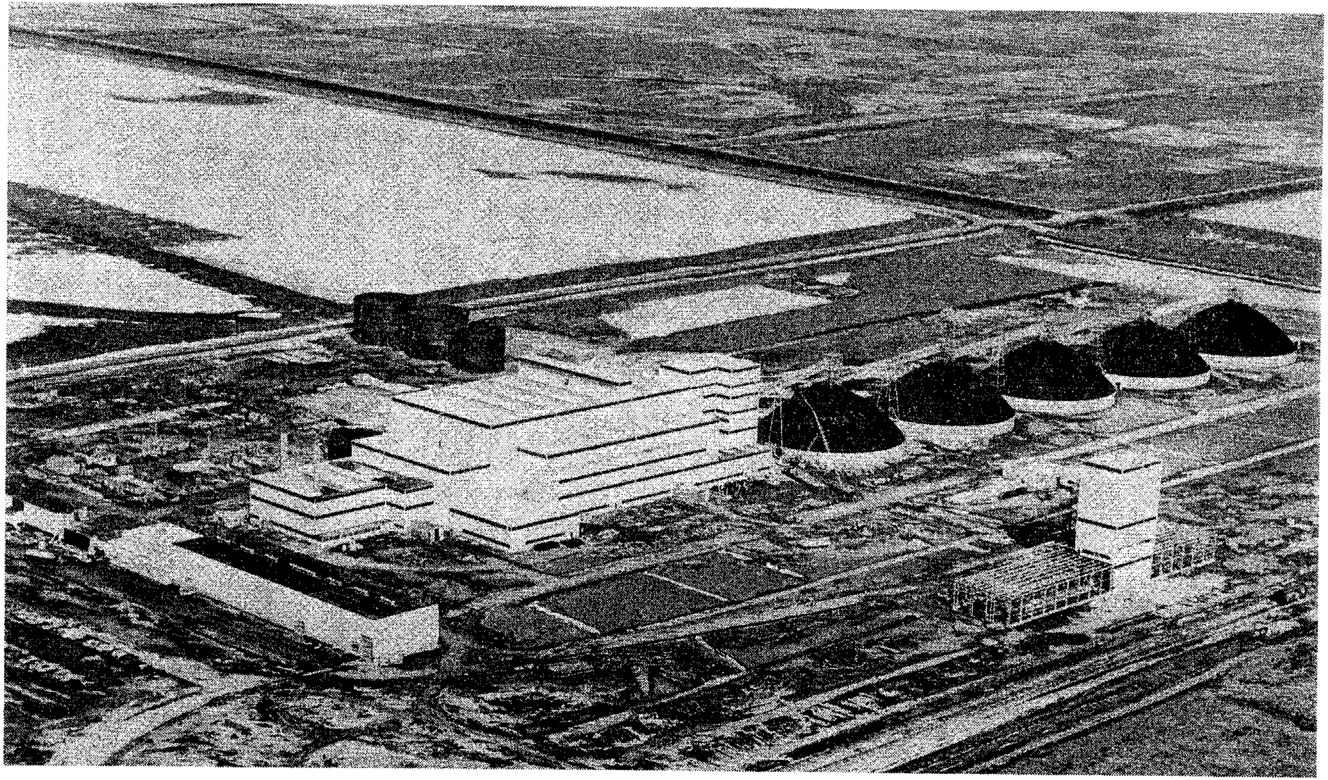

Figure 23.29: Potash recovery plant in Canada.

Trona

The mineral trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, because of its bicarbonate content, could have precipitated in nature only in the presence of abundant CO_2. This was provided by the by-product of decaying organic remains of plants and animals which sank to the stagnant, reducing lake bottom. The CO_2 in the air also aided in this formation. Trona is usually converted into Na_2CO_3 by two methods:

The monohydrate process. The crushed trona is calcined in a rotary kiln to remove H_2O and CO,, the product is then dissolved in water, filtered to remove insoluble impurities, then heated in triple-effect evaporators whereby $Na_2CO_3 \cdot H_2O$ crystals form. These are then calcined to anhydrous Na_2CO_3 which is known in industry as the dense soda ash.

The sesquicarbonate process. In this process, the crushed trona is first dissolved to remove insoluble impurities and the solution crystallized to form the sesquicarbonate which can be used as such or calcined to soda ash of light or intermediate density.

The complex brines of the lower level of Searles Lake are also treated for Na_2CO_3 recovery. This is usually done by first treating the brine with CO_2 to crystallize the bicarbonate:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

'This is then calcined to Na_2CO_3. **A** second dissolution and crystallization may be necessary to get a high-purity product.

Borax

Borax or sodium borate, $Na_2B_4O_7 \cdot 10H_2O$, and other boron minerals are found in surface mines in California (Figure 23.30), underground mines in Turkey, or in surface waters, e.g., Searles Lake, Great Salt Lake, and Salar de Atacama. Surface or underground ore is purified by dissolution in water and filtration followed by vacuum crystallization. Boric acid is produced by acidification of the purified solution:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$$

Figure 23.30: Mining and processing of borax at the US Borax Mine, Boron, California.

Borax is also recovered from the upper level of Searles Lake by cooling to about 15 °C. After separating these crystals, a second cooling to about 5 °C is carried out to crystallize Glauber's salt.

Caliche

Caliche or huanu, natural sodium nitrate deposits found in Chile, were once an important source of nitrate fertilizers and nitric acid manufacture before the NH_3 synthesis process. The deposits contain a variety of other salts; NaCl, $CaCl_2$, $MgSO_4$, KNO_3, NaCl, $NaIO_3$, $Na_2B_4O_7$, as well as sand and clays. It is usually purified by dissolution, filtration, and crystallization. The deposits are also an important source of iodine.

Carnallite

For many years, Germany monopolized the potash industry until potassium salts were discovered in Searles Lake in 1930. The German deposits at Stassfurt contained mainly carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$. The salt is dissolved in water, filtered to remove insoluble impurities, then evaporated to crystallize KCl. The mother liquor contains $MgCl_2$, RbCl, and KBr from which they are also recovered.

Hydrometallurgical solutions

Few metal recovery operations involve crystallization from leach solutions; some have been displaced by solvent extraction methods. Industrial sulfates are also prepared from hydrometallurgical solutions.

Aluminum from clay

Methods for the recovery of aluminum from clay are based on the crystallization of an aluminum salt from the leach solution; this is then decomposed to Al_2O_3 (see chapter 16). Aluminum sulfate for water treatment is also prepared from clay.

Chrome alum

When chromium ores are leached for the production of metallic chromium or its salts, separation from leach solution is usually achieved by adding an ammonium salt and crystallization of chrome alum (see chapter 11).

.Nickel sulfate

An important amount of nickel sulfate used by the electroplating industry is recovered as a by-product of electrolytic copper refining. Nickel impurity in the copper is solubilized during refining and is recovered from a bleed solution of the electrolyte by crystallization.

Copper sulfate

Copper sulfate for industrial purposes is prepared by dissolving copper in aerated H_2SO_4 followed by crystallization of the pentahydrate. It is also a by-product of electrolytic refining of copper.

Ferrous sulfate

Ferrous sulfate is prepared by dissolving scrap iron in dilute H_2SO_4 followed by crystallization of the heptahydrate. It is also a by-product of numerous hydrometallurgical operations, e.g., ilmenite leaching.

Preparation of anhydrous beryllium fluoride

Formation of double salts is applied in hydrometallurgy as a mean of obtaining certain anhydrous salts. Preparation of pure anhydrous halides is an important step in the metallurgy of reactive metals since these compounds can be reduced directly to the metals. Anhydrous beryllium fluoride cannot be prepared by dissolving $Be(OH)_2$ in HF solution, because on evaporating the solution, a tetrahydrate ($BeF_2.4H_2O$) crystallizes, which on drying hydrolyzes to the oxyfluoride $5BeF_2 \cdot 2BeO$. However, on evaporating a solution containing an equimolecular amount of beryllium fluoride an an alkali fluoride, e.g., NH_4F, crystals of anhydrous ammonium fluoroberyllate, $(NH_4)_2BeF_4$, are obtained from which anhydrous BeF_2 can be obtained by thermal decomposition:

$$(NH_4)_2BeF_4 \rightarrow BeF_2 + 2NH_4F$$

Separation of the lanthanides

The great similarity in chemical properties of the lanthanides has made their separation a problem of extraordinary difficulty, and separation by fractional crystallization was the earliest method attempted. The solubilities of some salts of the lanthanides which have been extensively used for separations are shown in Table 23.9. The general scheme for carrying out fractional crystallizations is shown schematically in Figure 23.31. The solution is evaporated till crystals are separated. It is then filtered, the mother liquor is evaporated further till more crystals separate, while the crystals from the first step are dissolved in water and then evaporated till crystals again separate. Crystals from the second crop are combined with the mother liquor of the least soluble fraction, and evaporated. The process is repeated many times until finally three fractions are obtained; one containing the least soluble constituents, a second containing the most soluble constituents, and a third containing constituents of middle solubility.

The initial material for the preparation of concentrates of lanthanides is monazite sand, xenotime, or bastnasite. **A** lanthanide oxide is obtained, which is dissolved, and the lanthanides are separated from it by fractional crystallization.

Separation of cobalt from nickel

Cobalt and nickel are separated from solutions containing equal amounts of the metal sulfates by the so-called pentammine complex process (**see** page *644)*. The separation is based on the fact that cobalt in the trivalent state is not decomposed by H_2SO_4 while nickel is. Consequently, when NH_3 is added to a solution containing cobalt and nickel sulfates, and air is bubbled through, cobalt(II) ammine is oxidized to the stable cobalt(III) pentammine complex, $[Co(NH_3)_5]^{3+}$. ’When dilute H_2SO_4 is then added, nickel ammine complex decomposes forming nickel ammonium sulfate which crystallizes out, while cobalt(III) pentammine remains in solution:

$$[Ni(NH_3)_4]SO_4 + H_2SO_4 \rightarrow NiSO_4 \cdot (NH_4)_2SO_4 + 2NH_3$$

Table 23.9: Solubilities of some lanthanide compounds.

	$M_2(SO_4)_3 \cdot 8H_2O$ g/100 g H_2O at 20°C	$M(BrO_3)_3 \cdot 9H_2O$	Dimethyl **phosphate**	$2M(NO_3)_3 \cdot 2Mg(NO_3)_2 \cdot 24H_2O$
Pr	12.74	196.1	64.1	7.70
Nd	7.00	151.3	56.1	9.77
Sm	2.67	117.3	35.2	24.55
Eu	2.56			
Gd	2.89	110.5	24.2	35.23
Tb	3.56	132.2	12.6	
Dy	5.07		8.24	
Ho	8.18			
Y	9.75		3.53	
Er	16.00		3.36	
Yb	34.78		1.35	
Lu	47.27			

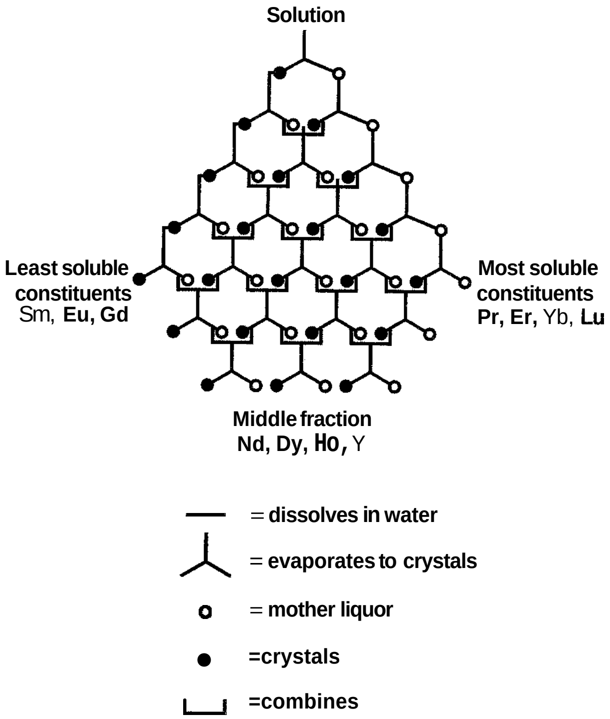

Figure 23.31: Fractional crystallization of the salts of the rare earths.

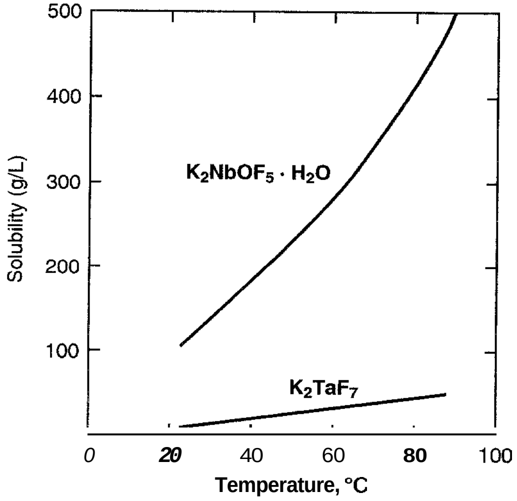

Figure 23.32: Solubility of complex fluorides in 1N HF.

Separation of niobium from tantalum

The difference in solubilities of K_2TaF_7 and K_2NbOF_5 has been used successfully to separate niobium from tantalum (Figure *23.32)*. The slurry containing the metal oxides is dissolved in 70% hydrofluoric acid, diluted, and heated near boiling. A potassium salt is added in sufficient quantity to form the complex fluorides of the niobium and tantalum present. The solution is filtered and allowed to cool. At room temperature, most of the tantalum salt crystallizes out while the niobium remains in solution.

Separation of zirconium from hafnium

Zirconium ores usually contain about 1% Hf. Separation can be achieved from HF leach solution by crystallization of the double fluoride K_2ZrF_6. The hafnium salt is more soluble and remains in solution. A pure airconium salt can be prepared by recrystallization (Figure *23.33)*.

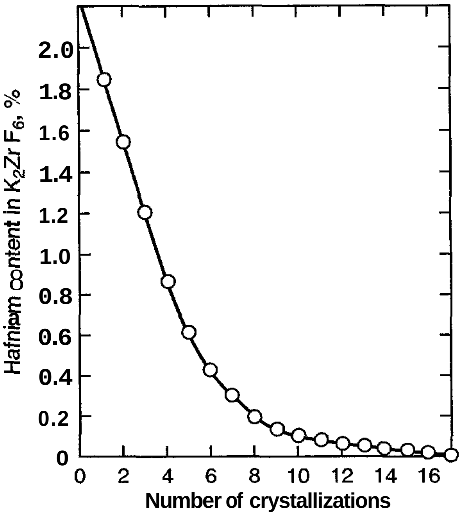

Figure 23.33: Separation of hafnium from zirconium by recrystallization of potassium fluorozirconate (Sajine and Pepeliaeva, 1955).

Chapter Twenty-Four

Hydrolytic and Ionic Precipitation

Introduction 593
Oxides. Hydrated Oxides. Hydroxides. and Hydroxy Salts .. 596
Oxides 598
Hydrated oxides 600
Hydroxides 600
Hydroxy salts 608
Polyacids and their Salts 610
Vanadates 611
Molybdates 611
Tungstates 613
Uranates 613
Dialuminates 616
Carbonates 616
Oxalates 618
Peroxides 618
Halides 618
Chlorides 618
Fluorides 621
Cyanides 622
Sulfides 623
Sulfites 625
Ammonium copper sulfites 625
Chevreul's salt 626
Metalloids 628
Summary 629

INTRODUCTION

Ionic precipitation is based on the fact that when a reagent is added to a solution containing metal ions. a compound is formed whose solubility is very low under these conditions that precipitation takes place immediately. For example. when sodium sulfide is added to a solution of $CuSO_4$, immediate precipitation of CuS takes place because Cu^{2+} ions and S^{2-} ions react to form a compound of very low solubility.

$$Cu^{2+} + S^{2-} \rightarrow CuS$$

This makes the difference between ionic precipitation and crystallization — in crystallization the compound precipitated has a high solubility and the proper conditions have to be found to allow it to form. The reagent used to effect the formation of a precipitate is called a *precipitant.* A variety of ionic precipitation methods are available.

The presence of phosphate ion in solution leads to the precipitation of most metals as *phosphates*:

$$3M^{x+} + xPO_4^{3-} \rightarrow M_3(PO_4)_x$$

This is undesirable since the phosphates produced must be processed further to separate the phosphate ion. The presence of arsenic in ores is also undesirable since it may contaminate the precipitates or cause disposal problems of solutions because of its toxicity. Therefore, its precipitation is of certain concern in hydrometallurgy. This is usually accomplished by precipitation as calcium or iron arsenate:

$$2AsO_4^{3-} + 3Ca^{2+} \rightarrow Ca_3(AsO_4)_2$$

$$AsO_4^{3-} + Fe^{3+} \rightarrow FeAsO_4$$

Table 24.1 gives the solubility of some phosphates and arsenates.

Table 24.1: Solubility of selected phosphates and arsenates.

	Compound	Solubility moles/1000 g H_2O
Phosphates	$AlPO_4$	7.6×10^{-10}
	$Ca_3(PO_4)_2$	8×10^{-7}
	$FePO_4$	1.1×10^{-11}
	$(UO_2)_3(PO_4)_2$	6.5×10^{-11}
Arsenates	$Ca(AsO_4)_2$	9.1×10^{-5}
	$FeAsO_4$	6.7×10^{-11}

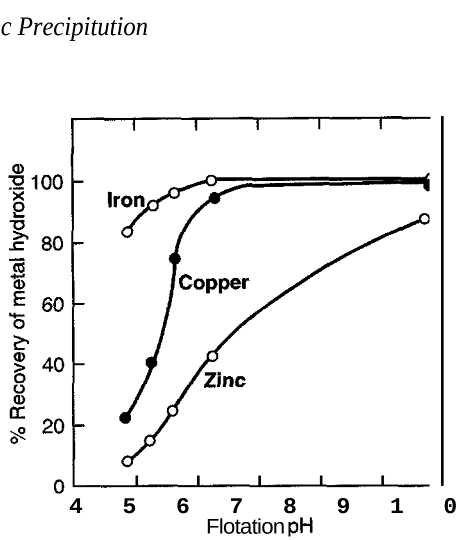

Figure 24.1: Effect of pH on the separation of metal hydroxides by flotation, using an ammonia collector; solutions contain 0.3 g/ L metal ion (Bearson and Ray, 1965).

Table *24.2:* Flotation of metal ions with soaps (Poltaramine, 1963).

Metals in solution	pH	Flotation time minutes
Fe	3.5–4.0	3
Cu	5.0–6.0	5
Zn	6.3–7.3	5–7
Co	8.5–10.0	7–10
Ni	9.0–10.0	15–20

Ion flotation is a technique that permits the recovery of metal ions from solution through the introduction of an appropriate cationic or ,anionic surface-active agent into the solution. The surface-active ,agent,called a collector, is added in stoichiometric amounts in relation to the metal content of the solution. It reacts with the metal ion to form an insoluble soap, and is levitated to the surface by gentle bubbling of air to form a foam which collapses into an insoluble scum. 'The optimum conditions for the ion flotation with soaps of C_{10} to C_{16} fatty acids are shown in Table *24.2.* When a metal is precipitated as the hydroxide, as little as one hundredth the stoichiometric amount of the collector, would be required to cause complete flotation of the precipitated hydroxide (Table *24.3).* It is possible to affect selective separations between different metals in solution by incremental pH control and stage flotation, the selectivity depending on the difference in pH values at which the metals precipitate and on the relative concentrations of the metals in solution (Figure 24.1).

Table *24.3:* Floatability of metal hydroxides (Baarson and Ray, 1965).

Metal	Concentration g/L	Flotation pH	Collector	Floatability index	Precipitant
Nickel	3.0	8.8	Armeen C	Fair	NH_4OH
Cobalt	3.0	9.1	Nro Fat 265	Fair	NH_4OH
Iron	0.25	5.8	Neo Fat 265	Excellent	NaOH
Chromium	*0.48*	6.0	ASLA[a]	Excellent	NaOH
Magnesium	0.125	10.8	ASLA[a]	Good	NaOH
Zinc	*0.1*	10.0	Neo Fat 265	Good	NaOH

a. Alpha-sulfolauric acid.

OXIDES, HYDRATED OXIDES, HYDROXIDES, AND HYDROXY SALTS

Metal ions in aqueous solution are highly solvated, i.e., they are bound to a number of H_2O molecules so oriented that the negative end of water dipole is directed toward the positively charged metal ion. The loss of H^+ from the bound water molecules takes place readily. That is why salt solutions are acidic. Stepwise dissociation of H^+ from the coordinated water molecules results in the successive replacement of H20 molecules by OH– groups. Each hydroxyl ion reduces the charge of the metal ion by one. For example, ferric ion reacts as follows:

$$[Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_5 \cdot OH]^{2+} + H^+$$

or simply:

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+$$

This process known as *hydrolysis* continues until an uncharged species is formed:

$$FeOH^{2+} + H_2O \rightarrow [Fe(OH)_2]^+ + H^+$$

$$[Fe(OH)_2]^+ + H_2O \rightarrow Fe(OH)_3 + H^+$$

When metal ions become electrically neutral, the ionic forces keeping them apart are thus removed, and therefore precipitation takes place.

It is evident that precipitation of a hydrolytic product can be favored by adding OH– ions which react with H^+ ions formed thus shifting the equilibrium to the right. When, however, the OH– ion concentration is high, some insoluble metal hydroxides react further to produce negative ions which are again soluble, e.g., aluminum and zinc hydroxides.

For each hydroxide there is, therefore, a narrow pH range within which its precipitation normally takes place from dilute solutions, as shown in Table *24.4*. According to this Table, separation of metals can be achieved by making use of the differences of pH at which the hydroxide precipitates. It should be noted, however, that the pH values given in Table *24.4* apply only to *0.02* molar solutions at room temperature. The relation between the pH at which the hydroxide precipitates and the concentration of the metal ion in solution can be derived from the following equilibrium:

$$M^{n+} + nOH^- \rightleftharpoons M(OH)_n$$

from which the equilibrium constant is given by:

$$K = \frac{1}{[M^{n+}][OH-]^n}$$

hence $-\log[M^{n+}] = n \times \text{pH} + \text{constant}$

Table *24.4:* pH for hydroxide precipitation from 0.02 molar solutions.

Metal	pH	Metal	pH	Metal	pH
Mg	*10.5*	Co(II)	*6.8*	Al	*4.1*
Ag	*8.0*	Y	*6.8*	Th	*3.5*
Mn(II)	*8.5*	Cd	*6.7*	In	*3.4*
La	*8.4*	Ni	*6.7*	Co(III)	*3.0*
Ce(III)	*7.4*	Pb	*6.0*	Ce(IV)	*2.7*
Hg(II)[a]	*7.3*	Be	*5.7*	Hg(II)[b]	*2.0*
Pr	*7.1*	Fe(II)	*5.5*	Sn	*2.0*
Nd	*7.0*	Cu(II)	*5.3*	Zr	*2.0*
Zn	*7.0*	Cr	*5.3*	Fe(III)	*2.0*

a. From chloride solution.
b. From nitrate solution.

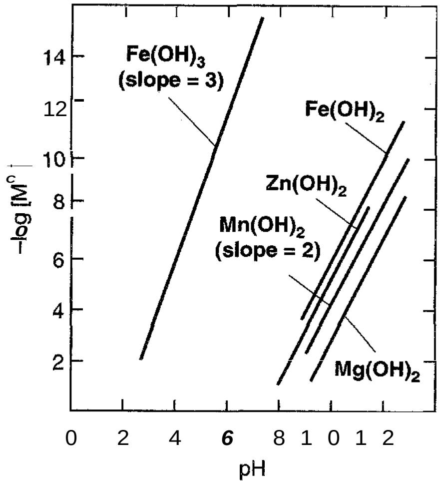

Figure *24.2:* Relation between pH and metal ion concentration for the deposition of hydroxides.

Therefore, the plot of $-\log[M^{n+}]$ against the pH gives a straight line with slope 1, 2, or 3 for mono-, di-, ot trivalent metals, respectively. This is illustrated in Figure *24.2.*

Hydrolytic reactions may lead to the precipitation of oxides, hydrated oxides, hydroxides, or hydroxy salts depending on temperature, concentration of solution, and the characteristics of the metal ion itself. High temperature increases greatly the rate of hydrolysis. Sometimes, the reaction is conducted in an autoclave to withstand the high pressure generated due to the vapor pressure of water when hydrolysis is conducted above the boiling point.

Oxides

The most important oxide precipitated industrially is TiO_2 and to a minor extent Cu_2O.

Titanium dioxide. One method of preparing pure TiO_2, used as a white pigment, is based on the hydrolysis of titanyl ion TiO^{2+} which is obtained by leaching the titanium raw material such as ilmenite or titanium slag. The hydrolytic reaction is:

$$TiO^{2+} + H_2O \rightarrow TiO_2 + 2H^+$$

Hydrolysis is usualy conducted by adding a seed of freshly precipitated TiO_2 from a previous batch to the solution and agitating the slurry for few hours at room temperature. When precipitation is complete, the slurry is filtered and the solids are dried. Figure 24.3 shows a typical TiO_2 powder as needed by the pigment industry. Titanium dioxide precipitated from sulfate medium is in form of anatase (density 3.84, refractive index 2.554). To obtain the rutile form which has a higher density (4.26) and a higher refractive index (2.903) and thus more suitable as a pigment, the anatase must be heated at 800 °C to effect this phase transformation.

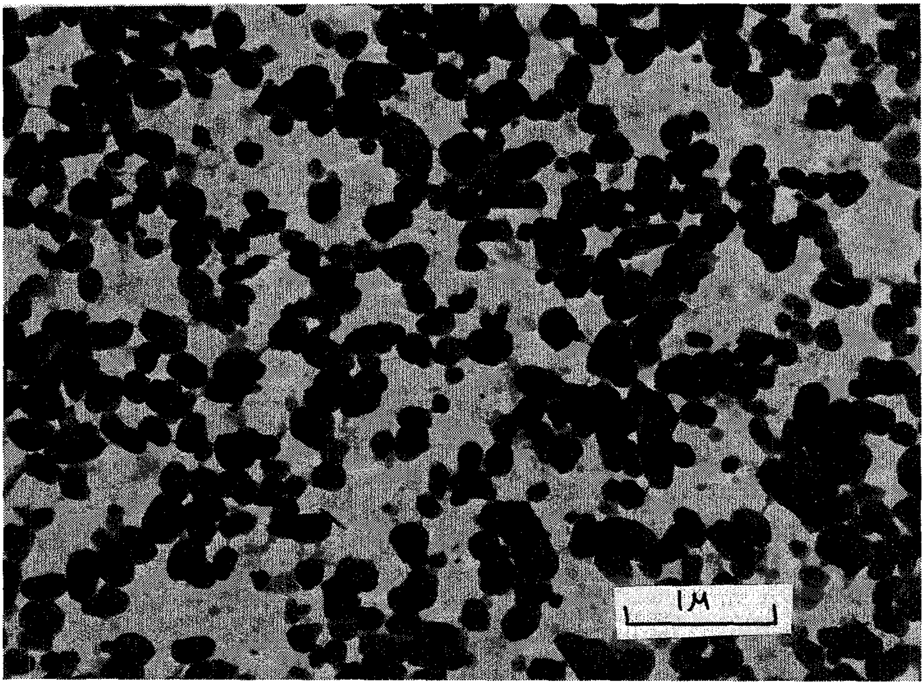

Figure *24.3:* Finely divided TiO_2 precipitate (average particle size 0.24 microns) needed for the pigment industry. Magnification 20 000 (Tioxide Canada).

Cuprous **oxide.** Cuprous chloride when reacted with calcium hydroxide precipitates red cuprous oxide:

$$CuCl_{(s)} \rightarrow Cu^+ + Cl^-$$

$$Cu^+ + OH^- \rightarrow CuOH$$

$$2CuOH \rightarrow Cu_2O + H_2O$$

The process was used on a commercial scale in Germany.

Hydrated oxides

Niobium and tantalum ores are usually leached with hydrofluoric acid then hydrated oxides are precipitated by adding ammonium hydroxide, e.g.:

$$NbF_6^- \rightarrow Nb^{5+} + 6F^-$$

$$2Nb^{5+} + (5+n)H_2O \rightarrow Nb_2O_5 \cdot nH_2O + 10H^+$$

or

$$2NbF_6^- + 10OH^- + nH_2O \rightarrow Nb_2O_5 \cdot nH_2O + 12F^- + 5H_2O$$

Hydroxides

Precipitation of hydroxides represents a major hydrometallurgical operation since aluminum is precipitated in this form and a large tonnage of this material is produced. Other hydroxides produced industrially are those of beryllium, magnesium, and cobalt.

Aluminum. In the Bayer Process for leaching bauxite, an alkaline sodium aluminate solution is obtained from which aluminum hydroxide is precipitated:

$$[AlO(OH)_2]^- + H_2O \rightarrow Al(OH)_3 + OH^-$$

The basis of this process is obtaining a crystalline product (Figure *24.4)* easy to filter and wash so that it is of the highest purity. The alkaline medium is the only medium suitable for obtaining the desired product. To obtain a thoroughly crystalline precipitate, the aluminate solution is stirred with a large excess of aluminum hydroxide “seed”. The seed has two functions:

- It reacts with the OH^- ions thus shifting the above equilibrium to the right and favoring precipitation.
- It acts as a nucleus on which $Al(OH)_3$ precipitates.

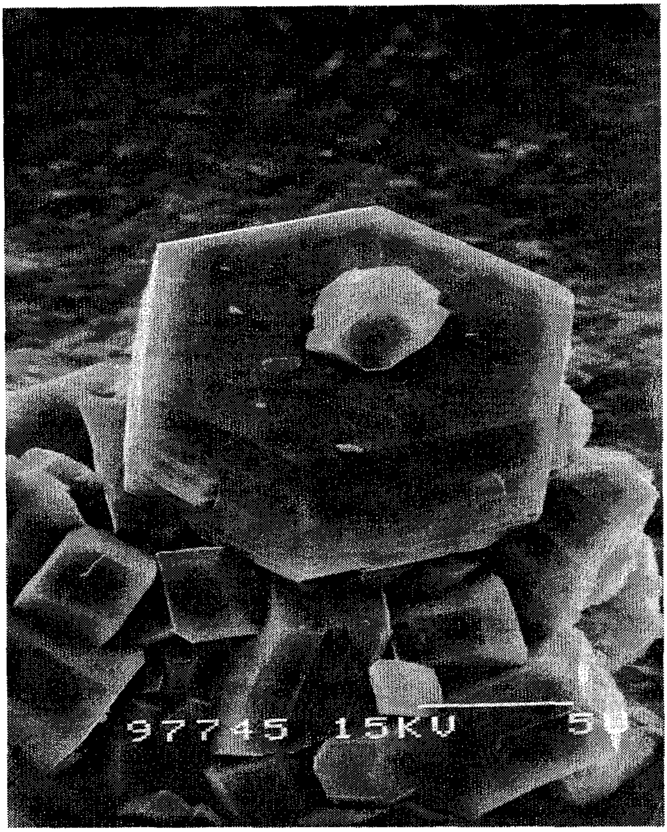

Figure 24.4: Electron photomicrograph showing the crystalline nature of aluminum hydroxide precipitated from the alkaline solution (Bayer Process). The edge of the hexagon is about 8 μ and its thickness is about 4 μ (Alcan).

The solution together with a seed is left in the vessel for about 4 days (Figure 24.5). Continuous agitation and cooling to 25–35 °C is necessary to permit the formation of coarsely crystalline products. A finely crystalline product is undesirable since it causes excessive dusting during calcination. In practice, the operation is conducted as follows: The slurry after precipitation is allowed to settle. The finely suspended crystals are recycled as seed, and coarsely settled crystals are withdrawn, filtered, washed, and calcined. The mother liquor is evaporated, and its alkalinity is adjusted and recycled for leaching another bauxite batch (Figure 24.6).

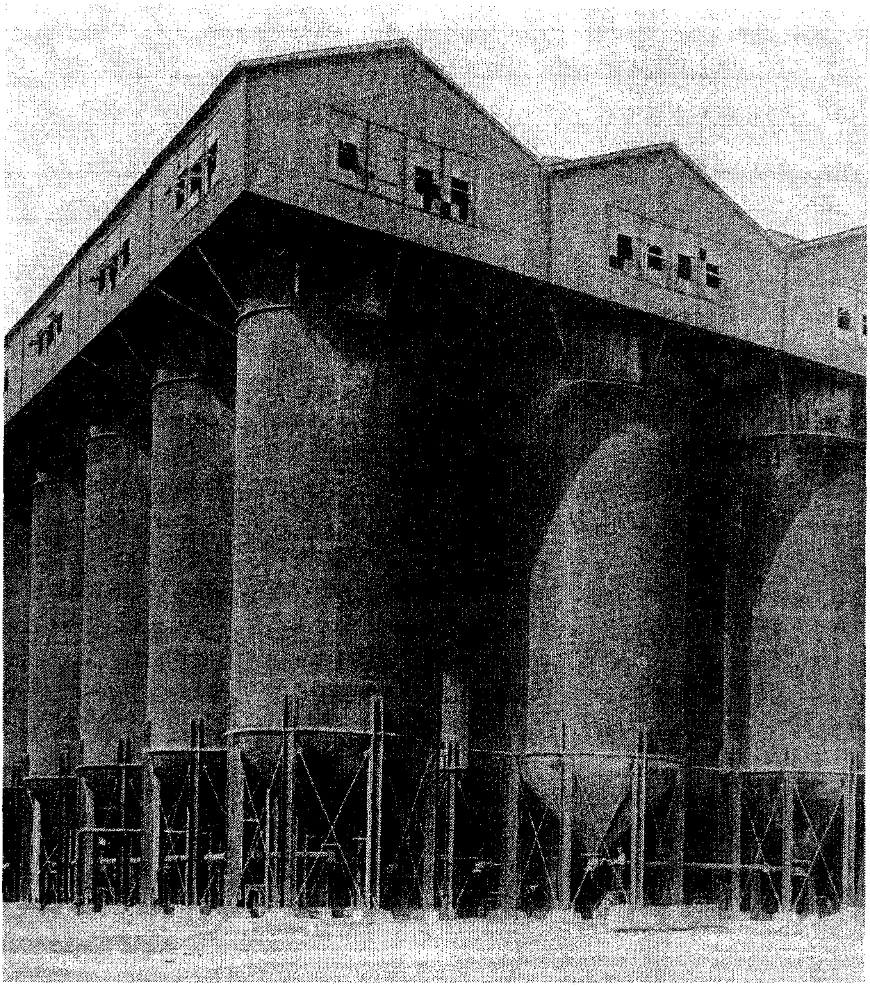

Figure *24.5:* Precipitating tanks for aluminum hydroxide.

A highly charged ion such as Al^{3+}, in acidic solution will be hydrated by six water molecules. Each hydrated water molecule will be hydrogen-bonded to other water molecules. If base is added to the solution, hydronium ions are removed and the positively charged hydrogen atoms on the hydrate water molecules progressively release electrons to the Al^{3+} and transfer through the hydrogen bond to a neighbor H_2O (or $OH-$) to form either H_3O^+ to be neutralized or H_2O directly. When three protons have been stripped from the hydrated ion in this way, it no longer has any net charge. The absence of electrostatic repulsion allows the $Al(OH)_3(H_2O)_3$ molecules to agglomerate through shared OH units and hydrogen bonding, which can include intermediate water molecules. Such a structure does not have the symmetry of a crystalline hydroxide. Since the hydrogen bonds are much weaker than covalent bonds or ionic attraction, the agglomerate is soft and ill-defined. In an alkaline medium, however, aluminum is present as $[Al(OH)_4]^-$ ion. The hydrolyzing power of Al^{3+} is nullified by the excess negative change. Therefore, aluminum precipitates as a crystalline material.

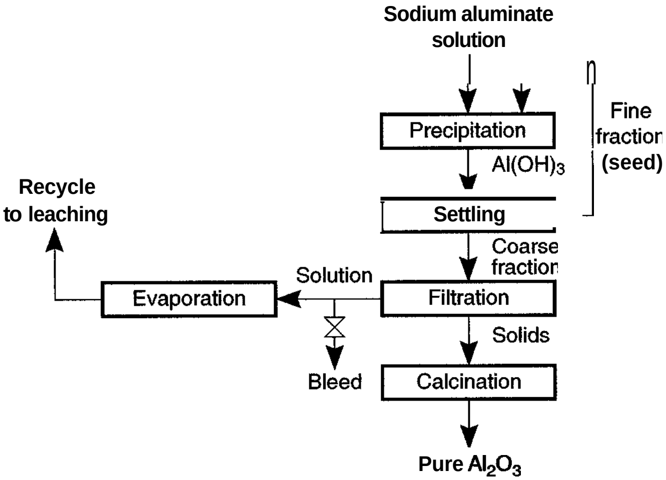

Figure *24.6:* Precipitation of $Al(OH)_3$ from sodium aluminate solution.

Beryllium. Beryllium is usually recovered from acid leach solutions by precipitation as a hydroxide. To get the crystalline hydroxide, precipitation should be carried out from alkaline medium. This is achieved by dissolving the hydroxide in excess alkali then boiling the beryllate solution to precipitate the crystalline hydroxide as follows:

$$Be^{2+} + 2OH^- + nH_2O \rightarrow \underset{\text{amorphous}}{Be(OH)_2 \cdot nH_2O}$$

$$Be(OH)_2 \cdot nH_2O + OH^- \rightarrow [Be(OH)_3]^- + nH_2O$$

$$[Be(OH)_3]^- \xrightarrow{\text{Boiling}} \underset{\text{crystalline}}{Be(OH)_2} + OH-$$

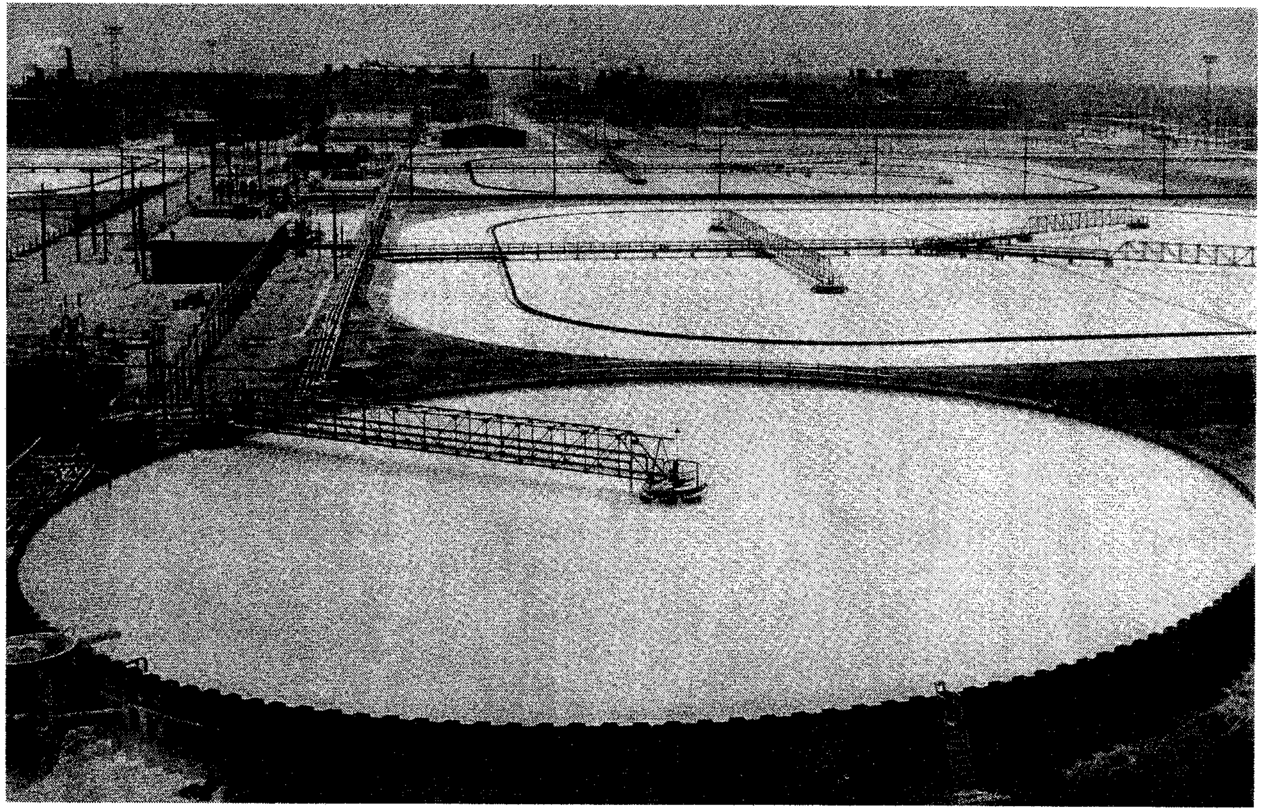

Figure 24.7: Recovery of magnesium from sea water at Dow Magnesium Corporation, Gulf of Mexico.

Separation of beryllium from aluminum, the major impurity in beryllium ores, is achieved by adding ethylene diamine tetraacetic acid (EDTA) together with NaOH to form beryllium and aluminum hiydroxides which redissolve on adding excess NaOH. On boiling the solution, only β-$Be(OH)_2$ is precipitated, while aluminum is not, due to the presence of EDTA.

Magnesium. Sea water contains about 1.3 g/L magnesium. Magnesium recovery is achieved by precipitation as a hydroxide:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

The precipitating agent may be either lime prepared by calcining oyster shells, or calcined dolomite (i.e., $CaO \cdot MgO$). The suspension is delivered to settling tanks (Figure 24.7). There, the precipitated magnesium hydroxide settles and is drawn off as a slurry containing about 1.2% $Mg(OH)_2$. The slurry is filtered, and the filter cake, containing aibout 25% $Mg(OH)_2$, is either dried and calcined to MgO for use as a refractory, or neutralized with HCl to get $MgCl_2$ solution; the metal is prepared by the electrolysis of fused anhydrous $MgCl_2$. Figure 24.8 shows a flowsheet of a typical operation.

Cobalt. Cobalt is usually recovered from acid leach solutions by precipitation as a hydroxide:

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2$$

Since the pH of precipitation is about 6.8, the solution must be purified of all metal ions that precipitate below this pH to avoid contamination. This is usually conducted by adding lime at pH 3 to precipitate iron and aluminum hydroxides. Thus, from the cobaltiferrous copper ores of Katanga, cobalt is leached together with copper but not deposited during the electrolytic recovery of copper. The solution leaving the electrolytic cells contains 25 g/L Cu and 15–25 g/L Co. It is purified from iron and aluminum by precipitation with lime at pH 3, then decopperized by cementation with metallic cobalt. Cobalt hydroxide is then precipitated by lime at pH 6.8 (Figure 24.9).

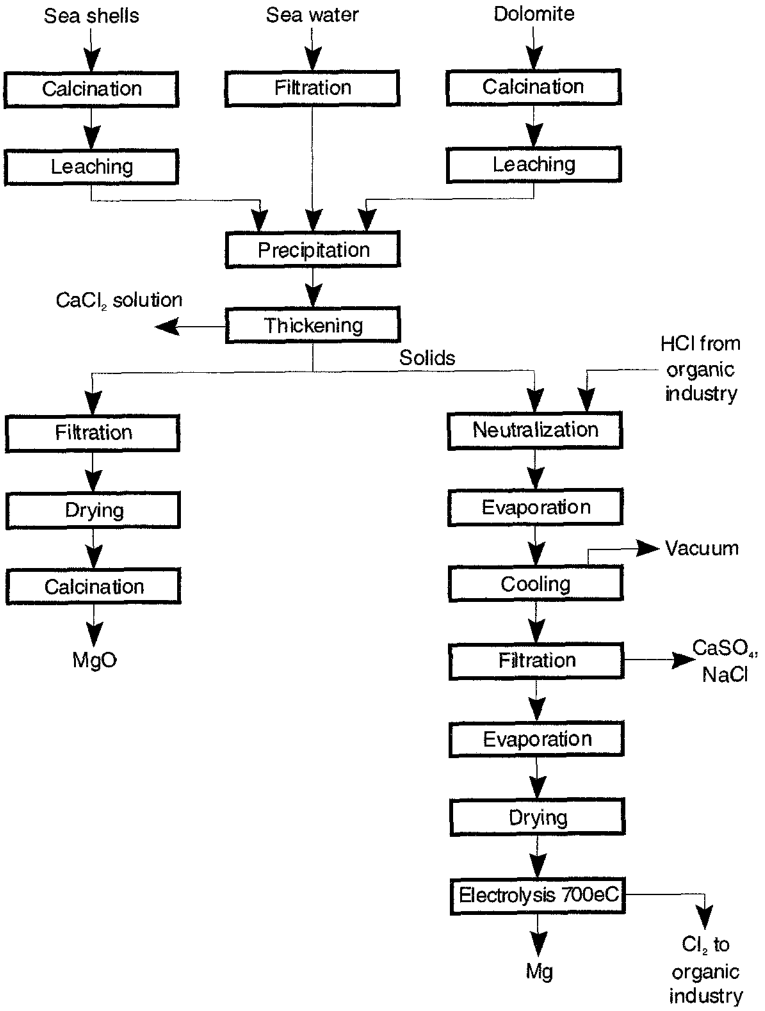

Figure 24.8: Recovery of magnesium from sea water.

Speiss leach solution containing Ni, Cu, Ag, Fe, as well as Co, is purified by adding NaCl to precipitate AgCl, metallic iron to precipitate copper, and lime to precipitate iron (some Co and Ni are also precipitated). A typical solution contains about 10 g/L Co and 3 g/L Ni. Separation of cobalt from nickel is usually achieved by oxidizing Co^{2+} to Co^{3+} using chlorine; Co^{3+} ion precipitated at pH 3 which is much lower than that necessary for Ni^{2+}:

$$Co^{3+} + 3OH^- \rightarrow Co(OH)_3$$

Under these conditions, about 90% of cobalt is precipitated free from nickel. Also, cobalt is sometimes precipitated as the hydroxide from pyrite cinder leach solutions.

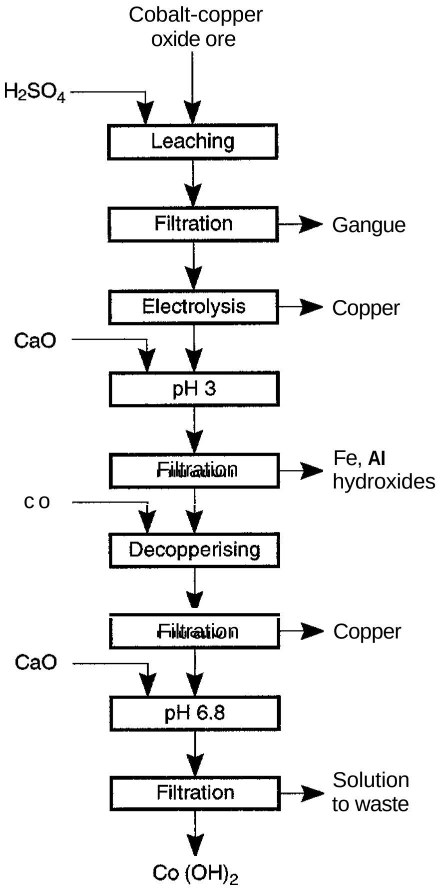

Figure *24.9:* Recovery of copper and cobalt from Katanga ore.

Hydroxy salts

Under certain conditions of pH, temperature, and concentration of metal ion in solution, hydroxy or basic salts are obtained instead of hydroxides. For example, pale blue hydroxy copper sulfate is precipitated according to:

$$2Cu^{2+} + SO_4^{2-} + 2H_2O \rightarrow Cu(OH)_2{\cdot}CuSO_4 + 2H^+$$

Similarly, the hydroxy chlorides and hydroxy carbonates:

$$2Cu^{2+} + 2Cl^- + 2H_2O \rightarrow Cu(OH)_2{\cdot}CuCl_2 + 2H^+$$

$$2Cu^{2+} + CO_3^{2-} + 2H_2O \rightarrow Cu(OH)_2{\cdot}CuCO_3 + 2H^+$$

Hydroxy carbonates are also precipitated when a metal ammine complex in a ammoniacal ammonium carbonate solution is heated to distill off NH_3:

$$\begin{aligned} &2[M(NH_3)_n]^{2+} + 4OH^- + (NH_4)_2CO_3 \rightarrow \\ &\qquad M(OH)_2{\cdot}MCO_3 + 2(n+1)NH_3 + 2H_2O \end{aligned}$$

A variety of hydroxy salts can be obtained, and many of these occur in nature either as anhydrous or as hydrated salts; Table 24.5 lists some of these. The precipitation of hydroxy iron sulfates has received the greatest attention since they are applied as a mean of eliminating iron from leach solutions because these compounds are crystalline and easy to filter and wash. For example, ferrihydroxy sulfate precipitates according to:

$$3Fe^{3+} + 3SO_4^{2-} + 3H_2O \rightarrow Fe(OH)_3{\cdot}Fe_2(SO_4)_3 + 3H^+$$

Table *24.5:* Hydroxy salts of divalent metals.

Medium	Hydroxy salt	Examples
Carbonate	$xM(OH)_2{\cdot}yMCO_3$	$Cu(OH)_2{\cdot}CuCO_3$ $Zn(OH)_2{\cdot}ZnCO_3$ $Ni(OH)_2{\cdot}NiCO_3$
Sulfate	$xM(OH)_2{\cdot}yMSO_4$	Cu(OH), .$CuSO_4$
Chloride	$xM(OH)_2{\cdot}yMCl_2$	$3Cu(OH)_2{\cdot}CuCl_2$

This precipitate can also be represented as: $Fe_2O_3{\cdot}2SO_3{\cdot}H_2O$ or $Fe(OH)SO_4$. In fact, there are numerous hydroxy ferric sulfates that form under different conditions and can be represented by the fornnula $Fe_2O_3 \cdot xSO_3 \cdot yH_2O$ as shown in Table *24.6*. At the special composition when $x = {}^4/_3$ and $y = 3$, the compound formed is known as hydronium jarosite'. In this compound, monovalent ions such as Na^+, K^+, NH_4^+, or Ag^+ may replace the hydrogen while divalent ions such as Pb^{2+} and Hg^{2+} may replace the iron as shown in Table *24.7*. Under such circumstances, the formation of jarosite may be a nuisance because it represents a loss of the non-ferrous metal and a contamination of the ferrihydroxy sulfate. Figure *24.10* shows the conditions for the precipitation of hydroxy salts of iron.

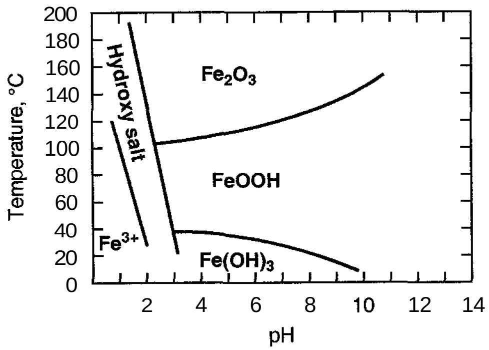

Figure 24.10: Conditions for the precipitation of iron oxide, oxide hydroxide, hydroxide, and hydroxy salts from 0.5M ferric sulfate solution (Babcan, 1971).

Table 24.6: Typical compounds derived from hydronium jarosite.

Jarosite	Formula
Hydronium	$(H_3O)Fe_3(SO_4)_2(OH)_6$
Sodium	$NaFe_3(SO_4)_2(OH)_6$
Potassium	$KFe_3(SO_4)_2(OH)_6$
Silver	$AgFe_3(SO_4)_2(OH)_6$
Ammonium	$(NH_4)Fe_3(SO_4)_2(OH)_6$
Thallium[a]	$TlFe_3(SO_4)_2(OH)_6$
Lead	$Pb_{0.5}Fe_3(SO_4)_2(OH)_6$
Mercury[a]	$Hg_{0.5}Fe_3(SO_4)_2(OH)_6$

a. Does not occur in nature.

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1. The mineral alunite $KAl_3(SO_4)_2(OH)_6$ is analogous to potassium iron jarosite $KFe_3(SO_4)_2(OH)_6$.

Table *24.7:* Stable solid compounds in the system Fe_2O_3–SO_3–H_2O at Fe^{3+} ion and H_2SO_4 concentrations below 100 g/L in the temperature range *75–200°C.*

x	y	Solid phase $Fe_2O_3 \cdot xSO_3 \cdot yH_2O$	Formula	Name
0	0	Fe_2O_3	Fe_2O_3	Hematite
0	1	$Fe_2O_3 \cdot H_2O$	FeOOH	Goethite
1/2	5/2	$Fe_2O_3 \cdot {}^1/_2SO_3 \cdot {}^5/_2H_2O$	$Fe_4SO_4(OH)_{10}$	Glockerite
4/3	3	$Fe_2O_3 \cdot {}^4/_3SO_3 \cdot 3H_2O$	$(H_3O)Fe_3(SO_4)_2(OH)_6$	Hydronium jarosite
2	1	$Fe_2O_3 \cdot 2SO_3 \cdot H_2O$	$Fe(OH)_3 \cdot Fe_2(SO_4)_3$ or $FeSO_4(OH)$	Ferrihydroxy sulfate

Some hydroxy salts are easily reduced to metal, e.g., copper hydroxysulfate:

$$Cu(OH)_2 \cdot CuSO_4 + 3H_2 \xrightarrow{200\,^\circ C} 2Cu + SO_2 + 4H_2O$$

or decomposed to oxide:

$$Ni(OH)_2 \cdot NiCO_3 \rightarrow 2NiO + CO_2 + H_2O$$

POLYACIDS AND THEIR SALTS

Anions like carbonate, nitrate, manganate, and perchlorate always exist in this simple form; all other ions undergo a process of limited or extensive condensation to form polyions. For example, sulfate ion forms the disulfate, chromate forms dichromate, and uranate forms diuranate. These polyions are formed from the condensation of two anions with the loss of oxide ion, e.g.:

$$2SO_4^{2-} - O^{2-} \rightarrow S_2O_7^{2-}$$

or from the condensation of two acid molecules with loss of water:

$$2H_2SO_4 - H_2O \rightarrow H_2S_2O_7$$

Other anions capable of extensive condensation are phosphate, silicate, vanadate, molybdate, tungstate, borate, and others'. Of metal-

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1. When condensation of two different anions takes place, the product is a heteropoly ion, e.g., condensation of phosphate with molybdate leads to phosphomolybdate, $[P(Mo_3O_{10})_4]^{3-}$. Thus, ammonium phosphomolybdate, $(NH_4)_3[P(Mo_3O_{10})_4] \cdot 6H_2O$ is a yellow precipitate known in analytical chemistry for determination of phosphorus.

lurgical importance are those polyions that are insoluble in water or that can be crystallized readily and hence can be used for metal separation.

Vanadates

Vanadate ion, VO_4^{3-}, is stable at pH 12. When the pH is gradually decreased by adding acid, divanadate and other polyions are formed until at pH of about 12 the tetravanadate is precipitated:

Anion	VO_4^{3-}	$\rightarrow$	$V_2O_7^{4-}$	$\rightarrow$	$V_4O_{12}^{4-}$	$\rightarrow$	$V_6O_{17}^{4-}$	$\rightarrow$	V_2O_5 colloidal	$\rightarrow$	VO_2^+
pH	11–12		9–11		7–9		2.2		1.3		0.5

When the pH is decreased further, the tetravanadate dissolves forming pervanadyl ion, VO_2^+. In industry, vanadium in ores is solubilized in form of sodium vanadate and precipitated as sodium tetravanadate known as red ***cake:***

$$6VO_4^{3-} + 4Na^+ + 14H^+ \rightarrow Na_4V_6O_{17} + 7H_2O$$

This is filtered, washed, and dissolved in NaOH then saturated with ammonium chloride to precipitate ammonium vanadate:

$$4VO_4^{3-} + 4NH_4^+ + 8H^+ \rightarrow (NH_4)_4[V_4O_{12}] + 4H_2O$$

Ammonium vanadate is then decomposed by heating to vanadium pentoxide the product of commerce:

$$(NH_4)_4[V_4O_{12}] \rightarrow 2V_2O_5 + 4NH_3 + 2H_2O$$

Molybdates

Molybdate ion, MoO_4^{2-}, is stable above pH 7. When the pH is ,gradually decreased, insoluble polyions are formed:

Anion	MoO_4^{2-}	$\rightarrow$	$Mo_3O_{11}^{4-}$	$\rightarrow$	$H_3Mo_6O_{21}^{3-}$
pH	14–6.5		6.5–4.5		4.5–1.5

Molybdenite, MoS_2, the major source of molybdenum, is usually oxidized to MoO_3, and the oxide is dissolved in excess ammonium hydroxide to form molybdate ion:

$$MoO_3 + 2OH^- \rightarrow MoO_4^{2-} + H_2O$$

The solution obtained is subjected to a purification step which involves acidification to precipitate a series of hexaammonium molybdates:

$$6MoO_4^{2-} + 3NH_4^+ + 9H^+ \rightarrow (NH_4)_3[H_3Mo_6O_{21}]\cdot 3H_2O$$

$$6MoO_4^{2-} + 4NH_4^+ + 8H^+ \rightarrow (NH_4)_4[H_2Mo_6O_{21}]\cdot 3H_2O$$

$$6MoO_4^{2-} + 5NH_4^+ + 7H^+ \rightarrow (NH_4)_5[HMo_6O_{21}]\cdot 3H_2O$$

These precipitates may be considered to be composed of:

$$x(NH_4)_2MoO_4\cdot yH_2MoO_4$$

where $x = 1.5$, 2, and 2.5 when $y = 4.5$, 4, and 3.5, respectively. This is a commercial product which can be thermally decomposed to pure oxide then reduced to metal (Figure 24.11).

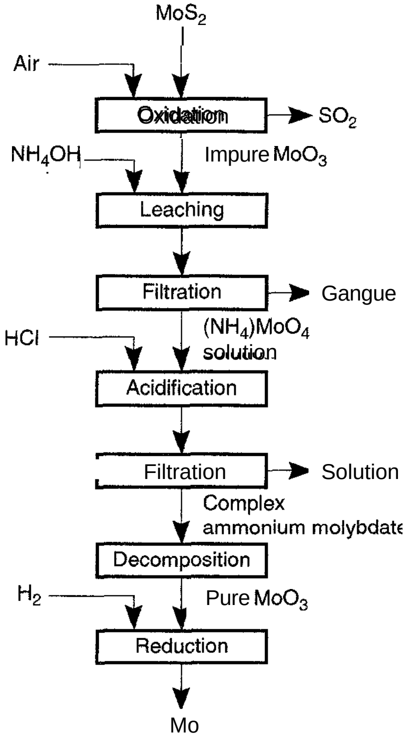

Figure 24.11: Recovery of molybdenum from molybdenite concentrate via the precipitation of complex ammonium molybdate.

Tungstates

Tungstate ion, WO_4^{2-}, is stable at pH > 8. When the pH is gradually decreased by adding *an* acid, numerous polyions form:

Anion	WO_4^{2-}	→	$W_2O_7^{2-}$	→	$W_3O_{10}^{2-}$	→	$W_4O_{13}^{2-}$	→	$WO_3 \cdot nH_2O$
pH	> 8								< 1.5

Before the precipitation of the hydrated oxides, however, tungstic acid and hexatungstic acid are supposed to form first by polymerization and splitting of water:

$$H_2WO_4 \rightarrow H_{12}W_6O_{24} \rightarrow H_{24}W_{12}O_{48} \rightarrow H_{10}W_{12}O_{41}$$

since stable crystals of sodium paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$, have been isolated (industrial product). In practice, wolframite concentrates, $FeWO_4$, are leached with alkali to form the soluble tungstate ion which is filtered then acidified to form hydrated tungsten oxide:

$$WO_4^{2-} + 2H^+ + xH_2O \rightarrow H_2WO_4 \cdot xH_2O \rightarrow WO_3 \cdot nH_2O$$

Scheelite concentrates, $CaWO_4$, are digested with acid to form $WO_3 \cdot nH_2O$ which is filtered, washed, and purified by dissolution in alkali then precipitation by acid (Figure 24.12).

Uranates

Uranates, MUO_4, and diuranates, $M_2U_2O_7$, are insoluble in water. The diuranate is obtained by adding an alkali hydroxide to a uranyl ion:

$$2UO_2^{2+} + 6OH^- + 2Na^+ \rightarrow Na_2U_2O_7 + 3H_2O$$

Magnesium oxide may also be added to neutralize the acid (H_2SO_4) and to precipitate magnesium diuranate:

$$MgO + 2H^+ \rightarrow Mg^{2+} + H_2O$$

$$2UO_2^{2+} + 3MgO \rightarrow MgU_2O_7 + 2Mg^+$$

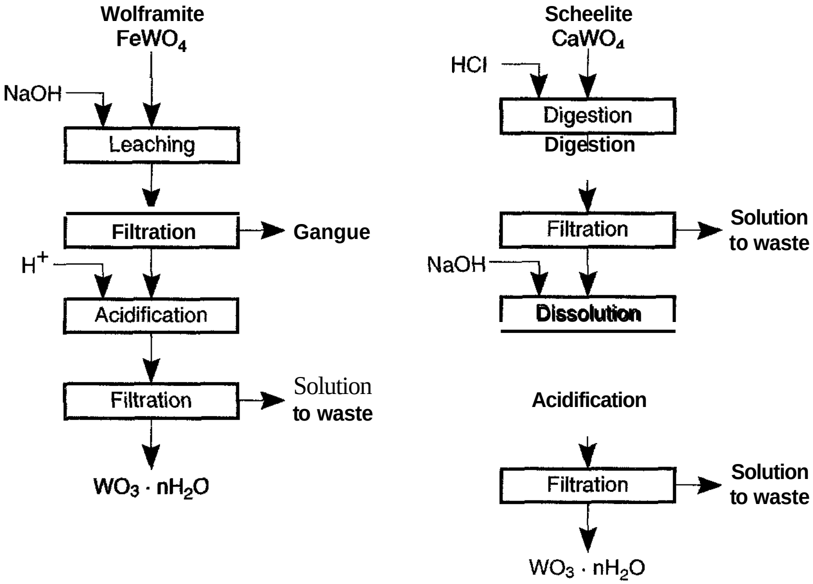

Figure *24.12:* Recovery of tungstic oxide from wolframite and scheelite.

Precipitation takes place at pH 6.5 and under these conditions most of the impurities are also precipitated. Lime cannot replace magnesia because calcium sulfate will also precipitate. Precipitation as uranates is mostly suitable for carbonate leach solutions, since sodium carbonate is regenerated and can be recycled:

$$2[UO_2(CO_3)_3]^{4-} + 6OH^- + 2Na^+ \rightarrow Na_2U_2O_7 + 6CO_3^{2-} + 3H_2O$$

A relatively pure uranate can be precipitated from eluate solutions of ion exchange or solvent extraction separation; in this case, ammonium or sodium hydroxide are used as a precipitating agent, e.g.:

$$2UO_2^{2+} + 2NH_4^+ + 6OH^- \rightarrow (NH_4)_2U_2O_7 + 3H_2O$$

Uranates are bright yellow in color and that is why they are known as *yellow cake.* This is usually the product of a uranium leaching plant (Figure *24.13);* the yellow cake is then sent to the refinery where it is dissolved in HNO_3 and purified by solvent extraction or other methods to get pure UF_4, the *green salt,* used for preparing the metal.

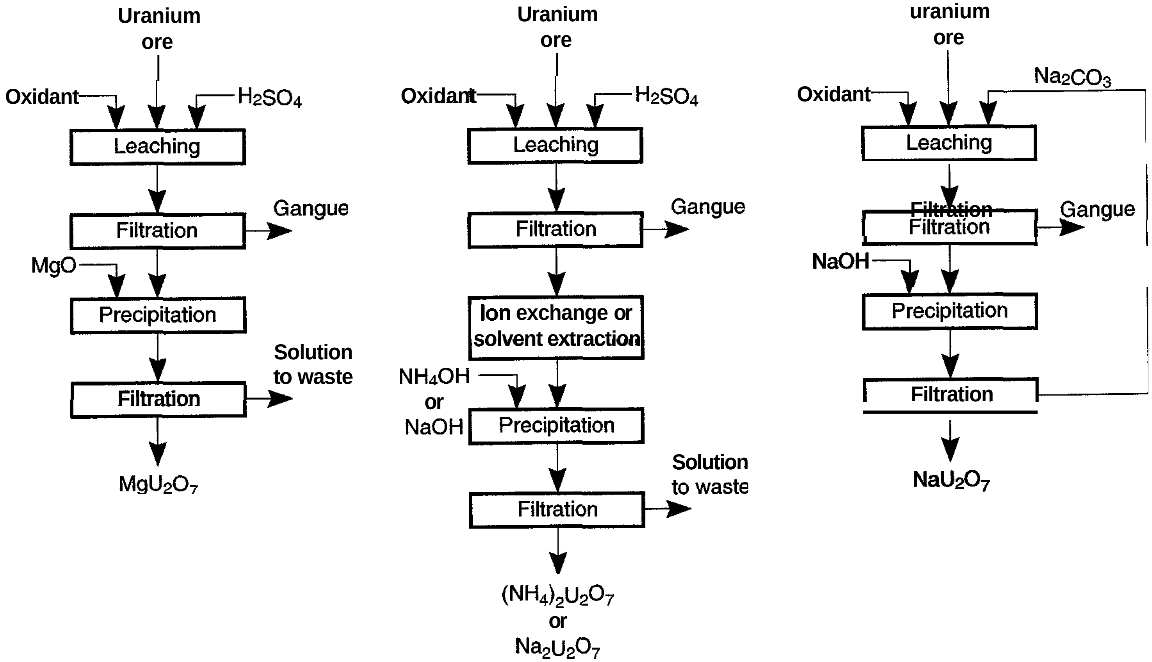

Figure *24.13:* Production of yellow **cake** from uranium **ores.**

Dialuminates

Aluminate ion, $[AlO(OH)_2]^-$, tends to polymerize to the dialuminate ion:

$$2[AlO(OH)_2]^- + 2H_2O \rightarrow [Al_2(OH)_7]^- + OH-$$

This polymeric ion can be crystallized from dilute aluminate solution containing Li+ion in form of the slightly soluble lithium dialuminate, $LiAl_2(OH)_7 \cdot 2H_2O$. This is the basis for a method suggested for the recovery of lithium from brines. The Dead Sea, for example, is relatively rich in lithium; it contains 20–50 ppm Li. The recovery of lithium can be achieved by adding an aluminum salt to the water followed by limewater.

CARBONATES

Lithium carbonate is the least soluble alkali carbonate (Table 24.8) and its solubility decreases with increasing temperature (Table 24.9). This is the basis of lithium recovery from solution:

$$2Li^+ + CO_3^{2-} \rightarrow Li_2CO_3$$

Table *24.8:* Solubility of alkali carbonates in water at 20 °C.

	g/100 g solution
Li_2CO_3	1.31
Na_2CO_3	17.6
K_2CO_3	53.2
Rb_2CO_3	very soluble
Cs_2CO_3	very soluble

Table *24.9:* Effect of temperature on the solubility of lithium carbonate.

°C	g/100 g H_2O
0	1.54
20	1.33
50	1.08
100	0.72

Lithium-containing solutions are obtained by treating spodumene ores or certain saline brine, e.g., in Nevada. Saline brine containing 0.25% LiCl is pumped from wells 90–250 meters deep to a multiple of solar evaporation ponds in series. When LiCl content increases to

0.8%, the brine is transferred to 50-acre ponds, where lime is added to precipitate magnesium and the concentration of LiCl reaches 2%. It is then transferred to a series of 10-acre ponds, where LiCl content reaches 6%. In these ponds, KCl and NaCl crystallize and precipitate. The concentrated brine is then transferred through heat exchangers to a series of rubber-lined tanks equipped with agitators, where sodium carbonate is added to precipitate lithium carbonate (Figure 24.14).

Magnesium may also be precipitated as a carbonate. Leach solution of the waste discarded by the talc or asbestos industries is sometimes treated in this way.

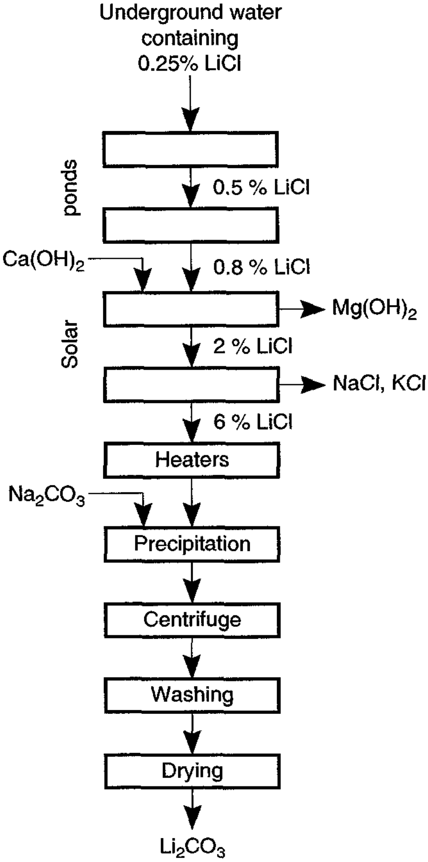

Figure 24.14: Recovery of lithium carbonate from subterranean water.

OXALATES

Separation of thorium and the lanthanides from sulfuric acid leach solution of monazite and xenotime concentrates is based on oxalate precipitation:

$$Th^{4+} + 2(C_2O_4)^{2-} \rightarrow Th(C_2O_4)$$

$$Ln^{3+} + 3(C_2O_4)^{2-} \rightarrow Ln_2(C_2O_4)_3$$

Uranium is not precipitated. The oxalate filter cake is then digested with NaOH solution to convert the oxalates into hydroxides and recover sodium oxalate for recycle:

$$Th(C_2O_4)_2 + 4OH^- \rightarrow Th(OH)_4 + 2(C_2O_4)^{2-}$$

$$Ln_2(C_2O_4)_3 + 6OH^- \rightarrow 2Ln(OH)_3 + 3(C_2O_4)^{2-}$$

The hydroxides are then calcined, and the resulting oxides dissolved in nitric acid for later separation of thorium by solvent extraction (Figure 24.15).

PEROXIDES

Precipitation as peroxides is used mainly for uranium and Plutonium. A yellow precipitate of uranium peroxide is obtained when hydrogen peroxide is added to a uranium(VI) solution:

$$UO_2^{2+} + O_2^{2-} + 2H_2O \rightarrow UO_4 \cdot 2H_2O$$

In the pH range 1.5–2.5, the reaction is quantitative. Traces of Zr, Hf, Th, and V may contaminate the precipitate. An insoluble green peroxide is formed when plutonium(IV) solution is treated with H_2O_2:

$$Pu^{4+} + 2O_2^{2-} \rightarrow PuO_4$$

HALIDES

Chlorides

The solubility of cuprous chloride in water is low, about 0.062 g/L, and this property is sometimes utilized to separate copper from leach solutions, since the precipitation is selective for copper:

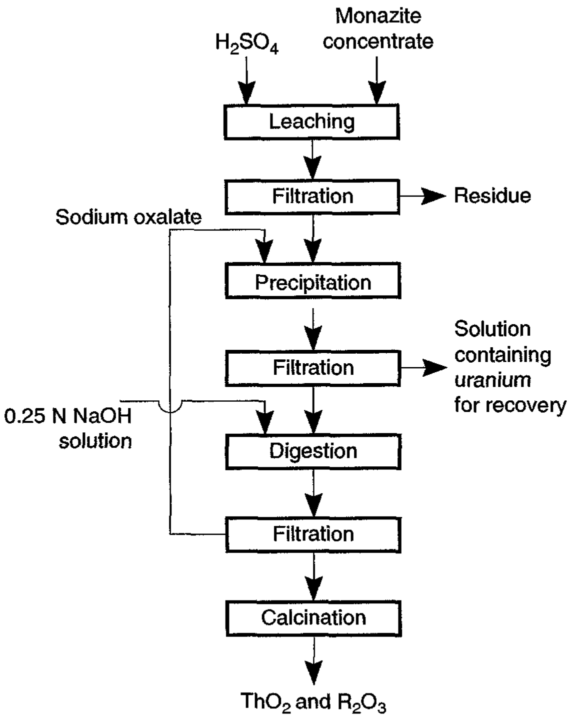

Figure 24.15: Recovery of thorium and rare earths from monazite sand by precipitation as oxalates.

$$Cu^+ + Cl^- \rightarrow CuCl_{(ppt.)}$$

AgCl and Hg_2Cl_2 are the only other insoluble chlorides ($PbCl_2$ partially soluble). Since copper is usually present as Cu^{2+} ions in leach solutions, reduction to Cu^+ is necessary before precipitation. This is achieved by heating with SO_2 or metallic copper in absence of air:

$$2Cu^{2+} + SO_2 + 2H_2O \rightarrow 2Cu^+ + 4H^+ + SO_4^{2-}$$

$$Cu^{2+} + Cu \rightarrow 2Cu^+$$

Precipitation of cuprous chloride is practiced at Mantos Blancos in Chile (Figure 24.16) since copper ore there contains appreciable amounts of chlorides and at Duisburger Kupferhütte in Germany for copper recovery from pyrite cinder leach solution.

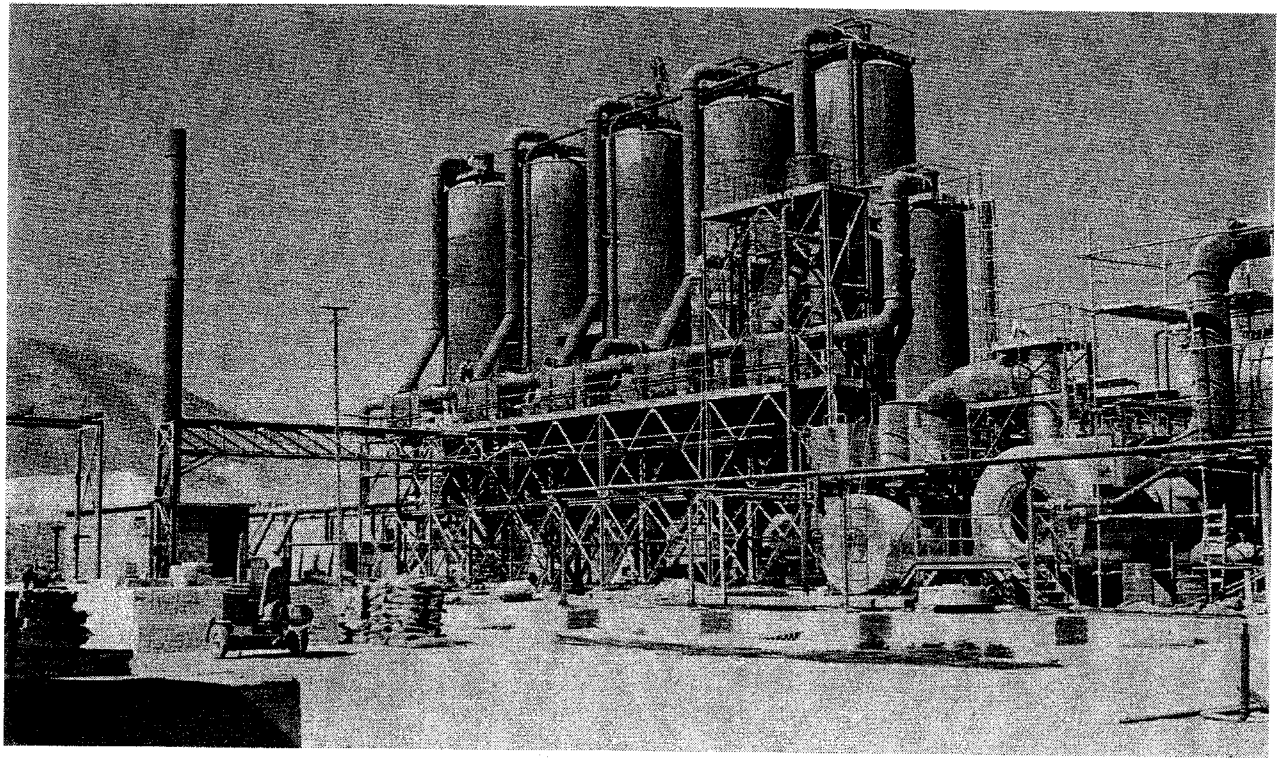

Figure 24.16: Cuprous chloride precipitation towers at Mantos Blancos, Chile (Lurgi).

Platinum is precipitated from solution as the ammonium hexachloroplatinate:

$$PtCl_4 + 2NH_4Cl \rightarrow (NH_4)_2[PtCl_6]$$

and the metal is recovered by thermal decomposition of the precipitate.

Fluorides

Preparation of anhydrous metal fluorides is an important step in the extraction of metals, since fluorides can be reduced to metals, or in the case of uranium, beside reduction to metals, it is processed further to UF_6 for isotope separation. There are two methods for preparing fluorides:

- Reaction of hydrogen fluoride gas with the oxide at high temperature
- Precipitation from aqueous solution.

The second method is more convenient since it is usually carried out at low temperature and in less corrosive media. Thus, plutonium trifluoride is prepared industrially by adding hydrofluoric acid to plutonium nitrate solution:

$$Pu^{3+} + 3HF \rightarrow PuF_3 + 3H^+$$

Table ***24.10:*** Uranium fluorides precipitated from aqueous solutions.

Temperature °C	Precipitating agent	Fluoride	Properties
25	HF	$UF_4 \cdot {}^5/_2H_2O$	Green, gelatinous, difficult to filter and wash.
90–100	HF	$UF_4 . {}^3/_4H_2O$	Green, dense, granular, easy to filter and wash.
	NaF	Na_2UF_6	
	NH_4F	$(NH_4)_2UF_6$	

Large crystals are obtained which are easily filtered, washed, and dried, and the anhydrous salt obtained is pure enough for subsequent reduction to plutonium metal. When, however, hydrofluoric acid is added to a uranous ion solution, different hydrates are formed depending on the conditions of precipitation (Table 24.10). These hydrates, however, are difficult to convert into the anhydrous form without side reactions:

$$UF_4 + 2H_2O \rightarrow UO_2 + 4HF$$

$$2UF_4 + O_2 + 2H_2O \rightarrow 2UO_2F_2 + 4HF$$

unless drying is carried out under high vacuum. To overcome this difficulty, the complex fluorides are usually prepared, since they precipitate without water of hydration, and therefore can be dried without decomposition. For example, sodium uranous fluoride is prepared by the reduction of uranyl ion with formic acid and SO_2, which, in the presence of an alkali fluoride, is precipitated as a complex fluoride:

$$U^{4+} + 6NaF \rightarrow Na_2[UF_6] + 4Na^+$$

The complex fluoride can be reduced by calcium to uranium metal. In a similar way, the complex ammonium fluorides can be prepared:

$$U^{4+} + 6NH_4F \rightarrow (NH_4)_2[UF_6] + 4NH_4^+$$

$$U^{4+} + 5NH_4F \rightarrow NH_4[UF_5] + 4NH_4^+$$

which can be decomposed to UF_4 by heating and the volatilized NH_4F recycled, e.g.:

$$NH_4[UF_5] \rightarrow UF_4 + NH_4F$$

CYANIDES

In acidic or neutral medium, cuprous cyanide is practically the only cyanide insoluble in water. Consequently, processes have been suggested for copper recovery from a leach solution by precipitation as cyanide, as follows:

- The low-grade ore is leached with sulfuric acid, SO_2 being added to the leach solution to reduce cupric to cuprous sulfate; then HCN is passed through the solution to precipitate cuprous cyanide:

$$HCN \rightleftharpoons H^+ + CN^-$$

$$Cu^+ + CN^- \rightarrow CuCN$$

- The low-grade ore is leached by sodium cyanide solution:

$$Cu_2O + 6CN^- + H_2O \rightarrow 2[Cu(CN)_3]^{2-} + 2OH^-$$

On acidifying the leach solution with dilute sulfuric acid, CuCN is precipitated, with simultaneous generation of HCN for recycle:

$$[Cu(CN)_3]^{2-} + 2H^+ \rightarrow CuCN + 2HCN$$

There is interference, however, in this case due to traces of iron which may co-precipitate as copper ferrocyanide, $Cu_2[Fe(CN)_6]$, and contaminate the product. This can be minimized by careful pH adjustment to isolate the complex cyanide prior to precipitating CuCN.

Cuprous cyanide is a white, easily filterable precipitate. Both methods are based on processing CuCN to metallic copper by reduction with hydrogen at about 400 °C, whereby HCN is regenerated for recycle:

$$2CuCN + H_2 \rightarrow 2Cu + 2HCN$$

SULFIDES

Metals such as copper, nickel, cobalt, and zinc are sometimes precipitated from leach solutions as sulfides when their concentration in the solution is low. This process is used as a purification as well as recovery step. Hydrogen sulfide, ammonium sulfide, and sodium sulfide are the most common precipitating agents used for this purpose. Figure 24.17 shows sulfide precipitating agents as a function of pH. Hydrogen sulfide is a poisonous and corrosive gas. In certain concentrations, it explodes in air. In precipitating metal sulfides by H_2S, the following points should be taken into consideration.

- *Acidgenerution.* Acid is generated during precipitation:

  $$M^{2+} + H_2S \rightarrow MS + 2H^+$$

  and can be used in the leaching circuit, or must be neutralized before disposal.

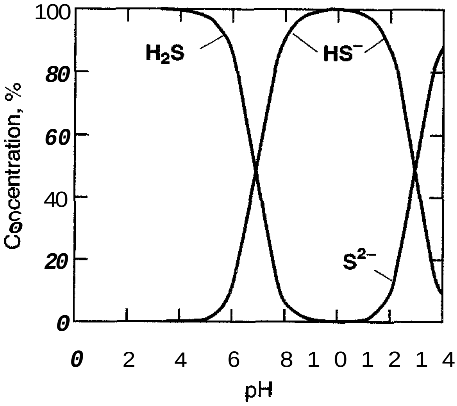

Figure 24.17: Sulfide precipitating agents as a function of pH.

- *Polymorphic precipitates.* Cobalt and nickel sulfides exist in several polymorphic forms with different solubilities. The alpha forms, obtained by precipitation from basic solutions, are amorphous and soluble in dilute acids. The beta forms, precipitated from weakly acid solutions, are crystalline and only slightly soluble in 0.1 M HCl.

- *Catalysis.* Precipitation may be greatly accelerated by the addition of a catalyst. Thus, the precipitation of nickel sulfide from weakly acidic solution is extremely slow, but the addition of small amounts of iron or nickel powder accelerates the reaction greatly especially at high temperature and pressure. A process developed at Moa Plant in Cuba for recovering nickel and cobalt was based on this principle. The ore containing 1.35% Ni and 0.15% Co is leached with sulfuric acid, filtered, and the solution treated with H_2S at 120 °C and 1000 kPa in the presence of iron powder as catalyst to precipitate NiS and CoS. Precipitation is conducted in pressure reactors. The mixed sulfide is then filtered, dried, and shipped for further processing.

- *Flotation of precipitates.* Sometimes, it is desirable to float the precipitated sulfide to economize the cost of filtration. This is especially the case when leaching low-grade copper ore containing fine particles (slimes). Precipitation can be conducted directly in the slurry and CuS is recovered by flotation thus by-passing a filtration step.

- *Selectivity.* Precipitation of sulfides can be selective. For example:

- At Outokumpu, in Finland, pyrite cinder is leached with water to get a solution at pH 1.5 analyzing 20 g/L Co, 6–8 Ni, 7–8 Cu, 10–12 Zn, and trace amounts of iron. The solution is purified by selective precipitation with H_2S to remove first copper, then zinc, nickel, and finally cobalt sulfides.
- At Nicaro, in Cuba, the ammoniacal solution containing nickel and cobalt in the ratio 15/1 is treated with a dosed amount of ammonium hydrogen sulfide to precipitate all the cobalt and a relatively small amount of nickel so that the precipitate contains nickel and cobalt in the ratio 3/1, and the solution contains only nickel.

SULFITES

Copper sulfites (Table 24.1 1) are of interest in hydrometallurgy because they can be readily precipitated from leach solutions in a pure form and can be treated in a variety of ways to yield pure metallic copper.

Table 24.1 1: Copper sulfites of interest to hydrometallurgy.

	cu, %	S, %	NH_3, %
$Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 10H_2O$	10.6	21.4	19.9
$Cu_2SO_3 \cdot (NH_4)_2SO_3$	39.3	19.8	10.5
$Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$ (Chevreul's salt)	49.2	15.5	nil

Ammonium copper sulfites

Ammonium sulfite solution (natural pH about 8) extracts copper from oxidized copper ores. When SO_2 is bubbled through the solution at room temperature until pH 7 is reached, the cupric species are reduced to the cuprous. The same behavior takes place when SO_2 is bubbled into a copper ammine solution (pH 10.5). The dark blue solution becomes colorless because of the oxidation–reduction reactions:

$$SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow SO_3^{2-} + 2H^+$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$\underset{\text{blue}}{[Cu(NH_3)_4]^{2+}} + e^- \rightarrow \underset{\text{colorless}}{[Cu(NH_3)_4]^+}$$

$$[Cu(NH_3)_4]^+ + 4H^+ \rightleftharpoons Cu^+ + 4NH_4^+ \text{ (pH 7, sulfite medium)}$$

Two products can be obtained from these solutions:

- By cooling, a double salt of cuprous ammonium sulfite having the composition $Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 10H_2O$ is formed. These are water-soluble transparent needle crystals (Figure 24.18); when acidified, they precipitate metallic copper by disproportionation:

  $$2Cu^+ \rightarrow Cu + Cu^{2+}$$

  while the sulfite ion forms SO_2:

  $$SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O$$

- When SO_2 is bubbled further until pH 3, then a double salt having the composition $Cu_2SO_3 \cdot (NH_4)_2SO_3$ is formed. These crystals are cream colored shiny hexagonal platelets that are insoluble in water (Figure 24.18). When acidified, they also precipitate metallic copper by disproportionation:

  $$Cu_2SO_3 \cdot (NH_4)_2SO_{3(s)} + 4H^+ \rightarrow$$
  $$Cu + Cu^{2+} + 2SO_2 + 2NH_4^+ + 2H_2O$$

When heated with water at 150 °C in an autoclave in absence of acid, complete conversion to metallic copper takes place:

$$Cu^+ + e^- \rightarrow Cu$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O$$

Overall reaction:

$$Cu_2SO_3 \cdot (NH_4)_2SO_3 \rightarrow 2Cu + SO_2 + 2NH_4^+ + SO_4^{2-}$$

Chevreul's salt

Named after its discoverer the French chemist Michel Eugène Chevreul, the salt is a red crystalline solid having the composition $Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$ (copper present in two valency states). It can be obtained in a variety of ways. For example:

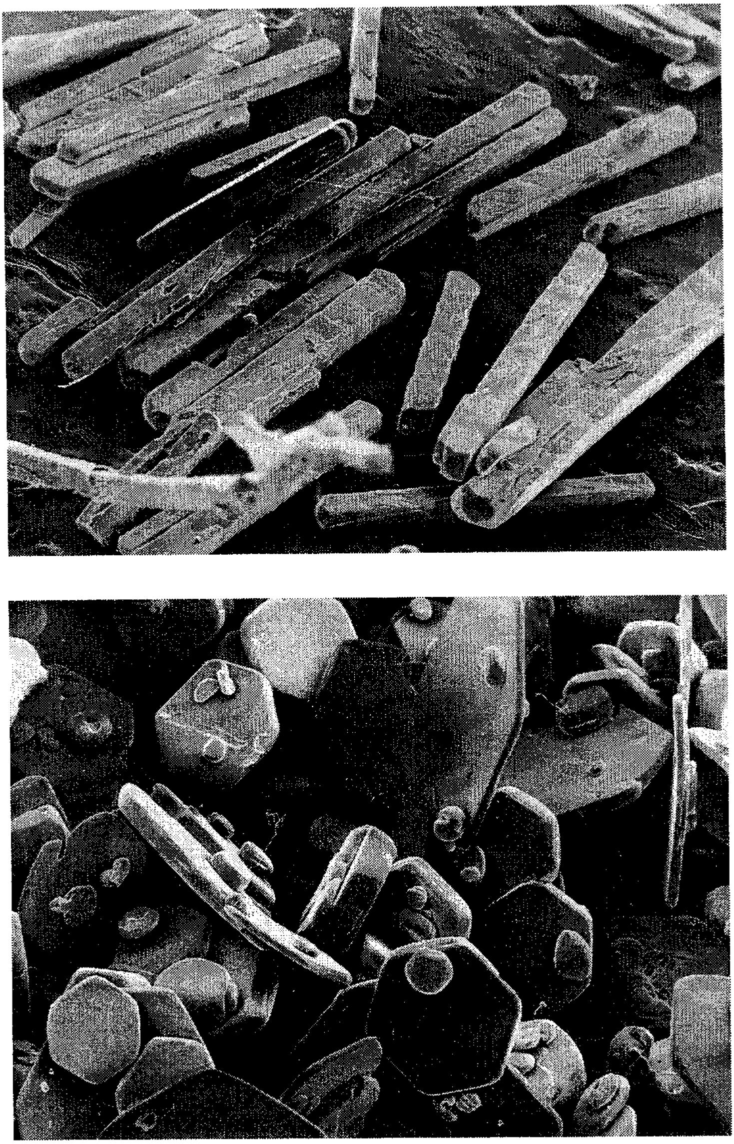

Figure ***24.18:*** Cuprous ammonium sulfites (Habashi). Top: $Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 10H_2O$; Bottom: $Cu_2SO_3 \cdot (NH_4)_2SO_3$.

- When copper oxide ore is dissolved in sulfurous acid, then the solution is heated:

  $$CuO + H_2SO_3 \rightarrow Cu^{2+} + SO_3^{2-} + H_2O$$

  $$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

  $$Cu^{2+} + e^- \rightarrow Cu^+$$

  Overall reaction:

  $$3CuSO_3 + 3H_2O \xrightarrow{\text{Heat}} Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O + H_2SO_4$$

- When $NaHSO_3$ is added to $CuSO_4$ leach solution at pH 1 to 3 then heated to 80 "C.
- When 1.5 M $(NH_4)_2SO_3$ is added to 1 M $CuSO_4$ solution at 60 "C:

  $$3Cu^{2+} + 4SO_3^{2-} + 2H_2O \rightarrow Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O + SO_4^{2-} + SO_2$$

  The salt can be decomposed at 200–300 "C in absence of air to yield oxide:

  $$Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O \rightarrow Cu_2O + 2H_2O + 2SO_2$$

METALLOIDS

Red amorphous selenium is usually purified by dissolution in sodium sulfite solution to form sodium selenosulfate (similar to thiosulfate $Na_2S_2O_3$). On acidification, pure selenium precipitates:

$$SeSO_3^{2-} + H^+ \rightarrow Se + HSO_3^-$$

$$HSO_3^- + H^+ \rightarrow H_2SO_3 \rightarrow H_2O + SO_2$$

Overall reaction:

$$SeSO_3^{2-} + 2H^+ \rightarrow Se + SO_2 + H_2O$$

A similar equation can be written for the acidification of sodium thiosulfate (Products: S, SO_2, and H_2O).

SUMMARY

Table 24.12 gives a summary of hydrolytic and ionic precipitation methods.

Table *24.12:* Summary of hydrolytic and ionic precipitation methods.

Precipitate	Precipitating agent	Examples
Oxides, hydrated oxides,	H_2O	TiO_2, $Al(OH)_3$, $Be(OH)_2$
hydroxides	OH^-	$Nb_2O_5 \cdot nH_2O$, $Ta_2O_5 \cdot nH_2O$, Cu_2O, $Mg(OH)_2$, $Co(OH)_2$
Hydroxy salts	OH^- + Anion	$Cu(OH)_2 \cdot CuCO_3$
Polyacids and their salts:		
Vanadates	H^+	$Na_4V_6O_{17}$, $(NH_4)_4[V_4O_{12}]$
Molybdates	H^+	$(NH_4)_4[H_2Mo_6O_{21}] \cdot 3H_2O$
Tungstates	H^+	$Na_{10}W_{12}O_{41} \cdot 28H_2O$
Uranates	OH^-, MgO	$(NH_4)_2U_2O_7$, $Na_2U_2O_7$, MgU_2O_7
Dialuminates	OH^- + Cation	$LiAl_2(OH)_7 \cdot 2H_2O$
Sulfides	S^{2-}	CuS, NiS, CoS, ZnS
Carbonates	CO_3^{2-}	Li_2CO_3
Chlorides	Cl^-	CuCl, $(NH_4)_2PtCl_6$, K_2TiCl_6
Cyanides	CN^-	CuCN
Fluorides	F^-	PuF_3, $UF_4 \cdot nH_2O$
Oxalates	$(C_2O_4)^{2-}$	$Th(C_2O_4)_2$, $Ln_2(C_2O_4)_3$[a]
Peroxides	O_2^{2-}	$UO_4 \cdot 2H_2O$, PuO_4
Sulfites	$(NH_4)_2SO_3$	Copper ammonium sulfites
Metalloids	H^+	Selenium from selenosulfate solution

a. Ln = Lanthanide or rare earth metal.

Chapter Twenty-Five

Reduction

Ionic *632*
  Sulfite ion *632*
  Hypophosphite *634*
  Others *635*
Non-ionic *636*
  Hydrogen *638*
  Precipitation of oxides *648*
  Carbon monoxide *649*
  Formaldehyde *649*
  Hydrazine *650*
Electrochemical *650*
  Activated charcoal *650*
  Metals *651*
Electrolytic *664*

In precipitation by reduction, the precipitating agent does not combine with the metal ion in solution *to* form an insoluble product as in ionic precipitation, but rather it is transformed into a higher oxidation state and at the same time reducing the metal ion in solution, i.e., it is an oxidation–reduction process:

Oxidation: Reduced species $\rightarrow$ Oxidized species + ne^-

Reduction: $\mathrm{M}^{n+} + ne^- + \mathrm{M}$

Overall reaction:

$$\mathrm{M}^{n+} + \text{Reduced species} \rightarrow \mathrm{M} + \text{Oxidized species}$$

The process may be *homogeneous* (the reduced species is ionic **or** non-ionic) or *heterogeneous* (reduction takes place on a solid surface). Heterogeneous processes may be electrochemical or electrolytic.

IONIC

Table 25.1 shows examples of metal precipitation by reduction of their aqueous solutions by ionic reducing agents. Reducing agents commonly used are ferrous, sulfite, dithionite, hypophosphite, formate, and oxalate ions.

Table 25.1: Precipitation by ionic reduction.

Reducing ion	Reaction	Application
Ferrous	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	$Au^{3+} + 3e- \rightarrow Au$ $Ag^+ + e^- \rightarrow Ag$
Sulfite	$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e-$	$Cu^{2+} + 2e- \rightarrow Cu$ $SeO_3^{2-} + 6H^+ + 4e- \rightarrow Se + 3H_2O$
Dithionite	$S_2O_4^{2-} \rightarrow 2SO_2 + 2e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$
Hypophosphite	$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e-$	$Ni^{2+} + 2e- \rightarrow Ni$ $Co^{2+} + 2e^- \rightarrow Co$
Formate	$HCOO- \rightarrow CO_2 + H^+ + 2e-$	$Pt^{4+} + 4e^- \rightarrow Pt$
Oxalate	$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$	$Pd^{2+} + 2e- \rightarrow Pd$ $Au^{3+} + 3e- \rightarrow Au$

Sulfite ion

Sulfite ion may be used as an aqueous solution of sulfur dioxide:

$$SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow 2H^+ + SO\$-$$

$$SO_3^{2-} + H_2O + SO_4^{2-} + 2H^+ + 2e^-$$

Precipitation of copper

On passing SO_2 into a solution of copper sulfate at room temperature, copper sulfite will precipitate. However, if precipitation is carried out at 150 °C and 350 kPa, metallic copper is precipitated according to:

$$Cu^{2+} + SO_3^{2-} + H_2O \rightarrow Cu + 2H^+ + SO_4^{2-}$$

The drawback to this process is the low yield of copper as shown in Figure 25.1; the corrosion problems due to the acidic environment, and the presence of small amounts of sulfur in the copper produced. The low yield may be due to the intermediate formation of cuprous ion which disproportionates precipitating half of the copper and regenerating the other half as cupric ion:

$$Cu^{2+} + e^- \rightarrow Cu^+$$

$$2Cu^+ \rightarrow Cu + Cu^{2+}$$

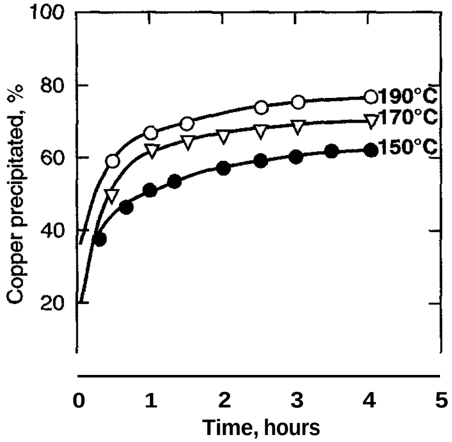

Figure 25.1: Precipitation of metallic copper from $CuSO_4$ solution by SO_2 (Okabe and Ito, 1964).

The decomposition of sulfurous acid at the reaction temperature to H_2SO_4 and elemental sulfur according to the equation:

$$3H_2SO_3 \rightarrow 2H_2SO_4 + S + H_2O$$

accounts for the presence of small amounts of sulfur in the copper produced.

This process can be improved by adding an ammoniacal solution of ammonium sulfite instead of SO_2, i.e., neutralizing the acid as soon as formed. The following reaction takes place:

$$Cu^{2+} + SO_3^{2-} + 2NH_3 + H_2O \rightarrow Cu + 2NH_4^+ + SO_4^{2-}$$

This results in complete precipitation of copper and has the advantage of operating under basic conditions thus eliminating corrosion problems. However, it has the inconvenience of producing ammonium sulfate which has to be marketed as fertilizer.

In a similar way, cuprous ion in a copper ammine sulfite solution can be reduced to metallic copper when the pH is adjusted to 3 by sulfurous acid to precipitate the double salt $Cu_2SO_3 \cdot (NH_4)_2SO_3$ which, when slurried with water and heated at 150 "C in an autoclave:

$$Cu^+ + e^- \rightarrow Cu$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O$$

Overall reaction:

$$Cu_2SO_3 \cdot (NH_4)_2SO_3 \xrightarrow{150\,°C} 2Cu + SO_2 + 2NH_4^+ + SO_4^{2-}$$

Precipitation of selenium

Sulfite ion in form of sulfur dioxide is also used to precipitate elemental selenium from selenous acid:

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$SeO_3^{2-} + 6H^+ + 4e^- \rightarrow Se + 3H_2O$$

Overall reaction:

$$SeO_3^{2-} + 2H^+ + 2SO_3^{2-} \rightarrow Se + 2SO_4^{2-} + H_2O$$

or $$H_2SeO_3 + 2SO_2 + H_2O \rightarrow Se + 2H_2SO_4$$

Selenous acid is obtained by water scrubbing of SeO_2 fumes evolved during the treatment of anodic slimes of copper electrolysis. During the Precipitation of selenium, the temperature of the solution should be kept at 25–30 "C so that selenium settles as a loose sludge which can be easily discharged. Above this temperature range, the sludge becomes plastic and is difficult to remove from the precipitators. The sludge obtained is then boiled to coagulate the red amorphous selenium and to convert it to the crystalline modification. Solutions of selenous acid usually contain tellurium in solution; the precipitation of selenium is, however, selective.

Hypophosphite

The reducing power of hypophosphite is due to the reaction:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^-$$

Nickel and cobalt are precipitated by hypophosphite:

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + 2H^+ + H_2PO_3^-$$

The reaction is vigorous and hydrogen gas is evolved by the side reaction:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + H_2$$

Nickel is obtained mainly as a dark powder, but occasionally it deposits on the walls of the container as a mirror, which is gradually detached and broken into thin flakes. These reactions are used at present to deposit nickel or cobalt films on articles equivalent to those obtained by electroplating. The process is thus known as *electroless electroplating* or *chemicalplating*. Nickel produced from neutral solutions contains as much as 12% P in form of nickel phosphide, Ni_3P. Ammonium salts decrease the rate of cobalt deposition to a great extent. Also, cobalt is not deposited from acid solution while nickel is deposited, thus a separation can be achieved. Complete precipitation of nickel powder can be achieved from solutions containing 50 g/L sodium hypophosphite and 200 g/L NH_4Cl.

Others

Ferrous, oxalate, and formate ions are used to precipitate precious metals from chloride leach solution of gold bullion:

$$AuCl_4^- + 3Fe^{2+} \rightarrow Au + 3Fe^{3+} + 4Cl^-$$

$$2Au^{3+} + 3C_2O_4^{2-} \rightarrow 2Au + 4H^+ + 6CO_2$$

$$Pt^{4+} + 2HCOO^- \rightarrow Pt + 2H^+ + 2CO_2$$

$$Pd^{2+} + HCOO- \rightarrow Pd + H^+ + CO_2$$

Based on these reactions, gold and the platinum metals are separated on a commercial scale from the spent electrolyte during the electrolytic refining of gold (Figure 25.2). Figure 25.3 shows a scanning photomicrograph of gold powder precipitated from gold chloride solution by ferrous sulfate solution.

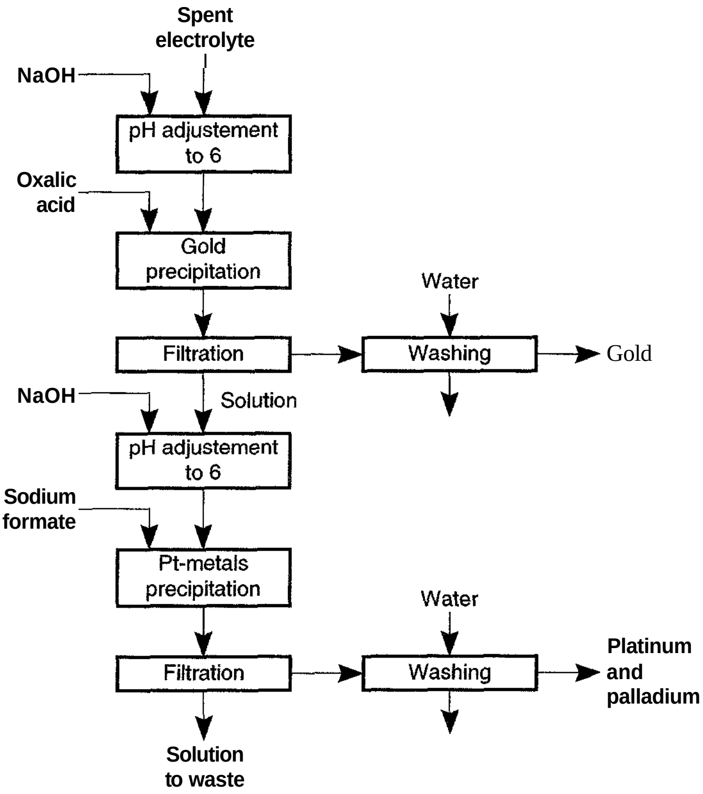

Figure *25.2:* Separation of gold and platinum metals from spent electrolyte.

Dithionite precipitates copper from $CuSO_4$ solutions:

$$S_2O_4^{2-} \rightarrow 2SO_2 + 2e^-$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Overall reaction:

$$Cu^{2+} + S_2O_4^{2-} \rightarrow c\ u + 2SO_2$$

NON-IONIC

Non-ionic reducing agents are hydrogen, carbon monoxide, formaldehyde, and hydrazine (Table 25.2). Their action may be represented by the equations:

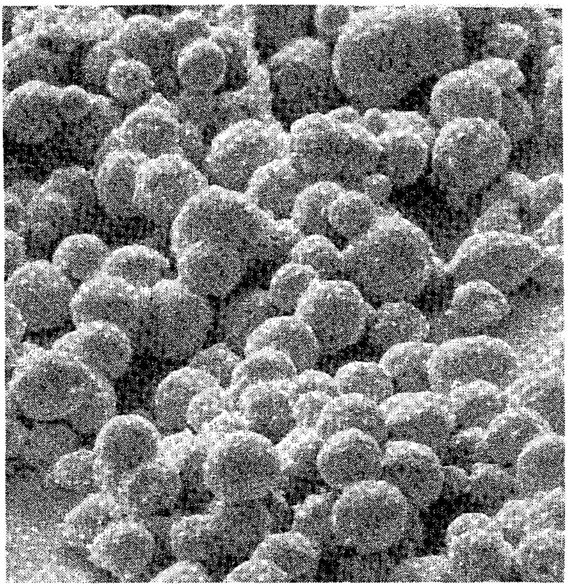

Figure 25.3: Scanning electron micrograph of gold powder precipitated from gold chloride solution by ferrous sultate. Magnification 1000**x** (courtesy Gold Bulletin).

$$H_2 \rightarrow 2H^+ + 2e-$$

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e-$$

$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^-$$

$$N_2H \cdot NH_2 \rightarrow N_2 + 4H^+ + 4e-$$

Table 25.2: Precipitation by non-ionic reduction.

Reducing agent	Reaction	Application
Hydrogen	$H^2 \rightarrow 2H^+ + 2e-$	$Ni^{2+} + 2e- \rightarrow Ni$
Carbon monoxide	$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e-$	$Ag^+ + e^- \rightarrow Ag$ $Cu^{2+} + 2e^- \rightarrow Cu$
Formaldehyde	$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^-$ $HCHO + 3OH^- \rightarrow HCOO- + 2H_2O + 2e^-$	$Cu^{2+} + 2e- \rightarrow Cu$
Hydrazine	$H_2N \cdot NH_2 \rightarrow N_2 + 4H^+ + 4e^-$ $2H_2N \cdot NH_2 \rightarrow N_2 + 2NH_4^+ + 4e-$	$Cu^{2+} + 2e^- \rightarrow Cu$

Hydrogen

Hydrogen at high temperature and pressure leads to the precipitation of metals or oxides. Cobalt, nickel, copper, and uranium dioxide are precipitated on industrial scale by this method. Reduction is usually carried out in horizontal stainless steel autoclaves equipped with agitators, baffles, heating or cooling coils, and the necessary connections for feed and gas inlets and outlets. The product of this technique is a high-purity powder that can be used as such, or in case of metals, hot pressed and rolled in form of strips. Precipitation may be conducted from aqueous as well as from non-aqueous media.

Precipitation of metals from aqueous medium

For the reaction:

$$M^{2+} + H_2 \rightarrow M + 2H^+$$

the equilibrium constant is given by:

$$K = \frac{[H^+]^2}{[M^{2+}] \cdot p_{H_2}}$$

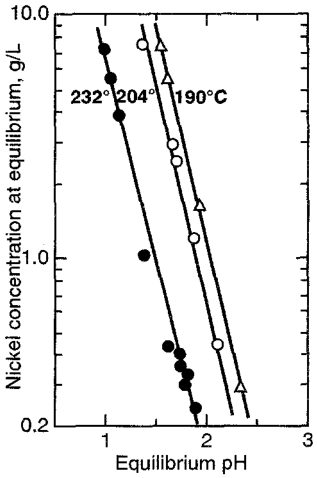

Figure *25.4:* Precipitation of nickel from nickel sulfate solution by hydrogen at 3,500 kPa, $[(NH_4)_2SO_4]$ = 112 g/L, equilibrium conditions (Schaufelberger and Roy, 1955).

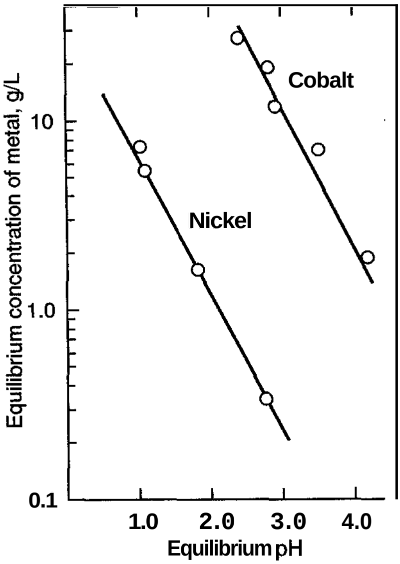

Figure *25.5:* Precipitation of cobalt and nickel from acid solution, temp. 190 °C, H_2 pressure 3500 kPa, $[(NH_4)_2SO_4]$ = 112 g/L (Schaufelberger and Roy, 1955).

'Therefore:

$$\log[M^{2+}] = -2\text{pH} - (\log K + \log p_{H_2})$$

This means that when precipitation is carried out at constant hydrogen pressure and constant temperature, then at equilibrium there is a linear relation between $\log[M^{2+}]$ and the pH of the solution, and the **dope** of this straight line equals –2. This was confirmed for the precipitation of nickel from $NiSO_4$ solution, as shown in Figure 25.4 and for cobalt as shown in Figure 25.5.

The precipitation of copper from $CuSO_4$ solution takes place through the disproportionation of cuprous ion which has been identified in the course of reaction:

$$2Cu^{2+} + H_2 \rightarrow 2Cu^{+} + 2H^{+}$$

$$2Cu^{+} \rightarrow c\ u + Cu^{2+}$$

This leads to low yields of metal.

It is clear from the above equation that more metal will be deposited if the hydrogen ions are removed as soon as they are formed. For copper, nickel, and cobalt, this is conveniently done by operating in ammoniacal medium:

$$[M(NH_3)_n]^{2+} \rightarrow nNH_3 + M^{2+}$$

$$M^{2+} + H_2 \rightarrow M + 2H^+$$

$$H^+ + NH_3 \rightarrow NH_4^+$$

It can be seen that increasing the ammonia concentration has two opposing effects:

- Precipitation is favored due to the neutralization of the liberated acid.
- Precipitation is hindered because of the decrease in the reducible metal ions M^{2+} due to the complexing action.

Therefore, there must be an optimum $[NH_3]/[M^{2+}]$ ratio at which these opposing effects are balanced. In the precipitation of nickel, the optimum molar ratio was found to equal two, which agrees with the overall reaction:

$$Ni^{2+} + 2NH_3 + H_2 \rightarrow Ni + 2NH_4^+$$

The amount of ammonia in solution also influences the rate of precipitation. In the case of cobalt, the rate of precipitation achieves a maximum when $[NH_3]/[Co^{2+}] = 2$, as shown in Figure 25.6. Similar results were also reported for copper.

Another way of removing the hydrogen ions as soon as they are formed during reduction is by reducing hydroxide slurries:

$$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$$

$$M^{2+} + H_2 \rightarrow M + 2H^+$$

$$OH- + H^+ \rightarrow H_2O$$

Overall reaction:

$$M(OH)_2 + H_2 \rightarrow M + H_2O$$

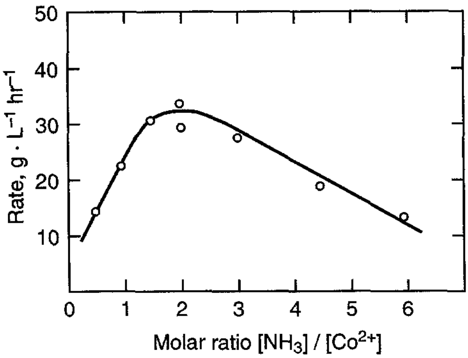

Figure 25.6: Effect of the molar ratio $[NH_3]/[Co^{2+}]$ on the rate of precipitation; temp. 200 °C, catalyst H_2PtCl_6 5.8×10^{-5} M, H_2 pressure 3000 kPa (Wimber and Wadsworth, 1961).

For nickel and cobalt, it was found that this reaction takes place at 270 °C which is a much higher temperature than normally used, but the product is of extremely fine particle size.

Nucleation. In some cases, the presence of a solid surface for precipitation is essential; such a solid is termed a *catalyst*[1].

- If no catalyst were provided, the internal surface of the autoclave itself acts as a catalyst and deposition of metals takes place on the walls or on stirrers. Deposition of metal on the internal surface of the reactor is undesirable because it causes operating difficulties in collecting the metal.
- A catalyst may be needed in one medium but not in another. For example, a catalyst is needed for precipitating cobalt and nickel from an ammoniacal sulfate but not from an acid medium. Nickel is precipitated catalytically from an ammoniacal sulfate medium but not from an ammoniacal carbonate medium.
- Precipitation of a metal may be autocatalytic. Thus, while copper can be precipitated from ammoniacal solution without the need of a catalyst, yet the deposited metal accelerates the process. A difference between the two processes however is that in non-catalyzed reduction, the rate depends on the initial metal ion concentration,

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[1] Strictly speaking, the process is heterogeneous (contact catalysis) but is different from the heterogeneous process described later.

while in catalyzed reduction it does not, but depends on the surface area of the catalyst.

- The commercial precipitation of nickel from the ammonium sulfate system nucleation is induced by adding a small amount of ferrous sulfate which, upon heating to the reaction temperature, hydrolyzes to ferrous hydroxide thus furnishing the catalytic surface required. Nickel deposited in the first step acts as a catalyst for the next. After each reduction, the nickel particles are allowed to settle to the bottom of the autoclave, while the spent solution is drawn off and replaced with fresh pregnant solution. In this way, the nickel particles grow to the desired size, at which point the suspension is discharged and the nickel powder then separated.
- There is no need for the ferrous sulfate catalyst in the ammonium carbonate system; as a result, the nickel powder produced in this medium has a lower sulfur and iron impurity level than powder produced from the ammonium sulfate system.

Role of additives. The presence of certain organic or inorganic substances in the aqueous phase greatly affects the physical nature of metal precipitated. It is possible to precipitate metal powder of certain physical property by simply adding a certain amount of additive. However, when organic additives are used, the carbon content in the powder produced is increased and a special heat treatment is necessary to lower it to 0.01%. Additives may be used for the following purposes:

- *Anti-agglomeration.* Agglomeration of the precipitated metal particles may take place, especially at high temperature. This is undesirable because the agglomerated particles entrap solution causing an impure product. Reagents are therefore added to control the particle size. These are the same as those commonly used to promote uniform growth of cathodes in the electrowinning of metals, e.g., ammonium polyacrylate, arabic gum, gelatin, dextrin, dextrose, and fatty acids such as oleic and stearic. These additives are adsorbed on the individual particles, thus preventing their agglomeration.
- *Smooth surface formation.* When anthraquinone or its derivatives is added during reduction, nickel particles produced are smooth and regular because of uniform deposition while in the absence of anthraquinone, they are coarse and irregular (Figure 25.7).

Anthraquinone has no effect on the precipitation of cobalt. The addition of this additive to ammoniacal nickel sulfate or carbonate solutions also accelerates the precipitation, and this effect increases with increasing anthraquinone concentration up to a certain value, beyond which it has no further effect.

- *Crystalline product.* Figure 25.8 shows hexagonal platelets of metallic cobalt precipitated in presence of a suitable additive.

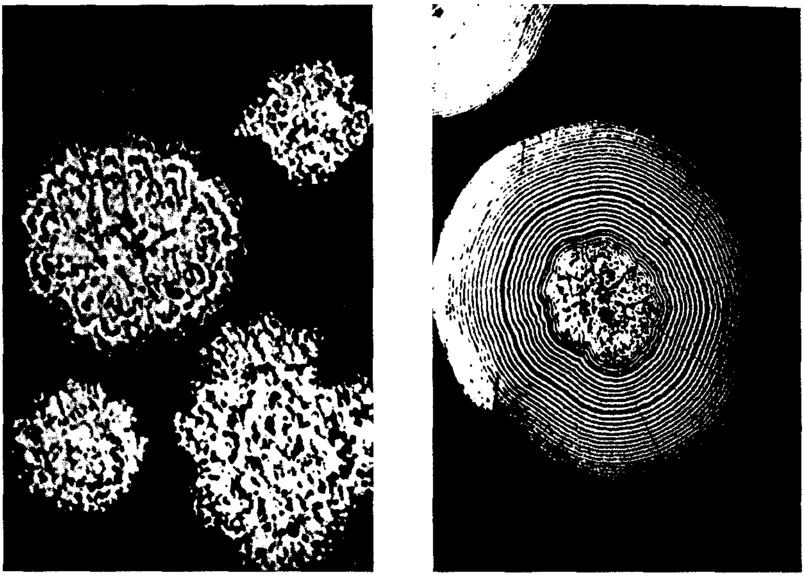
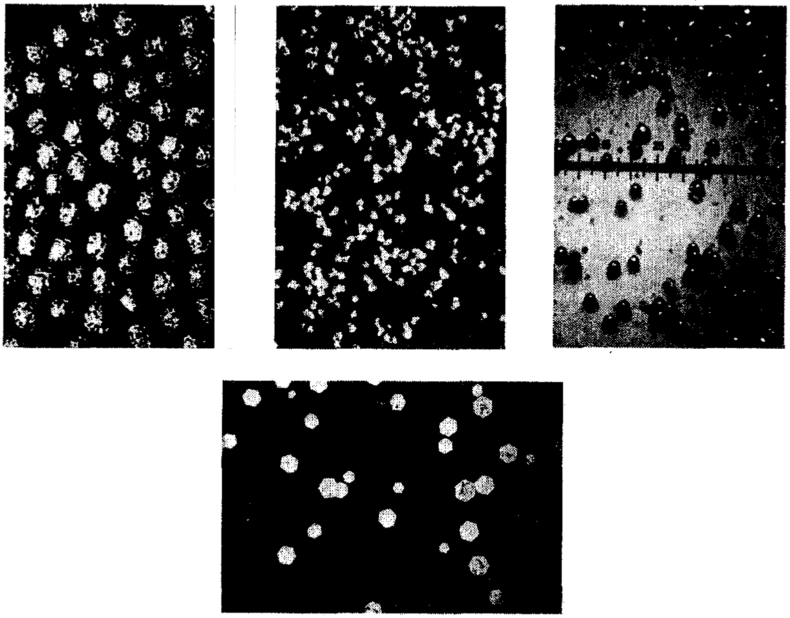


Figure 25.7: Effect of anthraquinone on the shape on nickel powder (320 x); *(a)* no anthraquinone, *(6)* in presence of anthraquinone, cross section through smooth nickel sphere after *40* successive depositions (Meddings and Mackiw, 1965).

Copper. Copper scrap or cement copper is dissolved either in ammoniacal ammonium carbonate at 60 "C at atmospheric pressure with continuous aeration, or in dilute sulfuric acid. When ammoniacal medium is used, the molar ratio $[NH_3]/[Cu^{2+}]$ should be equal to *2.4.* After filtration to remove insoluble material, a small amount of anti-agglomerating agent is added, then solution is heated to 200 "C under 6000 kPa hydrogen. The copper powder precipitated is filtered off, washed, and then dried in a reducing atmosphere at 600 "C.



Nickel

Fine, irregular rough powder Coarse, rough Smooth, 10 μ spheres

Hexagonal platelets

Cobalt

Figure 25.8: Different varieties of metal powders obtained by precipitation from aqueous solution by hydrogen (Mackiw, Benz, and Evans, 1961).

Cobalt and nickel. At the Sherritt-Gordon Plant (Figure 25.9), the purified leach solution obtained by ammoniacal pressure leaching of nickel–cobalt sulfide concentrate contains 45 g/L Ni, 1 g/L Co, 350 g/L ammonium sulfate, and enough free ammonia to give a $[NH_3]/[Ni^{2+} + Co^{2+}]$ molar ratio of 2. The purified solution is reacted with hydrogen at 3500 kPa and 200 °C. Nickel is precipitated prefentially until its concentration is reduced to about I g/L, while all the cobalt remains in solution (Figure 25.10). The spent solution containing 1 g/L Ni and 1 g/L Co is then treated with H_2S at 80 "C and atmospheric pressure, and the precipitated Ni–Co sulfides are filtered off for recovery. The solution is then evaporated to crystallize ammonium sulfate fertilizer. The mixed sulfides precipitated earlier are leached with H_2SO_4 at 120 "C in presence of air at 7200 kPa; acid is used instead of ammonia to avoid the formation of lower oxidation products of sulfur. The solution is purified from traces of iron by adjusting the pH to 5 and filtering off ferric hydroxide.

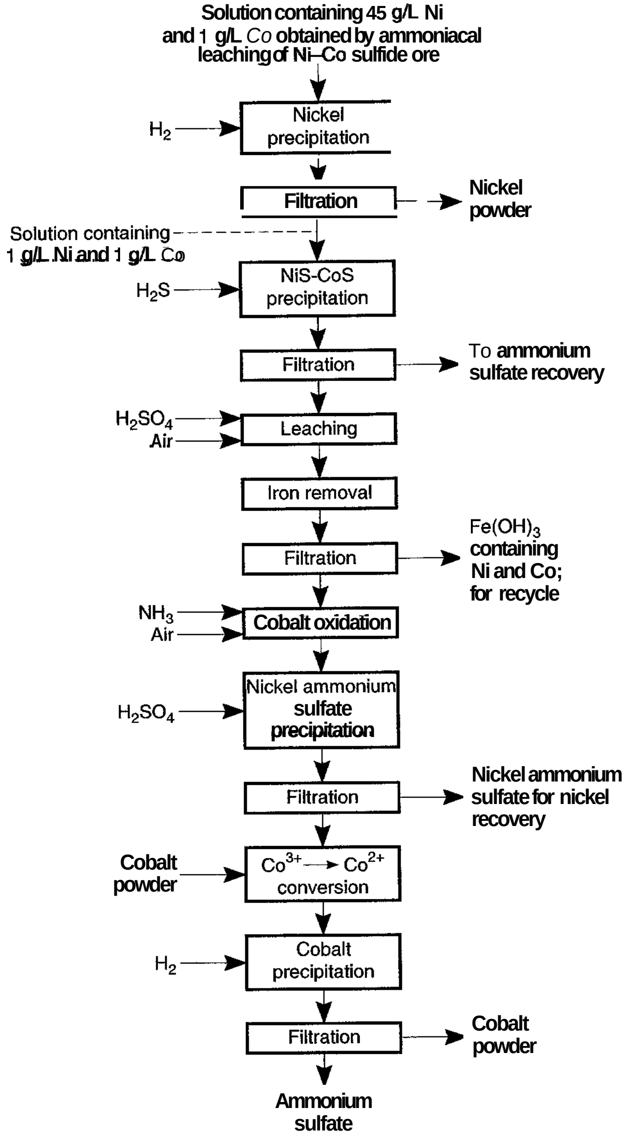


Figure **25.9:** Recovery of nickel and cobalt by precipitation with hydrogen: the Sherritt-Gordon process.

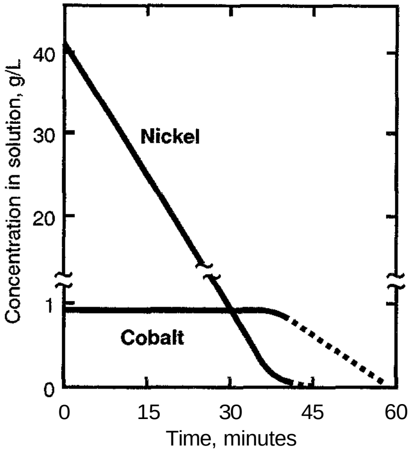


Figure 25.10: Precipitation of cobalt and nickel from ammoniacal solution by hydrogen under pressure (Forward and Halpern, 1956–1957).

The nickel–cobalt separation is carried out by oxidizing Co(II) to Co(III) to 70 °C by air at 700 kPa and in presence of excess ammonia:

$$[Co(NH_3)_5]^{2+} \rightarrow [Co(NH_3)_5]^{3+} + e-$$

$$^1/_2O_2 + H_2O + 2e- \rightarrow 2OH^-$$

On acidification, nickel ammine complex decomposes and precipitates as the double salt nickel ammonium sulfate:

$$[Ni(NH_3)_n]^{2+} + nH^+ \rightarrow Ni^{2+} + nNH_4^+$$

while cobalt remains in solution. The slurry is then filtered to recover nickel. The filtrate, containing cobalt in the cobaltic state, is converted back to the cobaltous state by cobalt powder. This step is essential otherwise a black precipitate of hydrated cobaltic oxide will precipitate during heating. Traces of iron are precipitated by ammonia as ferric hydroxide and separated. Metallic cobalt is then precipitated at 175 °C by hydrogen at 2000 kPa in the presence of 25 g/L Co powder as catalyst. After filtration, the solution is then evaporated to crystallize ammonium sulfate. Table 25.3 gives analysis of nickel and cobalt produced by this process.

Table ***25.3:*** Purity of nickel and cobalt produced by hydrogen reduction.

Nickel		Cobalt	
Ni	99.7–99.85	Co	95.7–99.6
Co	0.1–0.2	Ni	0.1–0.5
Cu	0.01	Cu	0–0.02
Fe	0.02	S	0.02–0.05

Copper and zinc. A flotation concentrate of copper–zinc–iron sulfide is leached with ammonia at 90 "C under an air pressure of 700 kPa. Copper and zinc pass into solution as ammines, while iron is precipitated as hydrated ferric oxide and filtered. Sulfamates formed during leaching are oxidized and hydrolyzed to sulfate at 230 "C and 3500 kPa with air. Prior to reduction by hydrogen to precipitate copper, the molar ratio of free ammonia to copper is decreased to 3/1 by adding sulfuric acid to the autoclave. Small amounts of ammonium polyacrylate are added to permit control of the physical characteristics of the powder produced. The solution is then treated with carbon dioxide under 700 kPa at 37 "C to precipitate zinc hydroxy carbonate, which is then filtered off:

$$2Zn(NH_3)_2SO_4 + CO_2 + 3H_2O \rightarrow$$
$$Zn(OH)_2 \cdot ZnCO_3 + 2(NH_4)_2SO_4$$

The clarified solution is evaporated to crystallize ammonium sulfate which is marketed as a fertilizer.

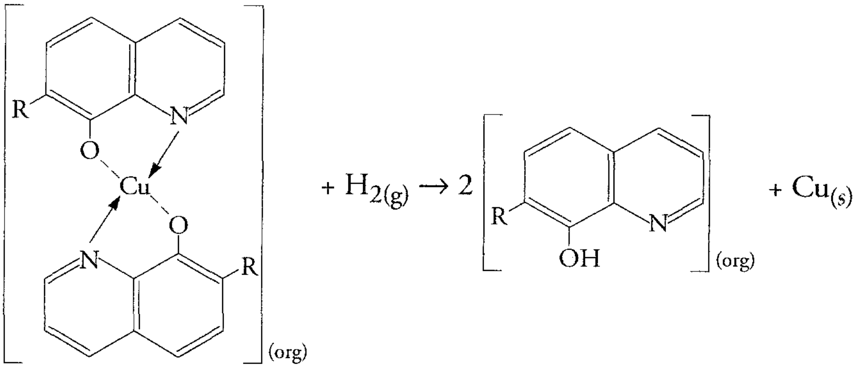
Precipitation of metals from non-aqueous medium

Many metal ions are extracted by organic solvents by forming a coordination bond. When this loaded organic phase is treated by hydrogen at high temperature and pressure in an autoclave, the metal precipitates in powder form and the organic phase is regenerated. The process may be described as *precipitation by substitution* since no ionic species are taking part in the reaction as compared to precipitation by hydrogen from an aqueous phase. The substitution reaction can be represented as follows:

$$H_{2(g)} \rightarrow H_{2(org)}$$

$$R_2M_{(org)} + H_{2(org)} \rightarrow 2RH_{(org)} + M_{(s)}$$

where RH is the organic solvent and M is a divalent metal. A typical example is the precipitation of metallic copper powder from hydroxyquinoline–kerosene phase containing copper:



Precipitation of oxides

Uranium dioxide is recovered from the uranyl carbonate leach solution by precipitation with hydrogen under pressure:

$$[UO_2(CO_3)_3]^{4-} \rightarrow UO_2^{2+} + 3CO_3^{2-}$$

$$UO_2^{2+} + 2e^- \rightarrow UO_2$$

$$H_2 \rightarrow 2H^+ + 2e^-$$

Overall reaction:

$$[UO_2(CO_3)_3]^{4-} + H_2 \rightarrow UO_2 + 2HCO_3^- + CO_3^{2-}$$

At Kalna in Yugoslavia, the reaction is conducted at 150 °C and 1500 kPa in vertical autoclaves containing pellets of partly sintered UO_2 as catalyst. The precipitate builds up on the catalyst pellets and each tower is operated continuously until 10 tons of product has accumulated. The reduction end solution which contains only 3 to 5 mg/L uranium is recycled to the pressure leaching state. The precipitation of the following oxides has been studied:

- Manganese dioxide from potassium manganate solution:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

- Molybdenum dioxide from ammonium molybdate solution:

$$MoO_4^{2-} + 4NH_4^+ + 2e^- \rightarrow MoO_2 + 4NH_3 + 2H_2O$$

Carbon monoxide

Carbon monoxide has been used for precipitating silver from $AgNO_3$ solution and copper from $[Cu(NH_3)_4]^{2+}$ solutions obtained by leaching brass scrap in ammoniacal ammonium carbonate[1]:

$$[Cu(NH_3)_4]^{2+} \rightarrow Cu^{2+} + 4NH_3$$

$$Cu^{2+} + CO + H_2O \rightarrow Cu + CO_2 + 2H^+$$

Precipitation takes place at 150 °C with CO partial pressure of 5,000 kPa. The solution is then boiled to precipitate zinc as basic carbonate. Precipitation of metals by CO is much slower than by hydrogen. This may be due to the fact that CO first reacts with water to form hydrogen:

$$CO + H_2O \rightarrow H_2 + CO_2$$

Formaldehyde

Formaldehyde, HCHO, is a water-soluble gas produced industrially by the oxidation of methyl alcohol which in turn is produced from coal or petroleum gases. It is mainly used for the manufacture of synthetic resins and as a reducing agent. It is effective in acid and in alkaline medium. In acid medium, formic acid is formed:

$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^-$$

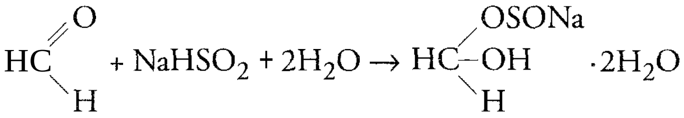
while in alkaline medium, formate ion forms:

$$HCHO + 3OH^- \rightarrow HCOO- + 2H_2O + 2e^-$$

Formaldehyde sodium sulfoxylate, known in industry as Rongalit C, is a crystalline solid having all the reducing properties of formaldehyde but the convenience of being easily handled. It is prepared by reacing formaldehyde with sodium sulfoxylate in alkaline medium:

---

1. An ammoniacal solution of cuprous chloride or cuprous formate can absorb a large amount of CO under pressure and *can* desorb it on reducing the pressure; $CuCl \cdot CO$ crystals form as intermediate product; a method used industrially to remove CO from gases for ammonia synthesis.



$$HCHO + NaHSO_2 + 2H_2O \rightarrow HC(OSONa)(OH)H \cdot 2H_2O$$

Hydrazine

Hydrazine, $H_2N{-}NH_2$, is a powerful reducing agent prepared industrially by the oxidation of ammonia by hypochlorite via the intermediate formation of chloramine:

$$NH_3 + OCl^- \rightarrow NH_2Cl + OH-$$

$$NH_3 + NH_2Cl + OH- + H_2N{-}NH_2 + Cl^- + OH-$$

Aqueous solutions of hydrazine are capable of reducing many metal ions to a lower valency state or to metals:

$$H_2N{-}NH_2 \rightarrow N_2 + 4H^+ + 4e^-$$

$$2H_2N{-}NH_2 \rightarrow N_2 + 2NH_4^+ + 2e-$$

Because of its high cost, its use in metallurgy is limited.

ELECTROCHEMICAL

Electrochemical reduction is a heterogeneous process in which the reducing agent is activated charcoal or a metal less noble than the metal ion in solution. Reactions take place through transfer of electrons at the surface of the solid.

Activated charcoal

The preparation and properties of activated charcoal have been described earlier (pp. 386–392). Activated charcoal has been used for many years for precipitating gold from solutions obtained by leaching gold ores with chlorine water:

$$AuCl_4^- \rightleftharpoons Au^{3+} + 4Cl^-$$

$$Au^{3+} + 3e^- \rightarrow Au$$

$$C + 2H_2O + CO_2 + 4H^+ + 4e^-$$

Overall reaction:

$$4Au^{3+} + 3C + 6H_2O \rightarrow 4Au + 3CO_2 + 12H^+$$

Gold precipitated on the surface of charcoal and was recovered by burning the charcoal. The process was abandoned in favor of the cyanide solution because chlorine water was incapable of solubilizing silver present in the ore.

Metals

Precipitation of a metal from an aqueous solution of its salts by another metal is known as *cementation,* because the precipitated metal is usually cemented on the added metal. The process can be predicted in terms of electrode potentials: The metal with the more positive (oxidation) potential, as given in Table 25.4 of the electromotive series, will pass into solution and displace a metal with a less positive potential provided the solutions are dilute and the metal ion is uncomplexed. The process is electrochemical in nature as shown in Figure 25.11.

A metal may also be recovered from an aqueous suspension of one of its insoluble salts by this method, e.g., silver from silver chloride:

$$\underset{\text{slurry}}{2AgCl} + Fe_{(s)} \rightarrow 2Ag_{(s)} + FeCl_{2(aq)}$$

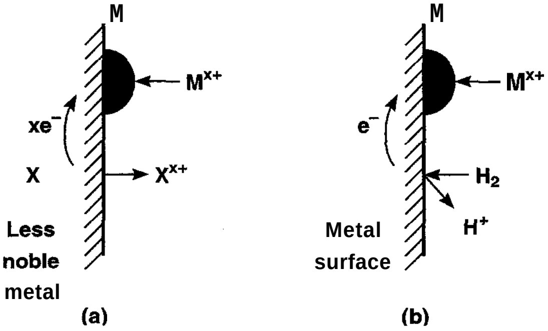


Figure 25.11: Representation of electrochemical precipitation reactions. *(a)* Displacement by metals; the less noble metal X dissolves. (6) Displacement by hydrogen; the metal surface acts as a nucleating agent.

Table *25.4:* Electrode potential series at 25°C and 1 M solutions.

Element	Volts	Element	Volts
Li/Li^+	+3.045	In/In^{3+}	+0.335
Cs/Cs^+	+2.923	Tl/Tl^+	+0.335
Rb/Rb^+	+2.925	Co/Co^{2+}	+0.30
K/K^+	+2.925	Ni/Ni^{2+}	+0.25
Ra/Ra^{2+}	+2.92	Mo/Mo^{3+}	+0.2
Ba/Ba^{2+}	+2.90	In/In^+	+0.14
Sr/Sr^{2+}	+2.89	Sn/Sn^{2+}	+0.140
Ca/Ca^{2+}	+2.87	Pb/Pb^{2+}	+0.126
Na/Na^+	+2.713	Fe/Fe^{3+}	+0.036
La/La^{3+}	+2.52	$H_2/2H^+$	0.000
Ce/Ce^{3+}	+2.48	Sb/Sb^{3+}	−0.1
Mg/Mg^{2+}	+2.37	Bi/Bi^{3+}	−0.2
Y/Y^{3+}	+2.37	As/As^{3+}	−0.3
Sc/Sc^{3+}	+2.08	Cu/Cu^{2+}	−0.337
Th/Th^{4+}	+1.90	Co/Co^{3+}	−0.4
Be/Be^{2+}	+1.85	Ru/Ru^{2+}	−0.45
U/U^{3+}	+1.80	Cu/Cu^+	−0.52
Hf/Hf^{4+}	+1.70	Te/Te^{4+}	−0.56
Al/Al^{3+}	+1.66	Tl/Tl^{3+}	−0.71
Ti/Ti^{2+}	+1.63	$2Hg/Hg_2^+$	−0.792
Zr/Zr^{4+}	+1.53	Ag/Ag^+	−0.800
U/U^{4+}	+1.4	Rh/Rh^{3+}	−0.8
Mn/Mn^{2+}	+1.19	Pb/Pb^{4+}	−0.80
V/V^{2+}	+1.18	Os/Os^{2+}	−0.85
Nb/Nb^{3+}	+1.1	Hg/Hg^{2+}	−0.854
Cr/Cr^{2+}	+0.86	Pd/Pd^{2+}	−0.987
Zn/Zn^{2+}	+0.763	Ir/Ir^{3+}	−1.15
Cr/Cr^{3+}	+0.74	Pt/Pt^{2+}	−1.2
Ga/Ga^{3+}	+0.53	Ag/Ag^{2+}	−1.369
Ga/Ga^{2+}	+0.45	Au/Au^{3+}	−1.50
Fe/Fe^{2+}	+0.44	Ce/Ce^{4+}	−1.68
Cd/Cd^{2+}	+0.402	Au/Au^+	−1.68

Although AgCl is insoluble in water, yet a certain amount of Ag^+ ions do exist in solution and their continuous removal by metallic iron shifts the equilibrium:

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

to the right resulting in the ultimate disappearance of AgCl. Similarly, copper may be recovered from cuprous chloride suspensions by metallic iron:

$$\underset{\textbf{slurry}}{2CuCl} + Fe_{(s)} \rightarrow Cu_{(s)} + FeCl_{2(aq)}$$

In some cases, the metal to be precipitated exists in solution as a complex ion, e.g., gold or silver in cyanide solution exist as the complex cyanide ions $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ respectively. Precipitation by metallic zinc takes place as a result of displacing the equilibrium of the complex ion according to:

$$[Au(CN)_2]^- \rightleftharpoons Au^+ + 2CN^-$$

$$2Au^+ + Zn \rightarrow 2Au + Zn^{2+}$$

$$Zn^{2+} + 4CN^- \rightarrow [Zn(CN)_4]^{2-}$$

Overall reaction:

$$2[Au(CN)_2]^- + Zn \rightarrow 2Au + [Zn(CN)_4]^{2-}$$

Iron used for cementation of copper is in form of scrap, cans, or sponge. Cans are heated in a rotary kiln to remove the tin plating and paint from the surface, and the solder from the seams. They are then passed through a hammer mill, a toothed roll, or a shredding machine to make them more compact and less bulky. Stockpiling of iron usually presents a problem: it occupies large areas and it oxidizes with rime. This oxidation not only means an iron loss, but also a decrease in the quality of cement copper produced from such material.

Applications. Cementation process is applied for the following purposes:

- Recovery of a metal from a leach solution, e.g., copper from sulfuric acid leach solution (Figure 25.12) and gold and silver from cyanide solution (Figure 25.13).
- Purification of a leach solution with the simultaneous recovery of the impurity, e.g., removal of cadmium and thallium from a zinc sulfate solution. In this case, it is very convenient to use metallic zinc as a cementing metal, since the zinc that goes into solution will be recovered at a later stage. Similarly, gallium can be recovered from aluminate leach solution by adding aluminum powder.

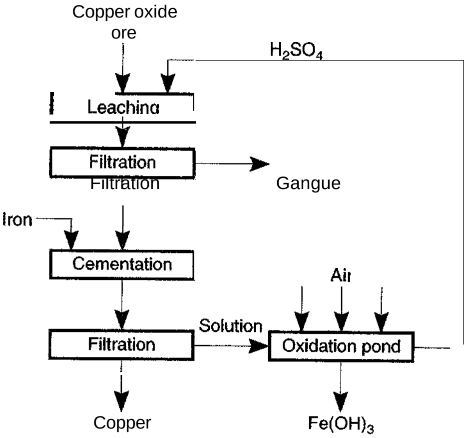


Figure 25.12: The recovery of copper by cementation.

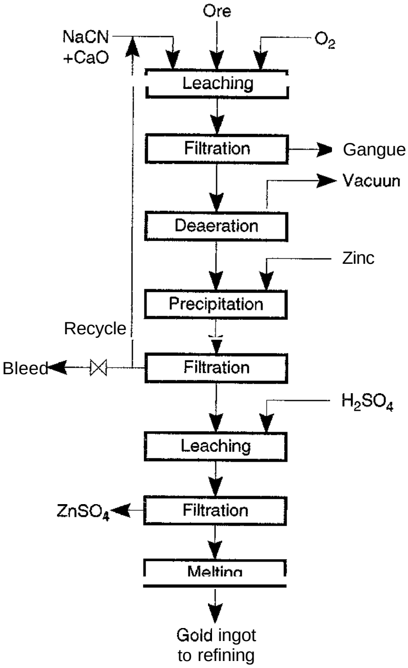


Figure 25.13: Recovery of gold from its ores by cyanidation and precipitation with zinc.

- Separation of two metals in leach solution, e.g., a leach solution containing cobalt and copper, is treated by adding metallic cobalt to precipitate copper, or, when the solution contains nickel and copper, nickel is added to precipitate copper. In both cases, the metal added to cement the copper is recovered at a later stage.

Side reactions during precipitation

The following side reactions take place during cementation:

- *Excessive dissolution of the precipitating metal.* **A** part of the precipitating metal usually dissolves by a secondary reaction without affecting precipitation, thus increasing metal consumption. For example, in the precipitation of copper by iron from sulfate solution, appreciable amounts of iron dissolve in the acid present with generation of hydrogen:

  $$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

  The presence of ferric ion in solution may also contribute to the dissolution of iron by the reaction:

  $$Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$$

  In practice, two to four times the theoretical amount of iron is consumed. In the precipitation of gold and silver from cyanide solution by metallic zinc, some zinc dissolves as a result of the high pH of the solution:

  $$Zn + 2OH^- \rightarrow ZnO_2^{2-} + H_2$$

  In all cases, more metal dissolves when it is in powder form than when it is coarse.

- *Re-dissolution of the precipitated metal.* Unless precautions are taken, the precipitated metal may re-dissolve on standing. For example, in the precipitation of copper by iron, copper may dissolve by the following reactions:

  $$Cu + Cu^{2+} \rightarrow 2Cu^+$$

  $$Cu + 2H^+ + {}^1/_2O_2 \rightarrow Cu^{2+} + H_2O$$

  Therefore, the precipitate should be removed as soon as possible from the solution, and excessive agitation should be avoided since it enhances these reactions. In the precipitation of gold and silver from cyanide solution, the solution must first be deaerated by applying vacuum to the tank containing the solution for few minutes to remove any dissolved oxygen thus preventing the re-dissolution of the metals.

- *Precipitation of hydrolytic products.* If the pH of the solution is not carefully controlled, precipitation of hydroxides or basic salts may take place and contaminate the metal precipitated thus decreasing its purity. For example, in the precipitation of copper by iron, the pH should be about 2 to prevent the hydrolysis of Fe^{2+} and Fe^{3+} ions.

- *Formation of toxic gases.* Due to the presence of trace amounts of arsenic and phosphorus as impurities in some of the precipitating metals, the conditions are favorable for the formation of arsine, AsH_3, and phosphine, PH_3, by the following reactions:

  $$M_3As_2 + 6H^+ \rightarrow 3M^{2+} + 2AsH_3$$

  $$M_3P_2 + 6H^+ \rightarrow 3M^{2+} + 2PH_3$$

  where M is a divalent metal, e.g., iron or zinc. Both gases are highly poisonous and were detected when using iron for precipitating copper, or zinc for precipitating cadmium.

- *Formation of alloys.* Under certain conditions, an alloy is precipitated instead of the pure metal. For example, when cadmium is added to $AuCl_3$ solution, $AuCd_3$ is. precipitated. During the precipitation of copper by iron, the main impurity is iron. There is an indication that this iron impurity occurs in alloy with copper. Cement copper containing 2% Fe is magnetic, and it is not possible to separate iron selectively by magnetic methods.

Table 25.5: Effect of [Cu^{2+}] on the particle size of copper precipitated by iron (Groves, 1964).

Screen analysis, %	Cu^{2+} concentration, g/L		
	3.7	15.0	27.0
+ 100 mesh	7.7	4.1	1.6
– 100 to + 150	11.6	9.2	6.0
– 150 to + 200	15.7	11.3	11.3
– 200 to + 270	14.0	10.8	12.2
– 270 to + 325	5.4	5.1	6.5
– 325	45.6	59.5	62.4

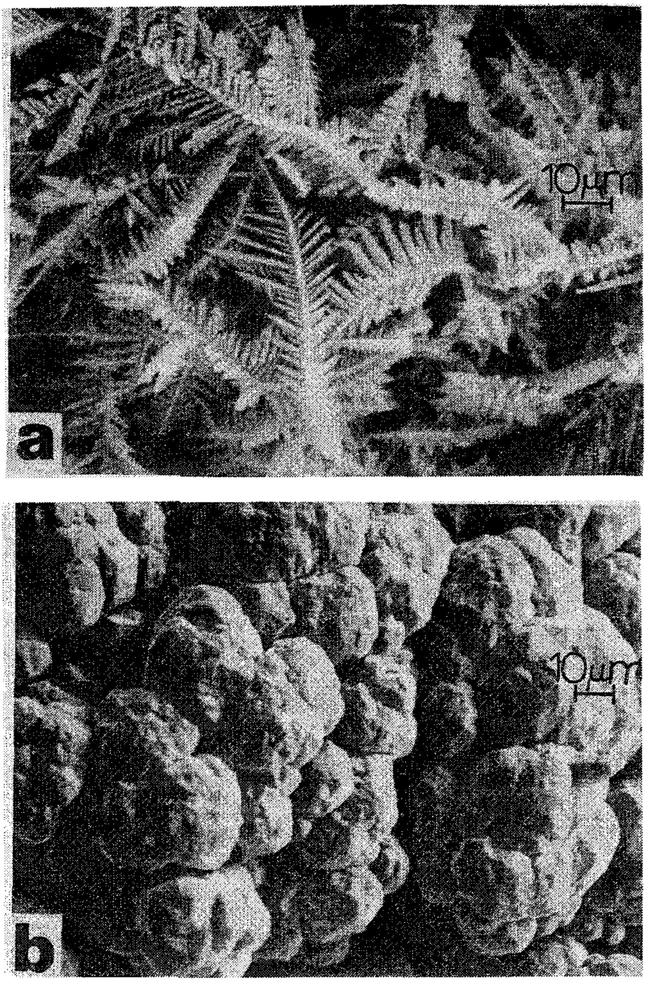


Figure 25.14: Morphology of copper precipitate from sulfate solution (*a*) aluminum, (6) iron (Murr et al., 1979).

Factors affecting the physical properties of precipitated metals

For the cementation of copper by iron, a finer powder is obtained at high Cu^{2+} ion concentration, as shown in Table *25.5.* Further, at a constant Cu^{2+} ion concentration, a fine powder is obtained at high H_2SO_4 concentration, as shown in Table *25.6.* Also, the form of the metal precipitated depends on the precipitating metal as shown in Figure *25.14.*

Table 25.6: Effect of H_2SO_4 on the particle size of copper precipitated by iron (Groves, *1964)*.

Screen analysis, %	H_2SO_4 concentration, g/L		
	8.9	*16.4*	29.9
+ 100 mesh	3.5	*4.6*	3.3
– 100 to + 150	*8.6*	*8.8*	2.9
– 150 to + 200	13.4	12.0	*11.9*
– 200 to + 270	13.4	12.3	11.4
– 270 to + 325	*6.5*	5.8	*6.4*
– 325	*54.6*	*56.5*	*64.1*

Purity and disposal of products

The metal precipitated usually contains appreciable amounts of the precipitating metal and therefore must be treated further to remove it. This is usually done by acid leaching. For example, excess zinc precipitated with gold or cadmium during cementation is removed by leaching with H_2SO_4. The metal is then melted and refined either pyrometallurgically or electrolytically

Cementation of copper from dilute leach solutions is conducted on a large scale as a cheap and rapid method of metal recovery. The product is an impure powder which is usually compacted and melted in a copper smelter. The process is now being challenged by solvent extraction–electrowinning. In some cases where the leach solution contains slimes, it is desirable to avoid the filtration step and therefore a process known as L–P–F, i.e., leach–precipitate–float is used. In this process, the leach solution containing slimes is contacted with iron to precipitate copper which is subsequently recovered by flotation. Drying cement copper is not an easy operation because of its tendency to form oxide. Typical analysis of cement copper produced by precipitation with scrap iron from leach solution is given in Table 25.7. In few cases, cement copper is purified and marketed as a powder. Purification methods yielding powder are:

- Dissolution in H_2SO_4 in presence of oxygen thereby Fe^{2+} is converted to Fe^{3+} which can be precipitated and filtered off. The pure copper sulfate solution is then treated by hydrogen under pressure and high temperature to yield pure copper powder.

Table 25.7: Typical analysis of cement copper.

	Launders, %	Cone precipitation, %
Cu	83.0	90–95
Fe	2.4	0.1–0.2
CaO	0.08	
S	0.52	
	1.15	0.1–0.2
SiO_2	0.42	0.1–0.2
H_2O	≈ 10	
	balance oxygen	balance oxygen

- Digestion with $CuSO_4$ solution, thus displacing the iron content by copper.

In the precipitation of gold from cyanide solution by zinc, mercury, if present in the ore, will also be co-precipitated. Its removal from the filter cake is usually achieved by distillation.

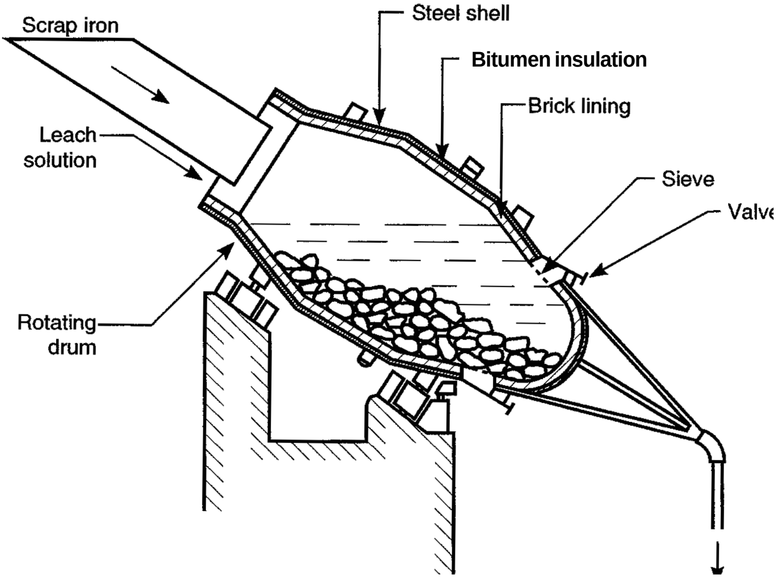


Figure 25.15: **A** rotating drum for cementation of copper.

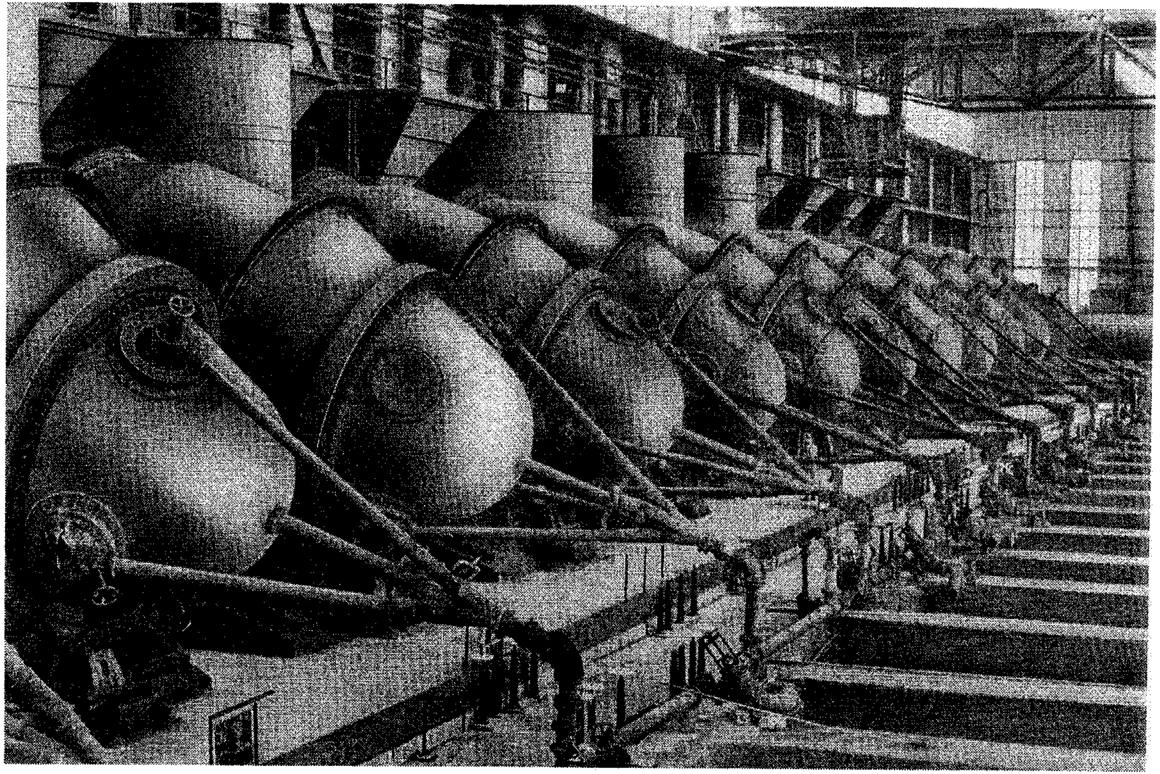


Figure 25.16: Rotating drums for the p of copper from solution by scrap iron (Duisburger Kupferhütte, Germany).

Methods and equipment

Small scale cementation reactions are usually conducted in agitated tanks or rotating drums. When agitated tanks are used, the leach solution is mixed with a certain amount of the precipitating metal powder in a *mechanically agitated tank.* When reaction is complete, the charge is emptied and filtered to recover the precipitated metal. This method is used for precipitating cadmium from zinc sulfate solution and gold and silver from cyanide solutions by zinc dust. In case of gold and silver, the solution must first be deaerated as mentioned earlier. Precipitation in rotating drums is a continuous process using pear-shaped vessels (Figures 25.15 and 25.16) charged from time to time with the precipitating metal in pieces. Due to the rotation, the precipitated metal flows out with the exit solution and is collected by filtration.

Large-scale cementation reactions are conducted principally for the recovery of copper from dilute solutions using scrap iron. This is conducted in launders or in the inverted cone reactors.

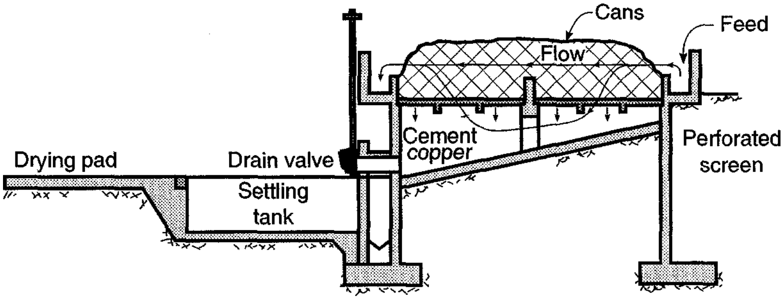


Figure 25.17: Precipitation of copper by iron cans in launders.

Launders. These are narrow tanks about 170 m long, 1.3–3 m wide, and 0.3–1.3 m deep, laid at a slope of about 2%. The launders are continuously charged with scrap iron cans, and the copper-bearing ,solution flows by gravity at the upper end of the launder (Figures 25.17 and 25.18). Fire hoses or hydraulic slushers are used to agitate the cans, knock the cement copper from the cans, and slush the copper along the launders to the settling tanks, where cement copper is then collected. The flow rate of the solution through the launder has an important effect on the quality of cement copper produced. **A** high flow rate helps to produce a uniform movement of solution through the iron in the launder. This prevents the formation of low-acid stagnant areas which favor deposition of hydrolytic products. Further, since the cementation reaction is fast, slow flow rate of solution will result only in excessive dissolution of iron by the acid.

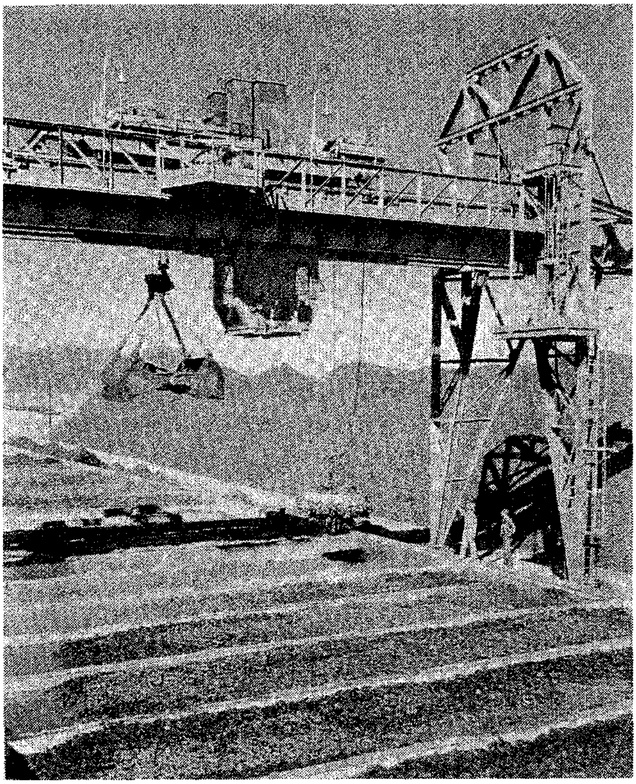


Figure **25.18:** Crane with electromagnet loads scrap iron into cementation tanks where a reaction between iron and $CuSO_4$ solution produces “cement” copper (Anaconda).

Inverted cones. The precipitation cone is **a** continuously operated unit. The vessel in Figure 25.19 consists of a tank of *4.2* m diameter and 7.3 m tall, into which is mounted an inverted cone of 3 m diameter and ***3*** m high. The outer tank contains a 45°-sloped false-bottom floor from one side of the tank to a bottom side discharge at the opposite side. The annular space between the inner cone and the tank is covered by a stainless steel screen mounted as a continuation of the cone and is anchored to the cone and tank. The cone supports a series of pressure nozzles arranged in such a manner as to create a vortex when the copper-bearing solution is pumped into the cone. The inner cone and the area of the tank above the stainless steel screens are filled with shredded detinned iron scrap. The injection of the solution through the mass of iron has the effect of not only rapidly precipitating copper, but also removing the metallic copper from the iron surface, thereby exposing clean, fresh iron. The pressure and velocity of the solutions in the lower conical section move the copper precipitated upward and out of the cone into a reduced velocity zone created by the larger diameter of the holding tank. The copper settles down through the stainless steel screen and accumulates on the sloped false bottom of the tank. Copper can then be discharged either intermittently or continuously. Table 25.7 compares the analysis of cement copper produced in launders with that produced in cones from which it can be seen that the product from cones is purer than that from launders.

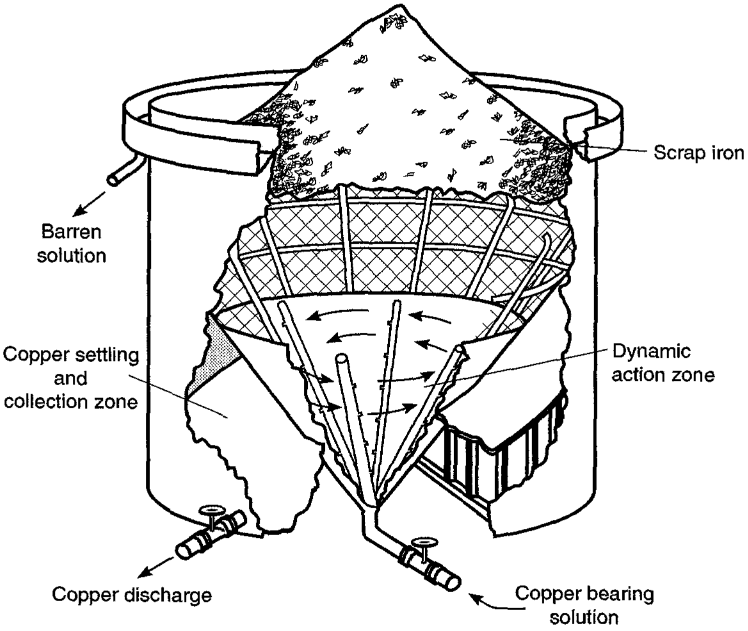


Figure 25.19: Inverted cone precipitator (Kennecott).

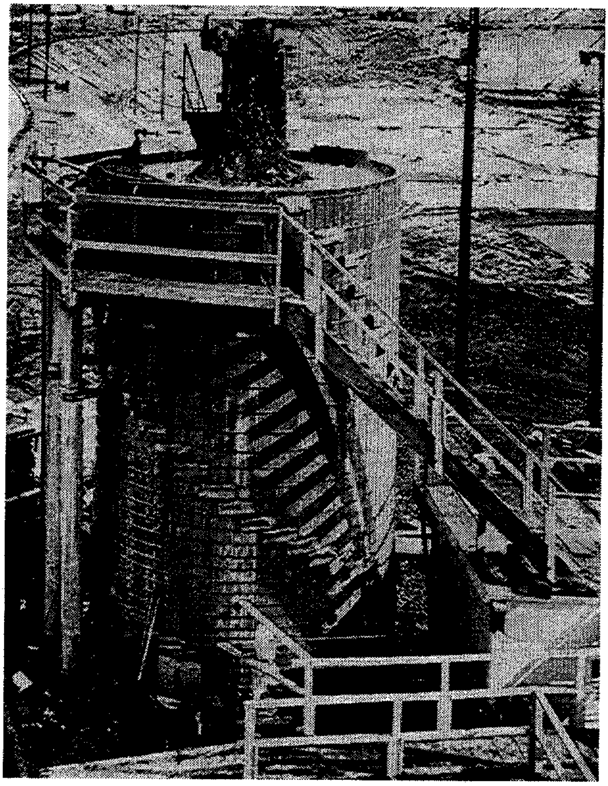


Figure 25.20: Inverted cone precipitator (Kennecott)

ELECTROLYTIC[1]

In precipitation by electrolytic reduction, inert electrodes[2] are immersed in the solution and a direct current is passed through. The reactions taking place for the precipitation of a metal can be represented by the equation:

$$\text{Cathodic: } M^{n+} + ne^- \longrightarrow M$$

---

[1] This is a specialized area of metallurgy — Electrometallurgy — and will be only briefly outlined. For more details, consult F. Habashi, *Principles of Extractive Metallurgy: Volume 4 —Amalgam and Electrometallurgy*, 1999 (available from Laval University Bookstore).

[2] The use of mercury as cathode is a specialized area of electrometallurgy — Amalgam Metallurgy — and will not be discussed here.

$$\text{Anodic: } H_2O \rightarrow {}^1/_2O_2 + 2H^+ + 2e^-$$

For example, copper, zinc, cadmium, manganese, chromium, nickel, cobalt, antimony, gold, silver, and tellurium are recovered industrially from leach solutions by this method — a process called *electrowinning.* Thus, the overall reaction for the electrowinning of copper from copper sulfate leach solution is:

$$Cu^{2+} + H_2O \rightarrow Cu + {}^1/_2O_2 + 2H^+$$

or

$$CuSO_4 + H_2O \rightarrow Cu + {}^1/_2O_2 + H_2SO_4$$

Sulfuric acid regenerated at the anode is recycled to the leaching step. Copper deposited on the cathodes is melted and casted.

In some cases, e.g., in the electrowinning of zinc, the $ZnSO_4$ leach solution must be extensively purified to avoid hydrogen evolution by the decomposition of water. The most important property that determines whether a metal can be deposited from aqueous solution is the relation of its potential to that of hydrogen. Metals having deposition potentials very much less noble than hydrogen cannot be deposited, because hydrogen is discharged preferentially and the cathode potential required for their deposition cannot be attained. It is true that due to the phenomenon of overvoltage, hydrogen does not discharge on many metals until the cathode potential is several tenths of a volt less noble than the reversible potential of hydrogen. That is why for example the deposition of zinc or manganese is possible from aqueous imedium although they are deposited at about 0.5 volt more negative (less noble) than the equilibrium potential of hydrogen. However, imany metals are apparently so much less noble than hydrogen that even the resistance of hydrogen over-voltage does not suffice to enable their deposition potentials to be attained.

Another factor which may be responsible for the failure to deposit some metals, especially beryllium and aluminum, from aqueous solutions is the extremely small size of the ions of these metals and the large positive charge associated with them resulting in their excessive hydration. Dehydration prior to neutralization of the charge at the cathode may be an extremely slow step that hydrolysis, instead, takes place, resulting in the precipitation of the hydroxide instead of the metal. Table 25.8 gives a summary of methods for precipitation of metals by electrolytic reduction.

Table 25.8: Precipitation of metals by electrolytic reduction.

Metal	Electrolyte	Cathode	Remarks
Antimony	NaOH + Na_2S	Steel	
Cadmium	Sulfate	Aluminum	By-product of zinc.
Chromium	Sulfate	Hastalloy	
Cobalt	Sulfate	Stainless steel	Co-product with copper in Zaire.
Copper	Sulfate	Copper	Leach solutions, or after concentration/purification by organic solvents.
Gallium	NaOH	Stainless steel	By-product of aluminum production from bauxite.
Gold	Cyanide	Steel wool	After enrichment on activated charcoal.
Manganese	Sulfate	Stainless steel	
Nickel	Sulfate	Nickel	
Silver	Nitrate	Silver or graphite	
Tellurium	NaOH	Stainless steel	
Zinc	Sulfate	Aluminum	
	NaOH	Stainless steel	Product in powder form

Appendix

Laboratory Autoclaves for Hydrometallurgical Research

Introduction *667*
Materials of Construction *668*
Engineering Aspects. 671
Acid Digestion Bombs *672*
Addresses of Suppliers. *673*

INTRODUCTION

Laboratory autoclaves for hydrometallurgical investigations are available in a variety of sizes, models, and materials of construction. They vary in sizes from *25* mL to *2* liters for laboratory studies and 5 to 50 gallons for pilot plant work. They are essential tools for studying dissolution of minerals at high temperature and pressure, and hydrothermal precipitation reactions. They can be equipped with gas inlet tube, cooling coil, agitators, etc. They may also incorporate an interchangeable chemically resistant lining covering all interior surfaces. Reactor operates up to 20 000 kPa and *250* °C. Berghof developed a special conical flange closure which assures uniform tightening and a reliable seal by means of two simple handscrews.

The Zipper Clave reactor by Autoclave Engineers is manufactured in ½, 1, 2 and *4* liters. It is claimed to be the fastest, easiest opening and closing pressure vessel ever offerred. No bolts to torque, no clamps or rings. Instead, just raise the body and push the spring section to close the cover. To open, just pull the spring and lower the body. Cover remains stationary, so there is no need to break cover connections. Closure is effected by resilient spring member (The Zipper) inserted through a circumferential groove in body and cover. Simply release the safety sleeve and pull the Zipper to remove the cover. A quick release/safety lock and cover safety device are provided to ensure that the spring is fully inserted. The maximum pressure and temperature at which any reactor can be used will depend upon the design of the vessel and its material of construction since all materials lose strength at elevated temperatures. Autoclave design is under continuous improvement for better reliability.

MATERIALS OF CONSTRUCTION

The choice of the material of construction (Table **A.**1) of an autoclave depends on the operating medium whether acidic or alkaline, the temperature range, and the presence or absence of oxidizing atmosphere. Table A.2 provides a set of multipliers which can be used to convert 350 °C pressure ratings for any T316SS vessel to higher or lower temperatures. It can also be used to determine the corresponding ratings for vessels of the same design made of other materials. No pressure vessel should be operated above these maximum temperature limits.

Table A.1: Materials of construction for Parr laboratory autoclaves.

	Major elements, %					
	Fe	Ni	Cr	Mo	Mn	Other
T316 Stainless Steel	65	12	17	25	2.0	Si 1.0
Carpenter 20Cb3	35	34	20	25	2.0	Cu 3.5, Nb 1.0 max.
Monel 400	1.2	66				Cu 31.5
Inconel 600	8	76	15.5			
Hastelloy B-2	2	66	1	28	1	*Co* 1.0
Hastelloy C-276	6.5	15.5	16	1		W *4.0, Co* 2.5
Nickel 200		99				
Titanium Grade *4*		Commercially pure titanium				Ti 99 min.
Zirconium Grade 705	Zr 95.5 min, Hf 4.5 max,Co 2.5					

Stainless Steel 316 Sulfuric, phosphoric, and nitric acids readily attack T316SS at elevated temperatures and pressures. Halogen acids attack all forms of stainless steel rapidly, even at low temperatures and in dilute solutions. Although T316SS offers excellent resistance to surface corrosion by caustic, stress corrosion cracking can occur. This phenomenon begins to appear at temperatures just above 100 °C.

T316SS offers good resistance to ammonia and to most ammonium compounds. Halogen salts can cause severe pitting in all stainless steels. Chlorides can cause stress corrosion cracking.

Table A.2: Pressure rating of reactors (Parr Instrument Company).

Material	Temperature, °C				
	25	100	200	300	350
T316 Stainless Steel	1.13	1.13	1.09	1.04	1.00
Monel 400	1.20	1.20	1.20	1.20	1.19
Inconel 600	1.20[a]	1.20[a]	1.20[a]	1.20[a]	1.20[a]
Hastelloy B-2	1.20[a]	1.20[a]	1.20[a]	1.20[a]	1.20[a]
Hastelloy C-276	1.20[a]	1.20[a]	1.20[a]	1.20[a]	1.20[a]
Nickel 200	0.60	0.60	0.60	0.60	0.60 at 316 °C
(Carpenter 20Cb3	1.20	1.20	1.17	1.16	1.16
Titanium Grade 2	0.75	0.64	0.51	0.36	0.34 at 316 °C
Titanium Grade 4	1.20	1.20	0.81	0.63	0.60 at 16°C
Zirconium Grade 705	1.20	0.98	0.76	0.65	0.61

[a] Standard designs cannot be rated higher than 1.20 without checking all aspects of the design.

Carpenter 20Cb-3. Carpenter 20Cb-3 is an enriched grade of stainless steel, designed specifically for use with dilute (up to 30%) sulfuric acid at elevated temperatures. It can also be used for nitric and phosphoric acid systems as well as for all systems for which T316SS is suitable.

Monel 400. Monel 400 is an alloy of two-thirds nickel and one third copper. For many applications it offers about the same corrosion resistance as nickel, but with higher maximum working pressures and temperatures and at a lower cost because of its improved machinability. It is used for caustic solutions because it is not subject ot stress corrosion cracking in most applications including the presence of chloride ions. It is also an excellent material for fluorine, hydrogen fluoride and hydrofluoric acid systems. As would be expected from its high copper content, Monel *400* is rapidly attacked by nitric acid and ammonia systems.

Inconel 600. Inconel 600 is a high nickel alloy offering excellent resistance to caustic and chlorides at high temperatures and high pressures when sulfur compounds are present. Although it can be recommended for a broad range of corrosive conditions its cost often limits its use to only those applications where its exceptional characteristics are required.

Hastelloy B-2. Hastelloy B-2 is an alloy rich in nickel and molybdenum which has been developed primarily for resistance to reducing acid environments, particularly hydrochloric, sulfuric and phosphoric. Its resistance to these acids in pure form is unsurpassed, but the presence of ferric and other oxidizing ions in quantities as low as 50 ppm can dramatically degrade the resistance of this alloy.

Hastelloy C-276. Hastelloy C-276 is a nickel chromium–molybdenum alloy having a broadest general corrosion resistance of all commonly used alloys. It was developed initially for use with wet chlorine, but it also offers excellent resistance to strong oxidizers such as cupric and ferric chlorides, and to a variety of chlorine compounds.

Nickel 200. Nickel 200 is one of the designations of commerically pure nickel. It offers the ultimate in corrosion resistance to host caustic environments, but its applications are severely restricted because of its poor machinability and resultant high fabrication costs.

Titanium. Titanium is an excellent material for use with oxidizing agents, such as nitric acid, aqua regia, and other mixed acids. It also offers good resistance to chloride ions. Sulfuric and hydrochloric acids, which have high corrosion rates in their pure form can have their corrosion rates in titanium reduced if small quantities of oxidizing ions, such as cupric and ferric are present to act as corrosion inhibitors. This phenomenon leads to many successful applications where sulfuric acid is used to leach ores and the extracted ions act as corrosion inhibitors.

It should be remembered, however, that titanium will burn vigorously in the presence of oxygen at elevated temperatures and pressures. While there have been many successful applications in hydrometallurgy where oxygen and sulfuric acid are handled in titanium equipment, the danger of ignition is always present and must be protected against.

Commercially pure titanium is available in several grades. Grade 2 is the material most commonly used for industrial equipment since it can be fabricated by welding. Grade 4, which has slightly higher trace levels of iron and oxygen, has higher strength than Grade 2 but it is not suitable for welding. Since Parr vessels are not welded, they usually are made of Grade 4 to obtain higher working pressures than can be obtained with Grade 2. Grade 7, containing small amounts of palladium, and Grade 12 containing small amounts of nickel and molybdlenum, offer enhanced resistance to certain environments and can be used for Parr reactors and pressure vessels if suitable billets can be obtained.

Zirconium. Zirconium offers excellent resistance to hydrochloric and sulfuric acids but as with Hastelloy B-2, oxidizing ions such as ferric, cupric, and fluorides must be avoided. Zirconium also offers good resistance to phosphoric and nitric acids, and to alkaline solutions as well. Grade 702 containing hafnium is the standard commercial grade offering the best resistance to most corrosive agents. Grade 705 containing small amounts of both hafnium and niobium has better strength than Grade 702, allowing higher working pressures, but the corrosion resistance of Grade 705 is not as good as Grade 702.

ENGINEERING ASPECTS

High-torque magnetic drives. These magnetically coupled systems use high energy permanent magnets in sealed enclosures with no rotating seals to eliminate the troublesome leakage problems which sometimes arise with a packing gland in severe service, permitting long continuous runs at pressures up to 30 000 kPa with little or no attention to the gland and drive. A water cooling sleeve attached to each drive protects the components from excessive temperatures arising from the reactor. The stirring shaft rotates in PTFE bearings and is rigidly connected to the internal magnet. Both of these components are inside the pressure vessel. The external magnet is supported by bearings and rotates outside the pressure chamber. As a result of the optimally utilized lines of force of the magnetic field, the internal magnet rotates in synchronization with the external magnet.

Valves. Valves used in autoclaves have non-rotating stems to minimize leakage. Because stem tip does not rotate on contact with body seat, the 2-piece Non-Rotating Stems designed by Autoclave Engineers eliminate the galling and scoring of stem and seat usually associated with conventional rotating stem valves. Thus, one of the major (causes of valve leakage and failure is avoided.

Accessories. The safety head houses the rupture disc. To prevent the action of corroding vapors, the discs can be coated on one or both sides with Teflon or gold. Such coatings and lining increase the minimum rupture ratings available in a given disc. A dial thermometer and a connecting tube are also shown.

ACID DIGESTION BOMBS

The acid digestion bombs are small non-agitated autoclaves that are meant for conducting rapid semi-quantitative tests at high temperature and pressure. They may be equiped with a heating mantle but more often they can be heated in a laboratory oven thus the temperature inside the bomb is not precicely known.

- Parr bombs contain a Teflon cup and are available in two sizes: 25 mL and 125 mL (Table **A.3).** They can be heated in an oven. The 125-mL bomb has a safety rupture disc built into the head which protects the bomb and the operator from the hazards of an unexpected explosion from accidental overloading. Should the pressure in the bomb accidentally reach the 23 000 kPa range, a pair of thin, frangible discs (Inconel + stainless steel) will rupture.
- Berghof bomb is a stainless steel pressure vessel with 10 mL Teflon sample holder, heated from below by a heating coil. Operating temperature up to 180 "C.
- Microwave acid digestion bombs are made of a microwave transparent polymer which has good mechanical strength at temperatures up to 150 "C, and serves as a heat insulator for the Teflon sample cup. Since heating is developed internally within the cup, temperatures in the outer, high strength body will seldom exceed 50°C. This type of autoclave is characterized by fast digestion times, can operate at temperatures up to 250 "C, and pressures to 8000 kPa.

Table A.3: Parr acid digestion bombs.

Size, mL	Maximum working pressure, kPa	Maximum working temperature, "C
25	8 000	150–250
125	14 000	150–250

ADDRESSES OF SUPPLIERS

Parr Instrument Company

211, Fifty-third Street
Moline, Illinois 61265
USA
Tel.: (309)762-7716
Fax: (309)762-9453

Autoclave Engineers, Inc.

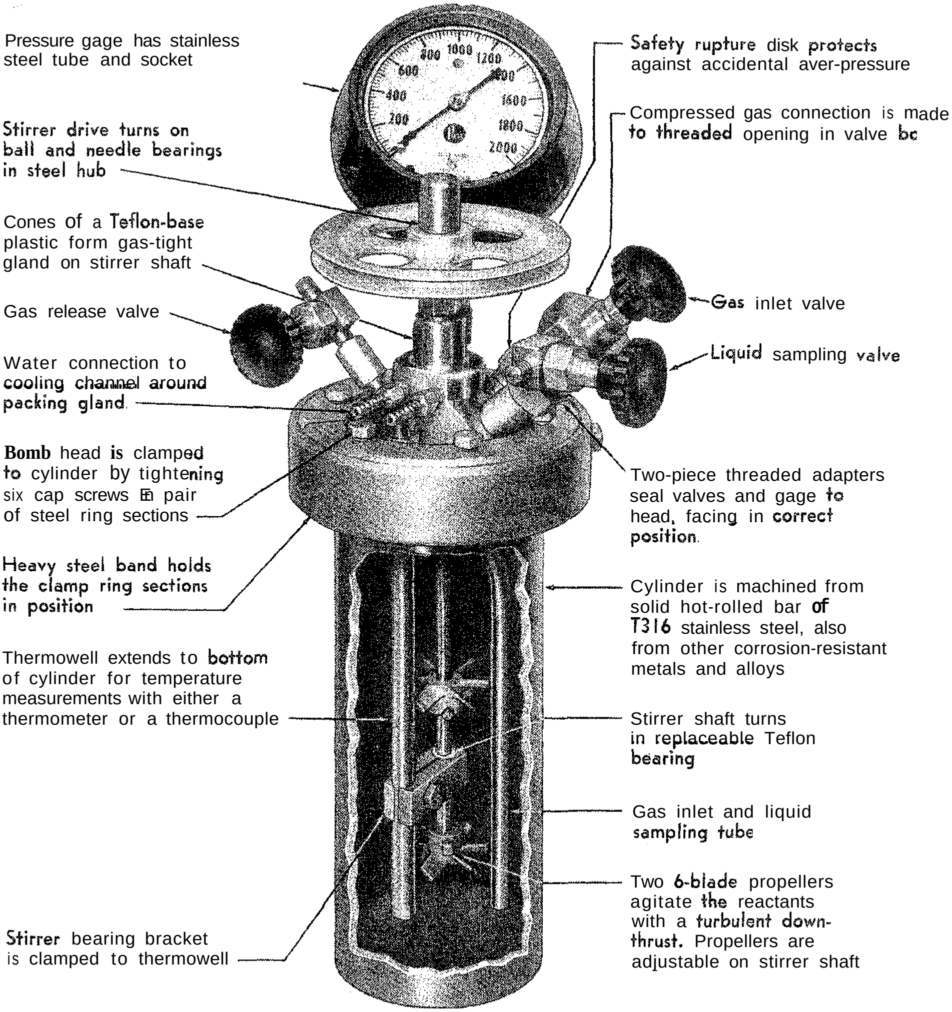
The Fred Gasche Building
2930 West 22nd Street
Erie, Pennsylvania 16512
USA
Tel.: (814)838-5700
Fax: (814)838-5855

Pressure Products Industries, Inc.

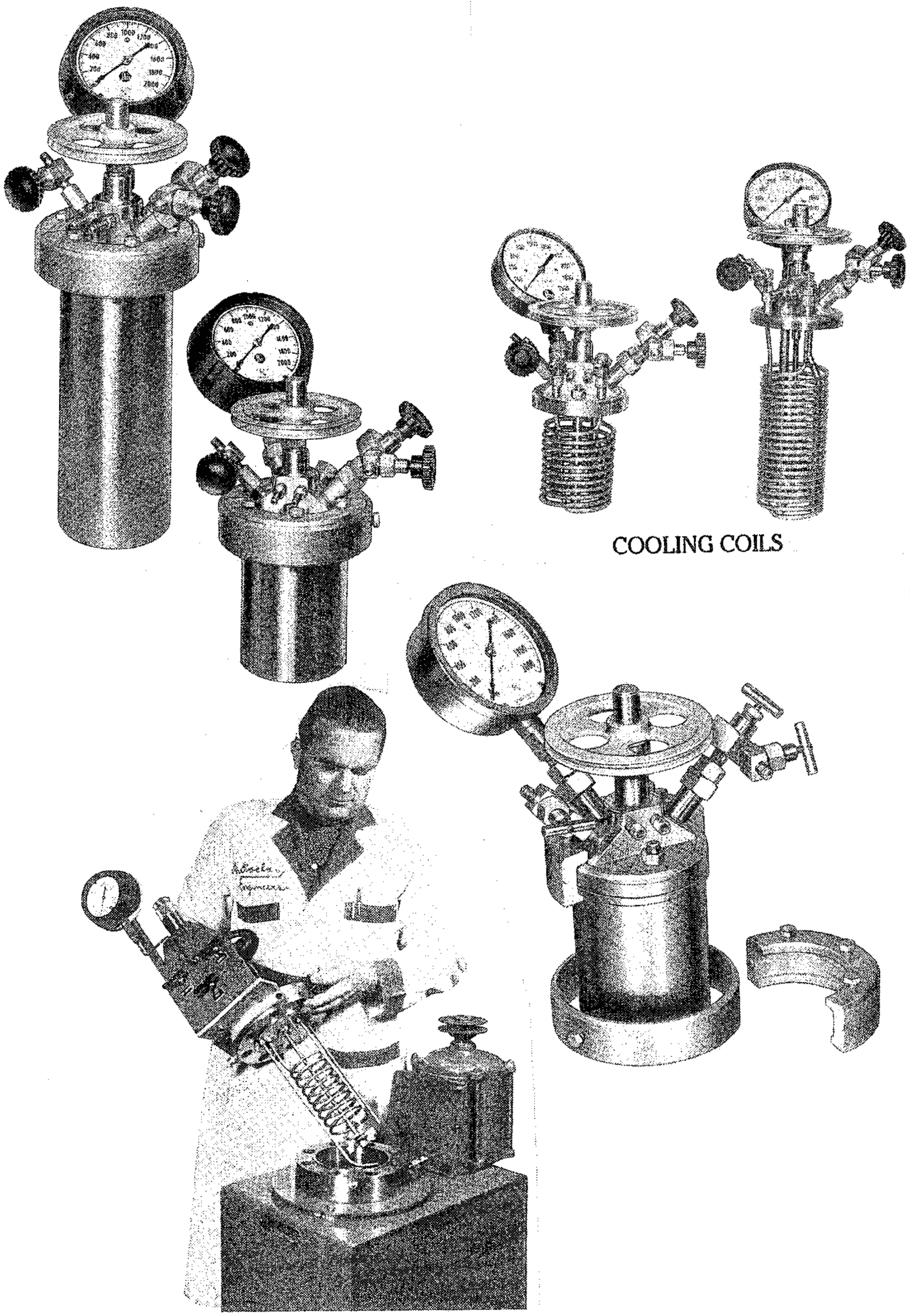
900 Louis Drive
Warminster, Pennsylvania 18974
USA
Tel.: (215)675-1600
Fax: (215)443-8341

Berghof America, Inc.

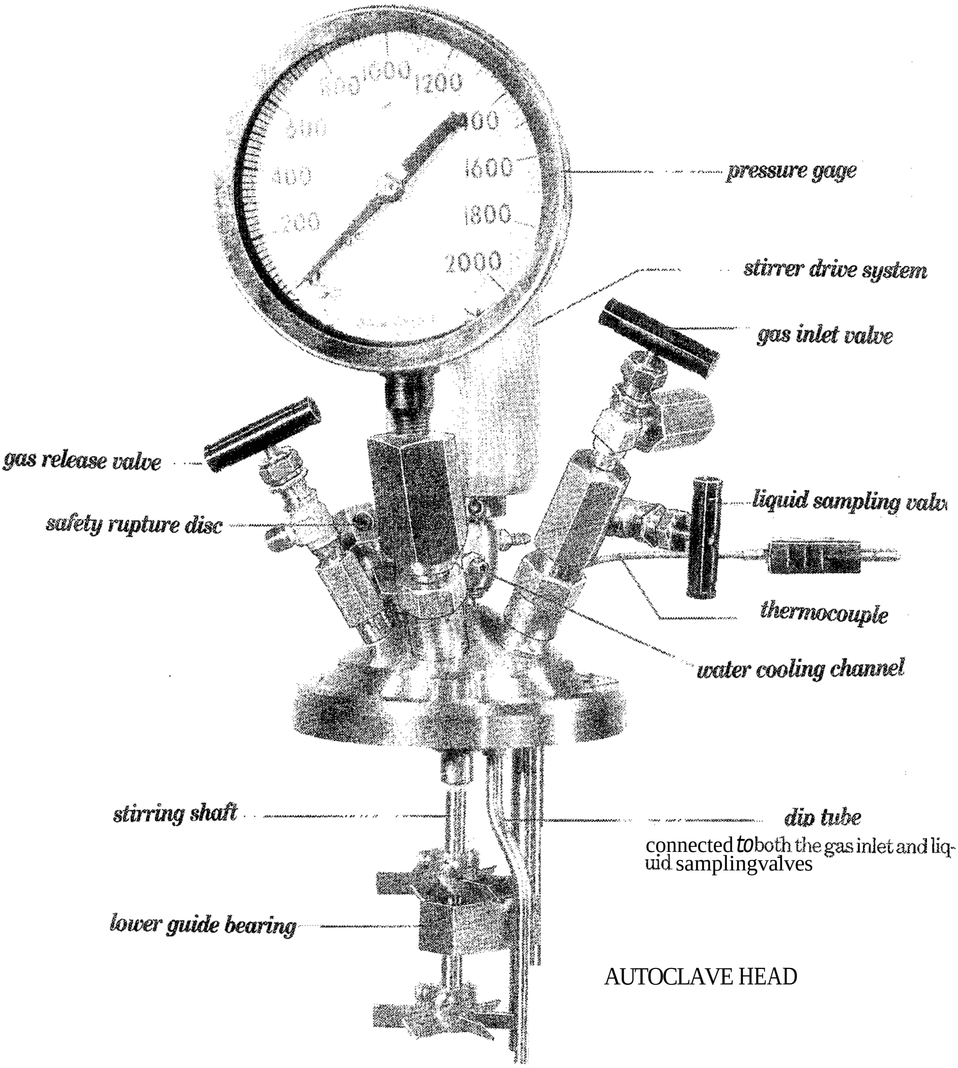
64550 Research Road
Bend, Orgon 97701, USA
Tel.: (503)389-4620



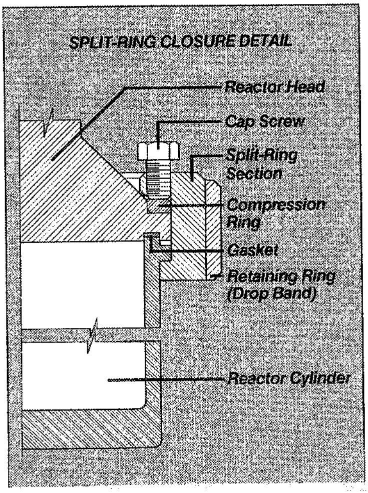
TWO LITERS **PARR** AUTOCLAVE

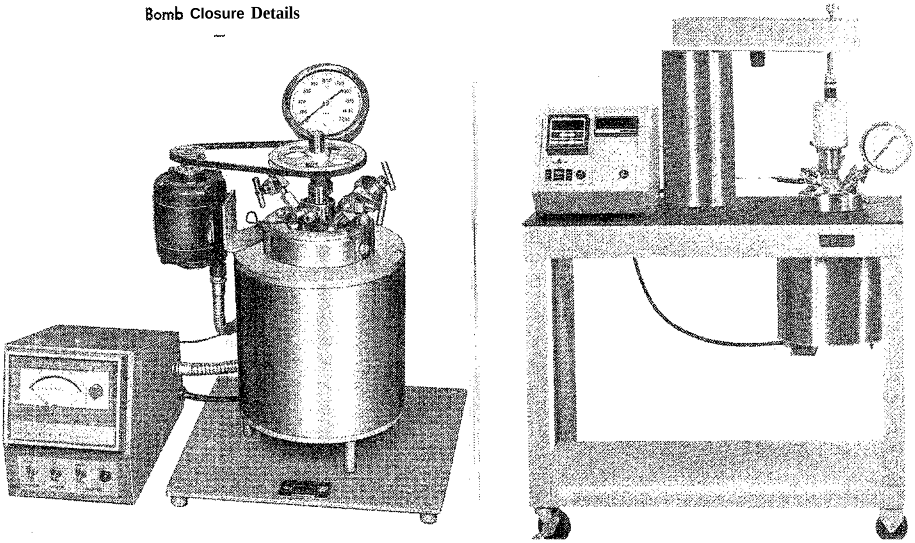


COOLING COILS

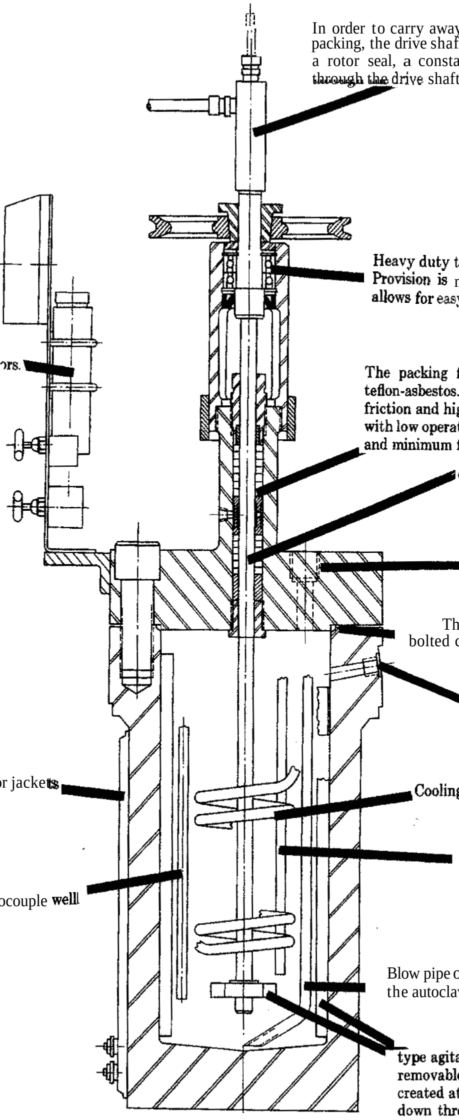

pressure gage
stirrer drive system
gas inlet valve
gas release valve
safety rupture disc
liquid sampling valv
thermocouple
water cooling channel
stirring shaft
dip tube
connected to both the gas inlet and liquid sampling valves
lower guide bearing
AUTOCLAVE HEAD

Bomb Closure Details





ASSEMBLED UNITS



In order to carry away friction heat generated at the packing, the drive shaft is drilled out, and by means of a rotor seal, a constant flow of water is circulated through the drive shaft in the packing section.

Heavy duty thrust bearings insure long-life operation. Provision is made for packing tension take-up, which allows for easy maintenance and long life.

oil seal helps protect the pressure gauge against corrosive vapors.

The packing for standard autoclaves is made from teflon-asbestos. The combination of low coefficient of friction and high-corrosion resistance provides packing with low operating temperature, long life, high strength and minimum frictional wear on the drive shaft.

drive shaft

Solids Charging

The standard closure bolted confined gasket type

safety head assembly

Electric heating or vapor jackets

Cooling coils

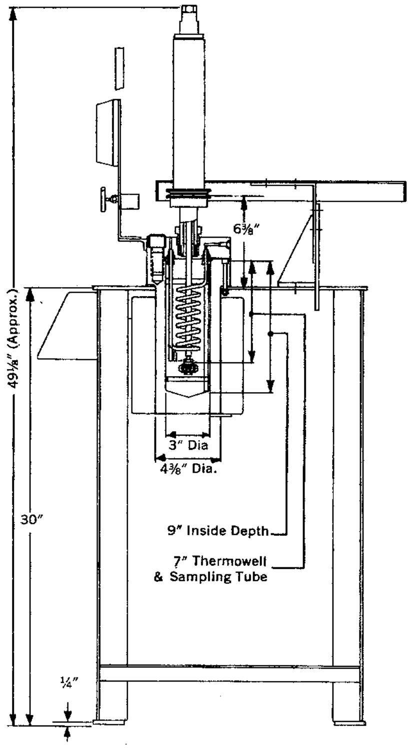
Sampling

A thermocouple within a thermocouple well

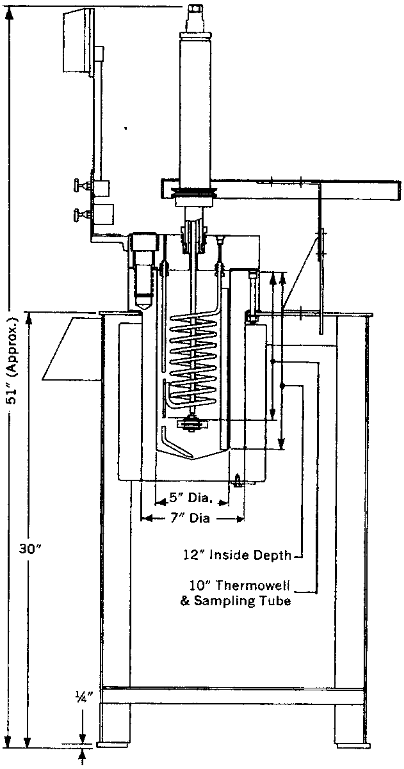
Blow pipe or drain connection can be provided for emptying the autoclave without removal of cover.

This is a turbine-**type agitator with a hollow shaft used in conjunction wi removable baffles. During operation, a low pressure area created at the turbine impellor. Gas is consequently drav down through the hollow shaft and dispersed througho the liquid. The gas bubbles are broken up by the baffl**

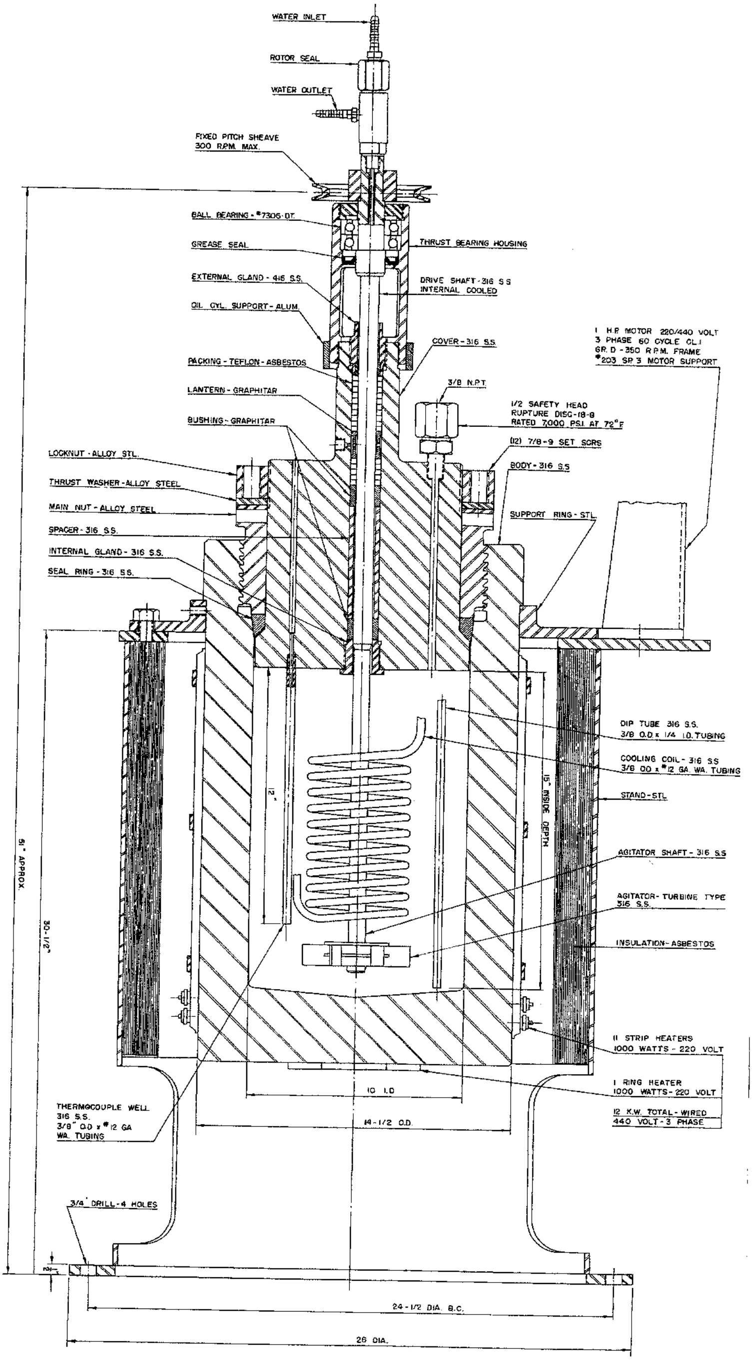
AUTOCLAVES **ENGINEERS**



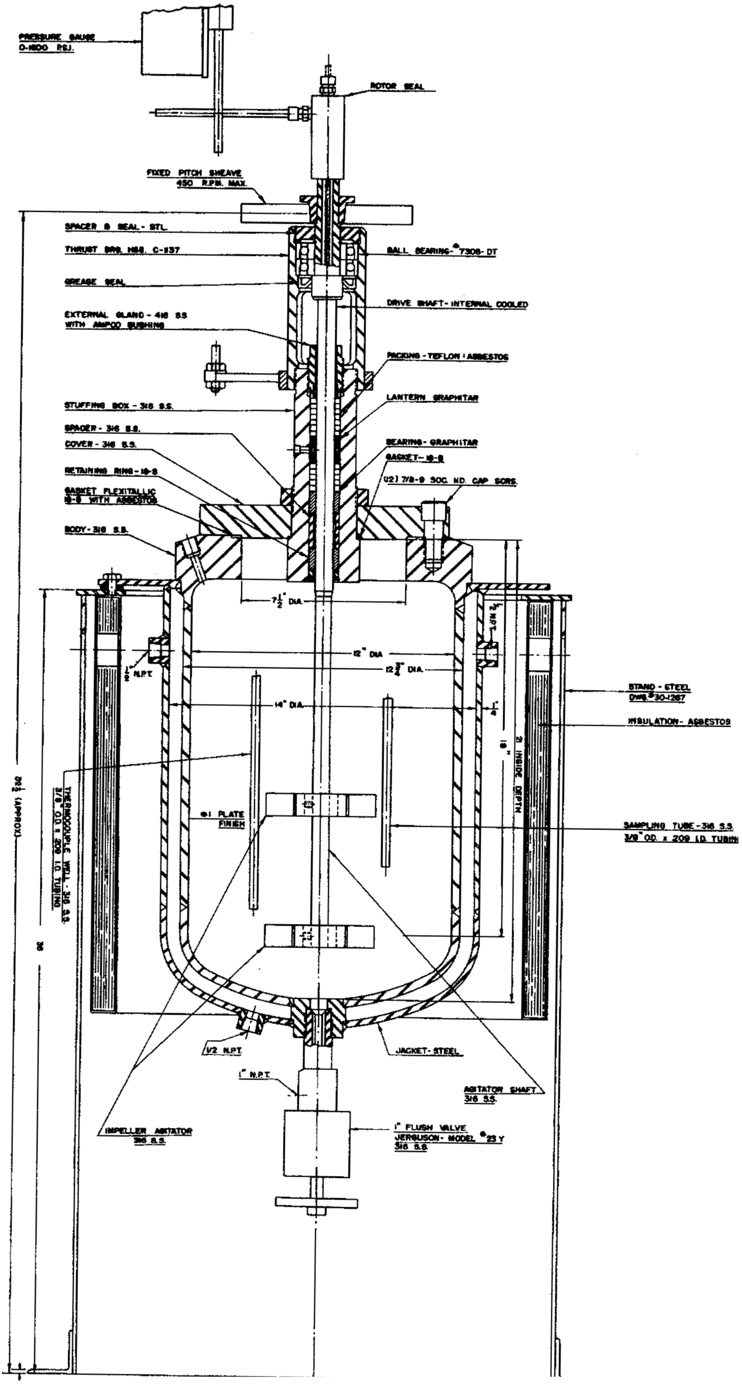
1 LITER



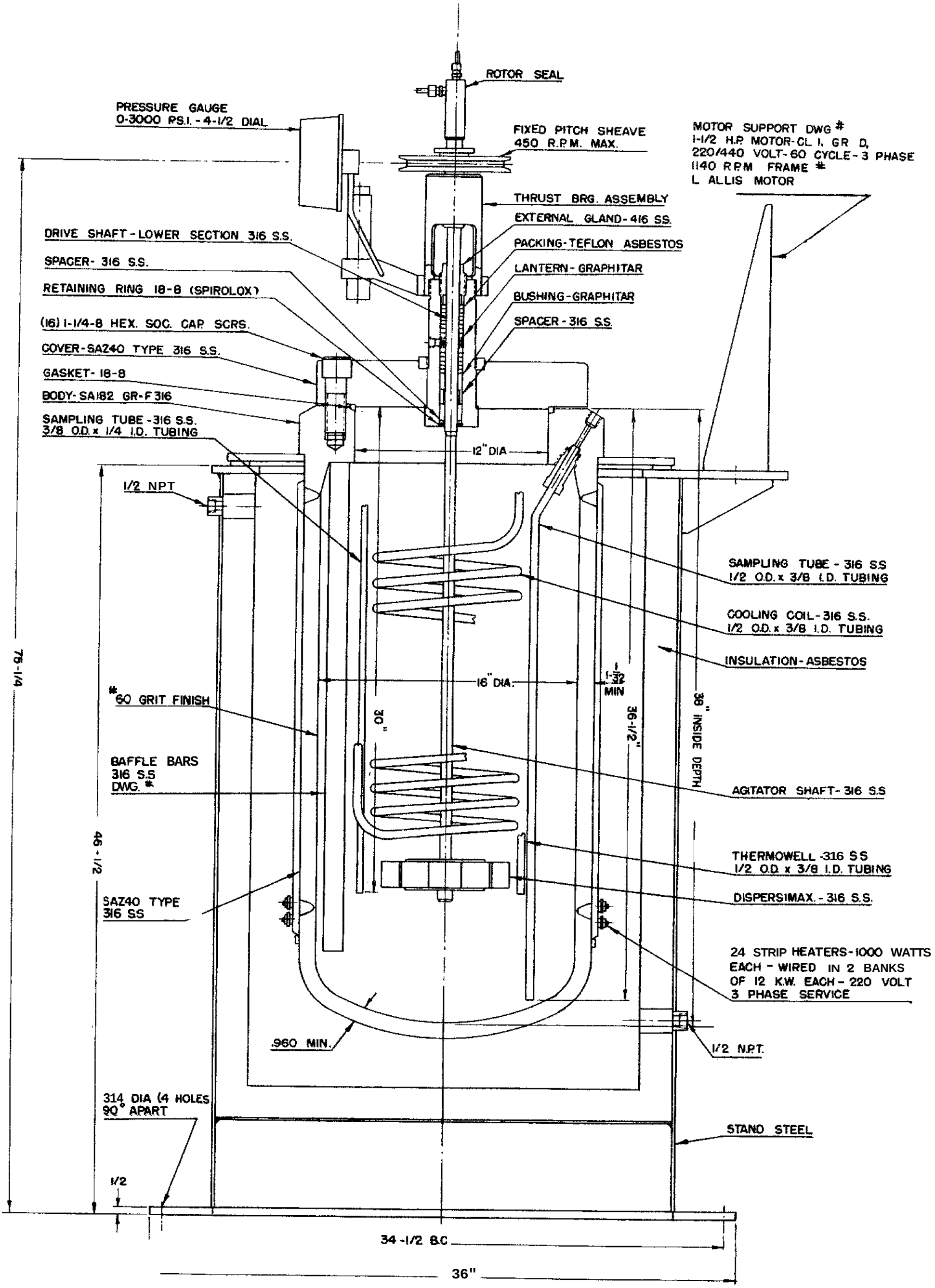
1 GALLON


WATER INLET
ROTOR SEAL
WATER OUTLET
FIXED PITCH SHEAVE 300 R.P.M. MAX.
BALL BEARING - #7306-DT.
GREASE SEAL
THRUST BEARING HOUSING
EXTERNAL GLAND - 416 S.S.
DRIVE SHAFT - 316 S.S INTERNAL COOLED
OIL CYL. SUPPORT - ALUM.
1 H.P. MOTOR 220/440 VOLT 3 PHASE 60 CYCLE CL.I GR. D - 350 R.P.M. FRAME #203 SP. 3 MOTOR SUPPORT
COVER - 316 S.S.
PACKING - TEFLON - ASBESTOS
3/8 N.P.T.
LANTERN - GRAPHITAR
1/2 SAFETY HEAD RUPTURE DISC - 18-8 RATED 7,000 PS.I. AT 72°F
BUSHING - GRAPHITAR
(12) 7/8-9 SET SCRS
LOCKNUT - ALLOY STL.
BODY - 316 S.S
THRUST WASHER - ALLOY STEEL
MAIN NUT - ALLOY STEEL
SUPPORT RING - STL.
SPACER - 316 S.S.
INTERNAL GLAND - 316 S.S.
SEAL RING - 316 S.S.
DIP TUBE 316 S.S. 3/8 O.D. x 1/4 I.D. TUBING
COOLING COIL - 316 S.S 3/8 O.D. x #12 GA. WA. TUBING
STAND - STL
12"
15" INSIDE DEPTH
51" APPROX.
30-1/2"
AGITATOR SHAFT - 316 S.S
AGITATOR - TURBINE TYPE 316 S.S.
INSULATION - ASBESTOS
11 STRIP HEATERS 1000 WATTS - 220 VOLT
1 RING HEATER 1000 WATTS - 220 VOLT
12 K.W. TOTAL - WIRED 440 VOLT - 3 PHASE
10 I.D.
14-1/2 O.D.
THERMOCOUPLE WELL 316 S.S. 3/8" O.D. x #12 GA WA. TUBING
3/4" DRILL - 4 HOLES
24-1/2 DIA. B.C.
26 DIA.

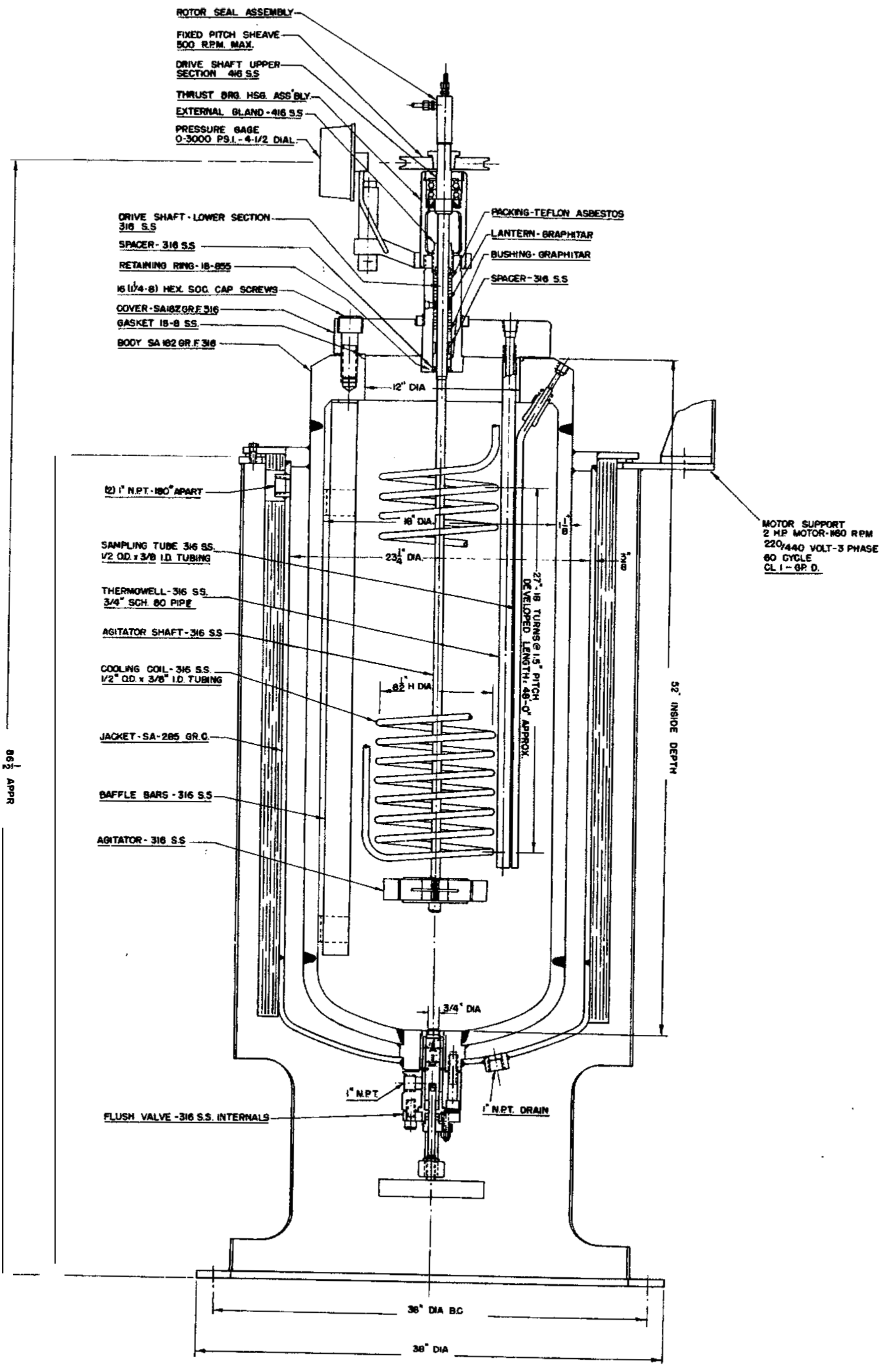
5 GALLONS


PRESSURE GAUGE 0-1800 PSI.
ROTOR SEAL
FIXED PITCH SHEAVE 450 R.P.M. MAX.
SPACER & SEAL - STL.
THRUST BRG. HSS. C-1137
BALL BEARING-#7306-DT
GREASE SEAL
DRIVE SHAFT- INTERNAL COOLED
EXTERNAL GLAND - 416 SS WITH AMPCO BUSHING
PACKING - TEFLON ; ASBESTOS
LANTERN GRAPHITAR
STUFFING BOX - 316 S.S.
SPACER - 316 S.S.
COVER - 316 S.S.
BEARING - GRAPHITAR
GASKET - 18-8
(12) 7/8-9 SOC. HD. CAP SCRS.
RETAINING RING - 18-8
GASKET FLEXITALLIC 18-8 WITH ASBESTOS
BODY - 316 S.S.
7½" DIA.
½" N.P.T.
12" DIA
12¾" DIA.
½ N.P.T.
14" DIA.
¼"
STAND - STEEL DWG.#30-1267
INSULATION - ASBESTOS
18"
21 INSIDE DEPTH
THERMOCOUPLE WELL - 316 S.S. 3/8" O.D. x 209 I.D. TUBING
51½ (APPROX)
36
#1 PLATE FINISH
SAMPLING TUBE - 316 S.S. 3/8" OD. x 209 I.D. TUBIN
1/2 N.P.T.
JACKET - STEEL
1" N.P.T.
AGITATOR SHAFT 316 S.S.
IMPELLER AGITATOR 316 S.S.
1" FLUSH VALVE JERGUSON - MODEL #23 Y 316 S.S.

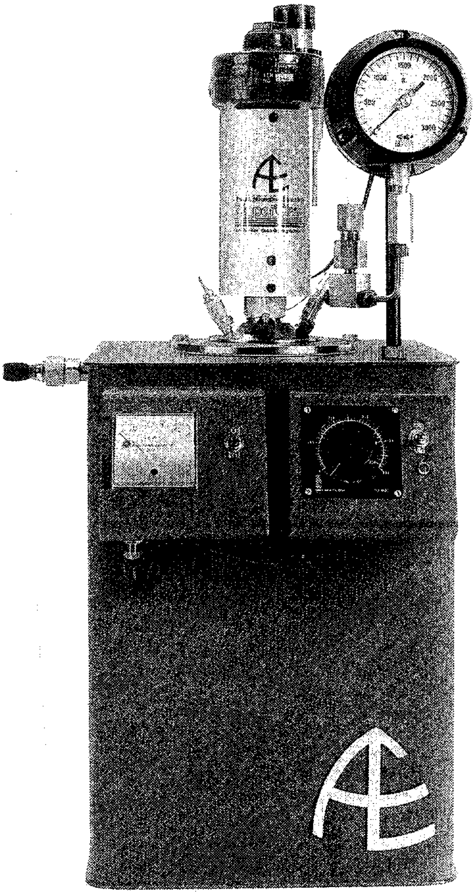
10 GALLONS

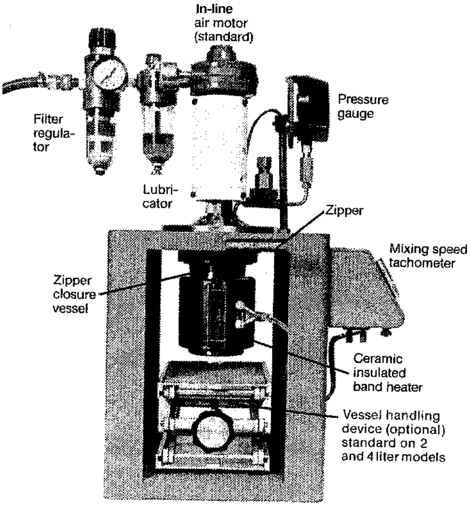

ROTOR SEAL
PRESSURE GAUGE 0-3000 P.S.I. - 4-1/2 DIAL
FIXED PITCH SHEAVE 450 R.P.M. MAX.
MOTOR SUPPORT DWG #
1-1/2 H.P. MOTOR-CL I, GR D,
220/440 VOLT-60 CYCLE-3 PHASE
1140 R.P.M. FRAME #
L ALLIS MOTOR
THRUST BRG. ASSEMBLY
EXTERNAL GLAND-416 SS.
PACKING-TEFLON ASBESTOS
LANTERN-GRAPHITAR
BUSHING-GRAPHITAR
SPACER-316 S.S.
DRIVE SHAFT-LOWER SECTION 316 S.S.
SPACER-316 S.S.
RETAINING RING 18-8 (SPIROLOX)
(16) 1-1/4-8 HEX. SOC. CAP. SCRS.
COVER-SA240 TYPE 316 S.S.
GASKET-18-8
BODY-SA182 GR-F316
SAMPLING TUBE-316 S.S. 3/8 O.D. x 1/4 I.D. TUBING
12" DIA
1/2 NPT
SAMPLING TUBE-316 SS 1/2 O.D. x 3/8 I.D. TUBING
COOLING COIL-316 S.S. 1/2 O.D. x 3/8 I.D. TUBING
INSULATION-ASBESTOS
75-1/4
16" DIA.
1-1/32 MIN
#60 GRIT FINISH
30"
36-1/2"
38" INSIDE DEPTH
BAFFLE BARS 316 S.S DWG. #
AGITATOR SHAFT-316 SS
46-1/2
THERMOWELL-316 SS 1/2 O.D. x 3/8 I.D. TUBING
DISPERSIMAX.-316 S.S.
SA240 TYPE 316 SS
24 STRIP HEATERS-1000 WATTS EACH - WIRED IN 2 BANKS OF 12 K.W. EACH-220 VOLT 3 PHASE SERVICE
.960 MIN.
1/2 N.P.T.
314 DIA (4 HOLES 90° APART
STAND STEEL
1/2
34-1/2 B.C.
36"

30 GALLONS


ROTOR SEAL ASSEMBLY
FIXED PITCH SHEAVE 500 R.P.M. MAX.
DRIVE SHAFT UPPER SECTION 416 S.S
THRUST BRG. HSG. ASS'BLY.
EXTERNAL GLAND - 416 S.S
PRESSURE GAGE 0-3000 P.S.I. - 4-1/2 DIAL.
DRIVE SHAFT - LOWER SECTION 316 S.S
SPACER - 316 S.S
RETAINING RING - 18-855
16 (1/4-8) HEX. SOC. CAP SCREWS
COVER - SA182 GR.F 316
GASKET 18-8 S.S.
BODY SA 182 GR.F 316
PACKING - TEFLON ASBESTOS
LANTERN - GRAPHITAR
BUSHING - GRAPHITAR
SPACER - 316 S.S
12" DIA
(2) 1" N.P.T. - 180° APART
16" DIA.
$1\frac{1}{8}$"
$23\frac{1}{4}$" DIA.
$\frac{3}{8}$"
27" - 18 TURNS @ 1.5" PITCH DEVELOPED LENGTH, 46'-0" APPROX.
SAMPLING TUBE 316 S.S. 1/2 O.D. x 3/8 I.D. TUBING
THERMOWELL - 316 S.S. 3/4" SCH. 80 PIPE
AGITATOR SHAFT - 316 S.S
COOLING COIL - 316 S.S. 1/2" O.D. x 3/8" I.D. TUBING
$8\frac{1}{2}$" H DIA
JACKET - SA-285 GR.C.
BAFFLE BARS - 316 S.S
AGITATOR - 316 S.S
MOTOR SUPPORT 2 H.P. MOTOR - 1160 RPM 220/440 VOLT - 3 PHASE 60 CYCLE CL I - GR. D.
52" INSIDE DEPTH
$86\frac{1}{2}$ APPR
3/4" DIA
1" N.P.T.
1" N.P.T. DRAIN
FLUSH VALVE - 316 S.S. INTERNALS
38" DIA B.C
38" DIA

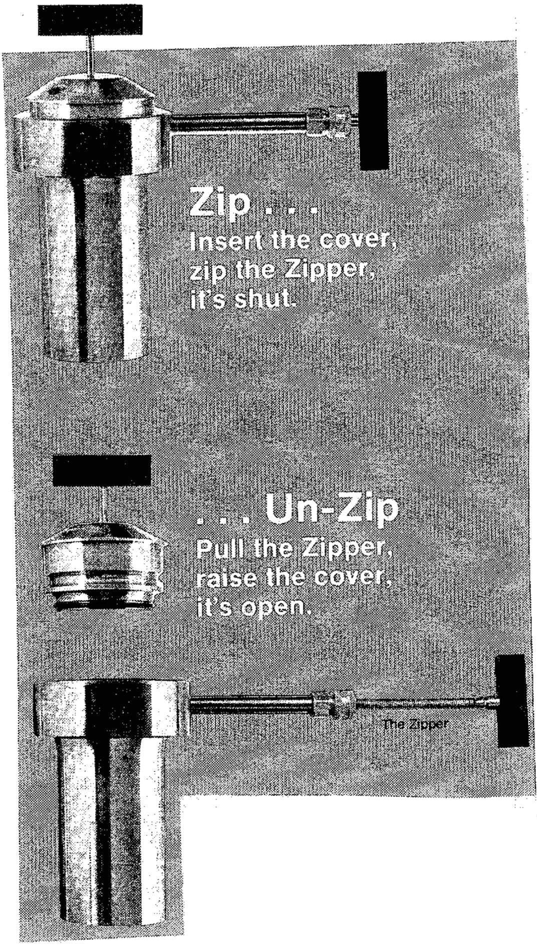
50 GALLONS

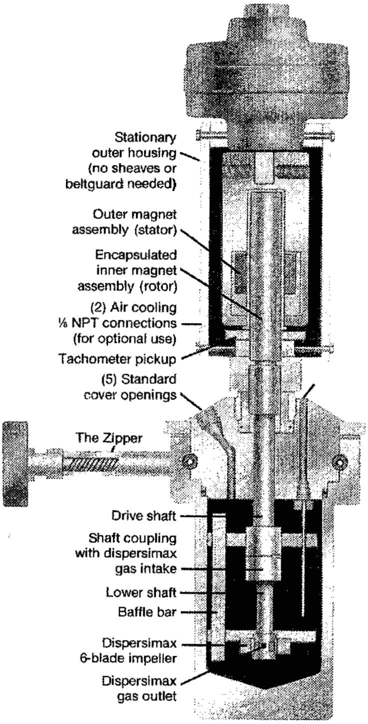




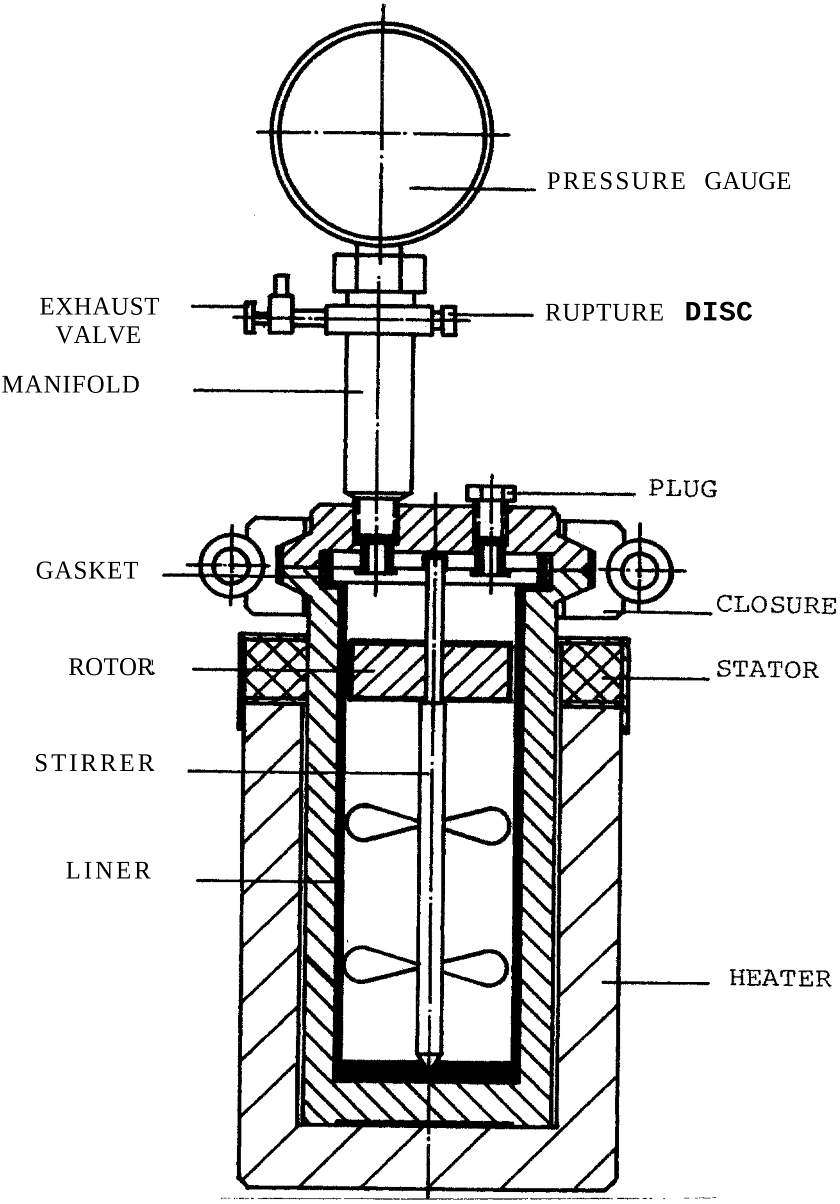
500 ml model

ZipperClave

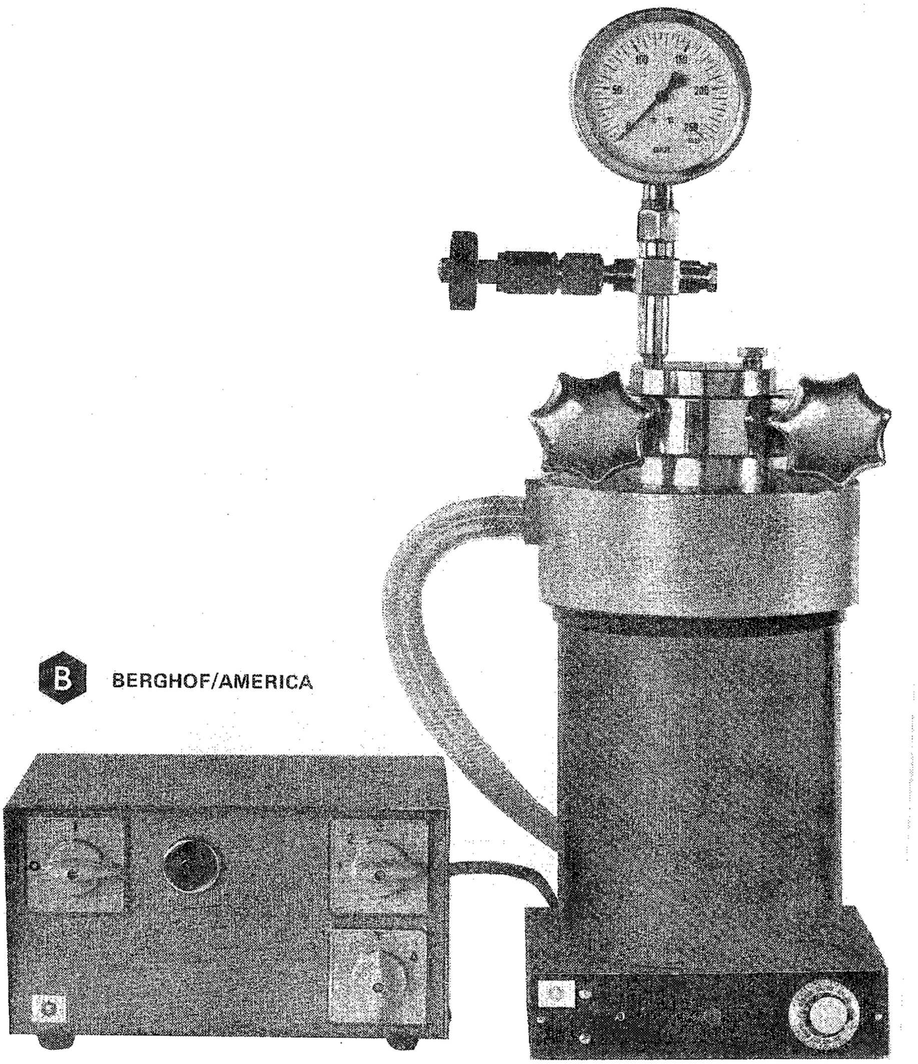


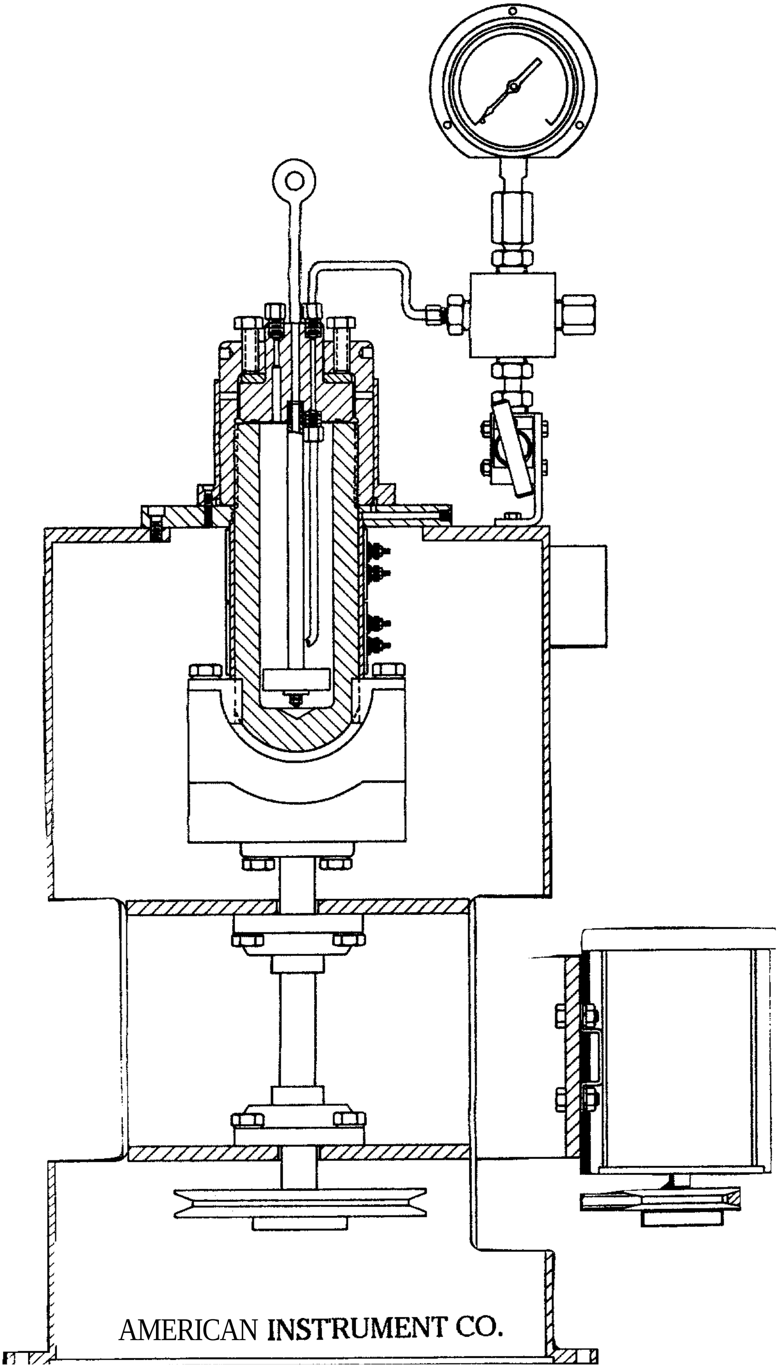


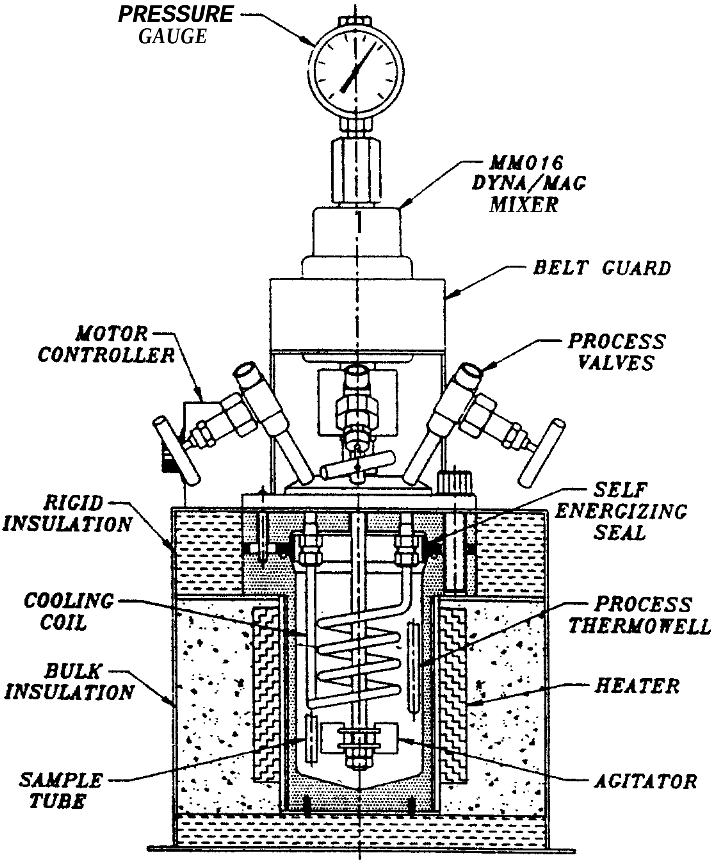
500 ml ZipperClave system



BERGHOF
America, Inc.


B
BERGHOF/AMERICA

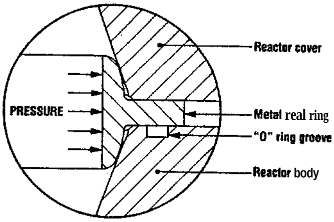

AMERICAN INSTRUMENT CO.

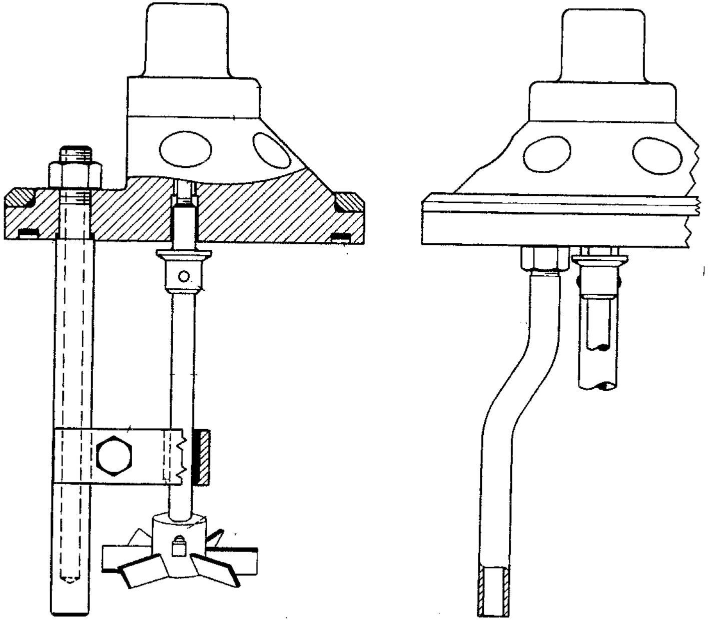


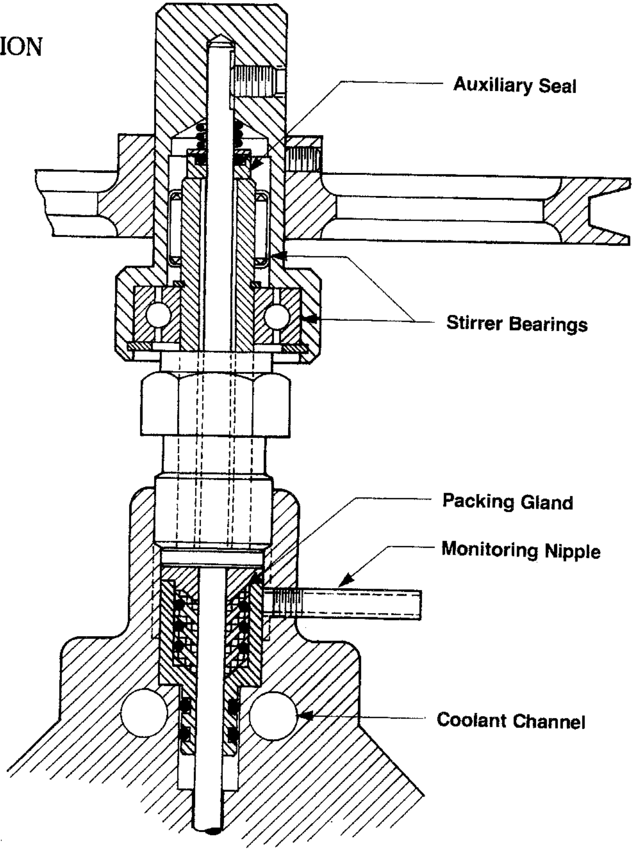
Pressure Products Industries, Inc.

2000 psig (138 bar) @ 350° C
300 ml, 500 ml
1, 2, and 4 liter sizes.

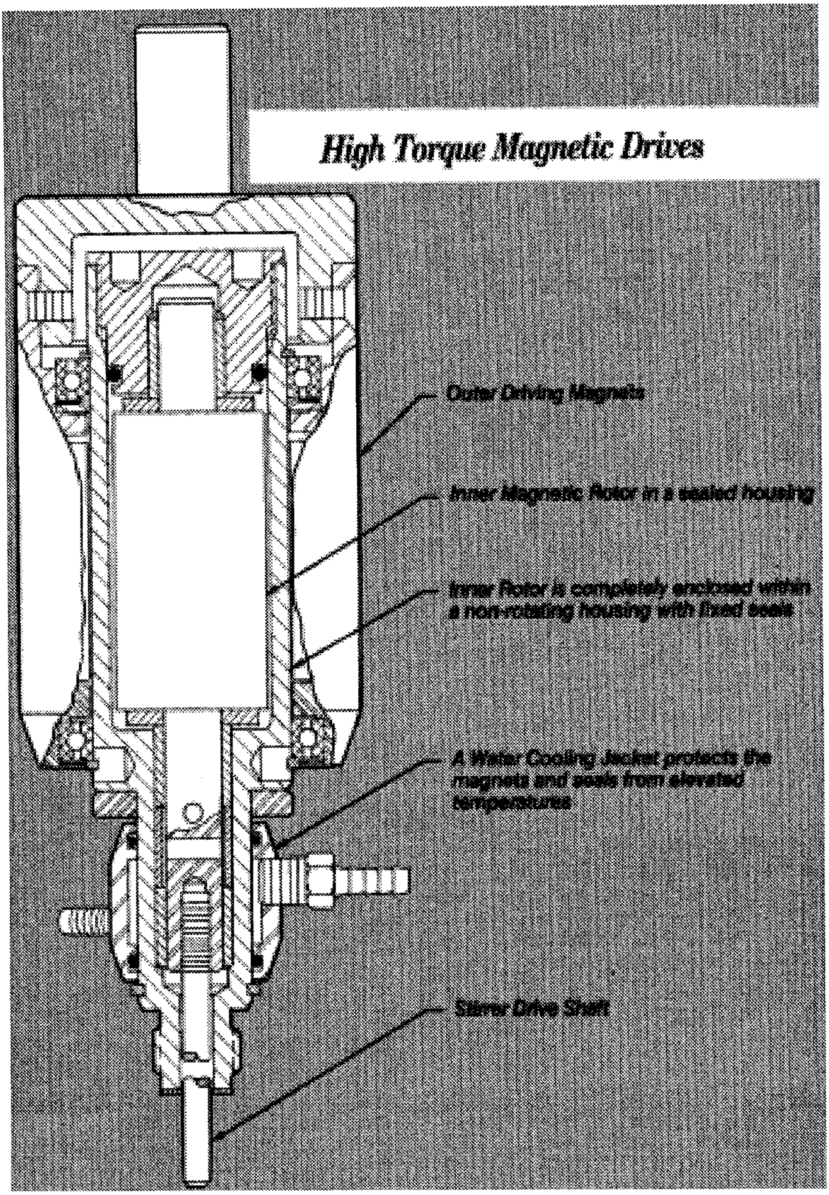
As the reactor cover and body are bolted together. the metal seal ring seats itself. Internal pressure increases the seal load and energizes the seal ring, assuring a tight, leak-free seal.

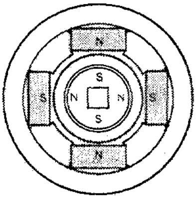




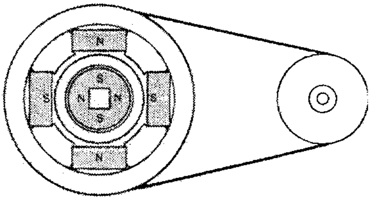


STIRRER DRIVE WITH SELF-SEALING PACKING GLAND

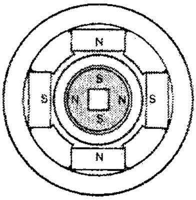

High Torque Magnetic Drives
Outer Driving Magnets
Inner Magnetic Rotor in a sealed housing
Inner Rotor is completely enclosed within a non-rotating housing with fixed seals
A Water Cooling Jacket protects the magnets and seals from elevated temperatures
Stirrer Drive Shaft



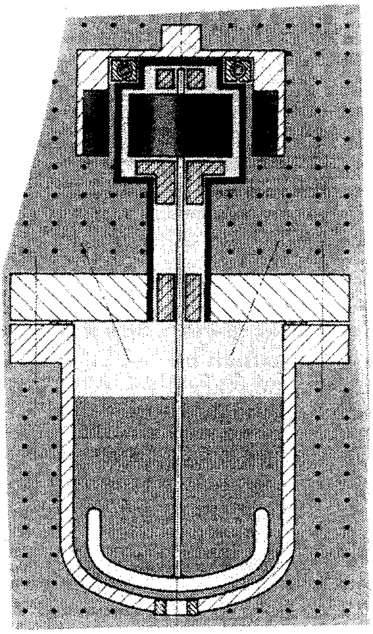
External **Driver** Magnet Assembly (as seen from above) consists of an outer steel housing that contains four equally spaced permanent magnets with attracting poles on their inner faces



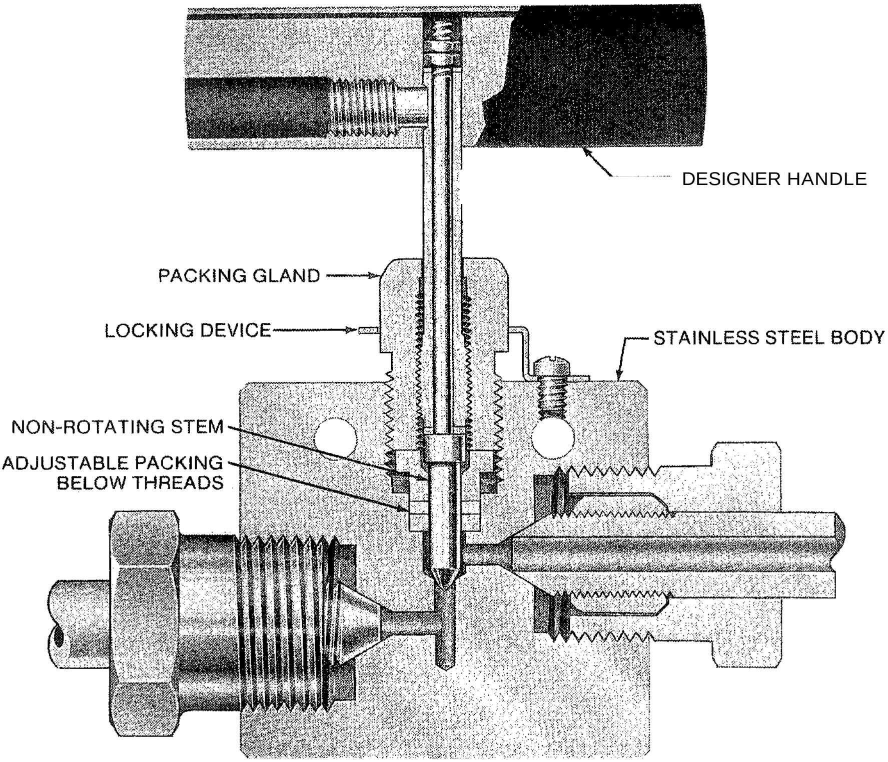
In operation. the Driver Magnet Assembly is rotated by a motor-driven V-belt, and the Driven Magnet Assembly rotates in response This action drives the rotor shaft to which the agitator is connected.



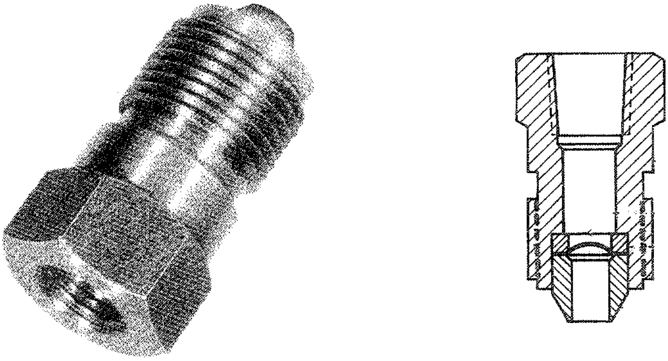
internal Driven Magnet Assembly is totally encapsulated it is made up of circular. ceramic-type permanent magnets encasing a square rotor shaft and enclosed in a leak-proof housing.



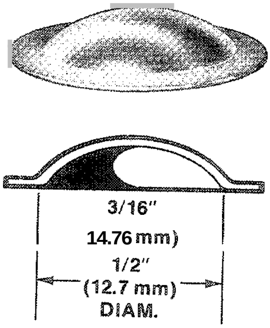
MagneDrive



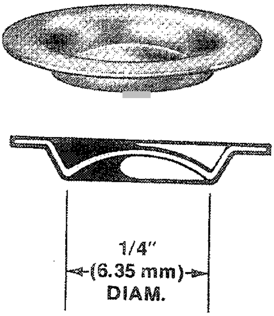
NON-ROTATING **STEM VALVE**



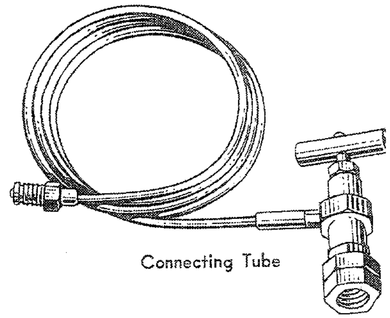
SAFETY HEAD



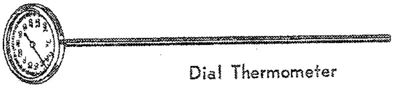
FLAT SEAT RUPTURE DISC



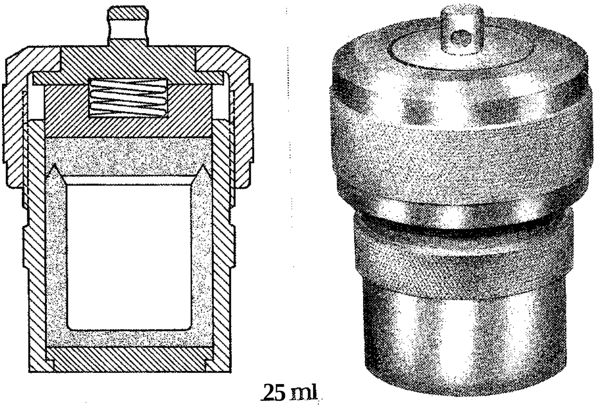
30° ANGULAR SEAT RUPTURE DISC



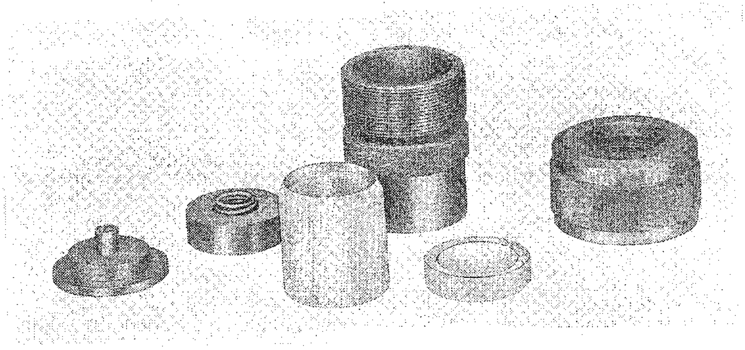
Connecting Tube



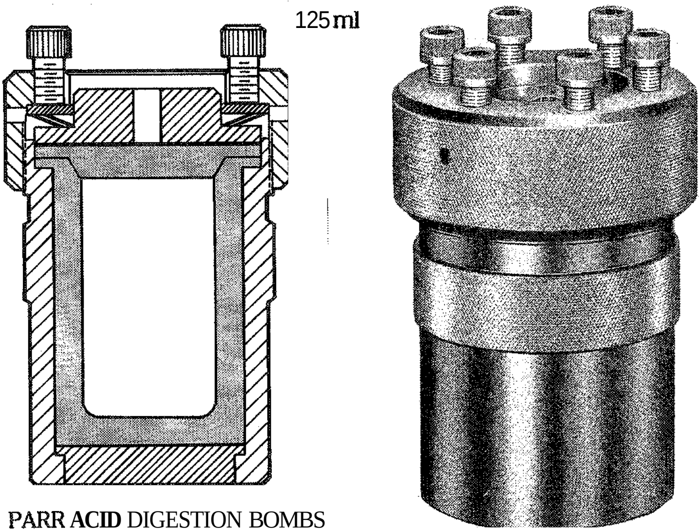
Dial Thermometer



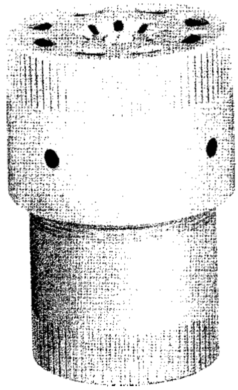
25 ml

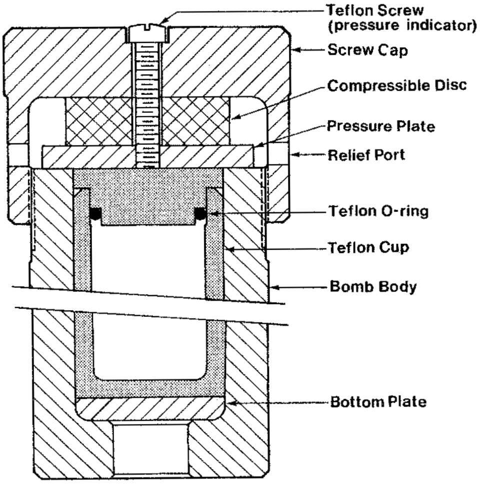


125 ml

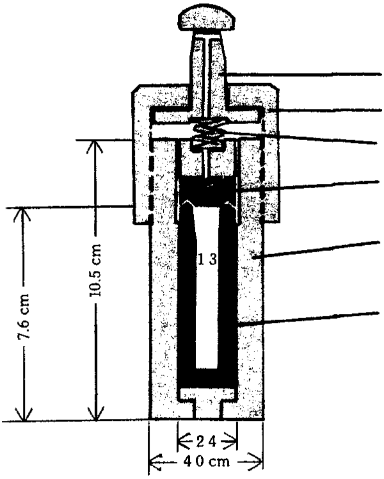


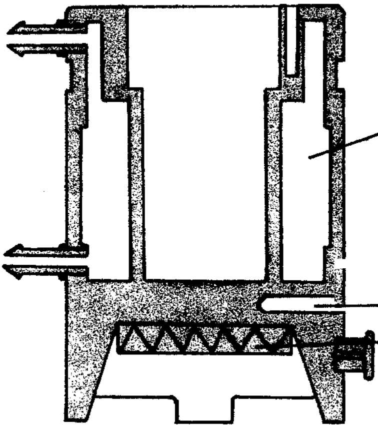
PARR ACID DIGESTION BOMBS



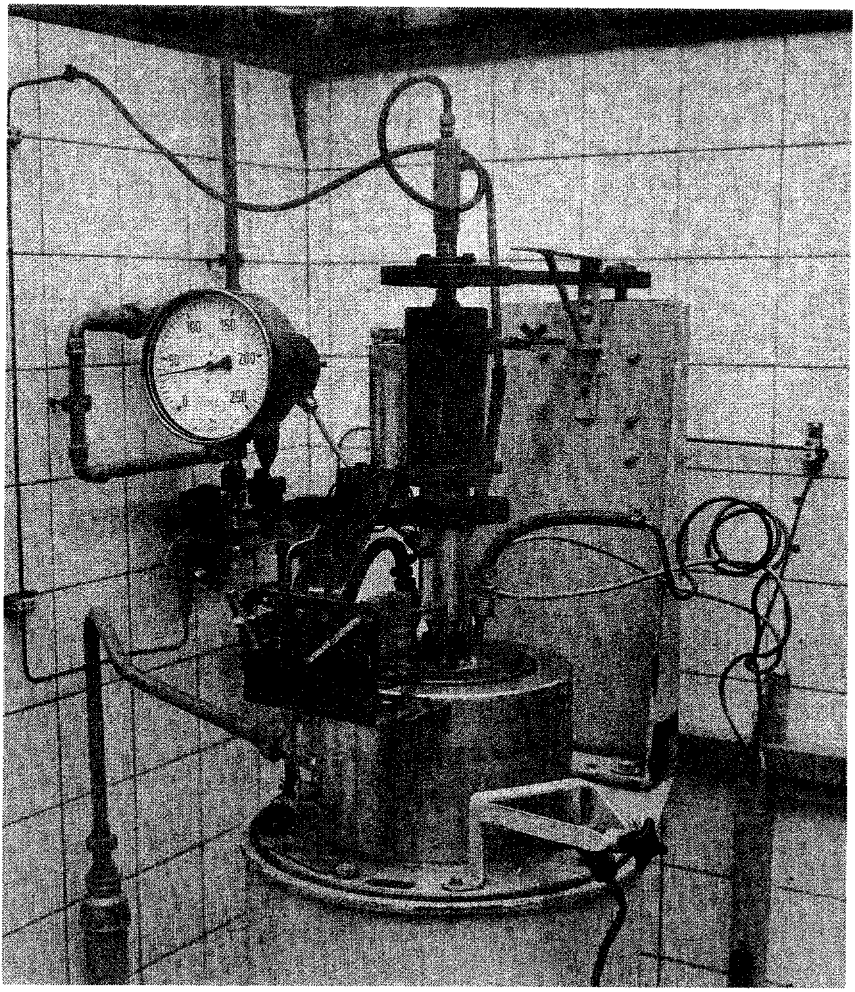


MICROWAVE
Acid Digestion Bombs

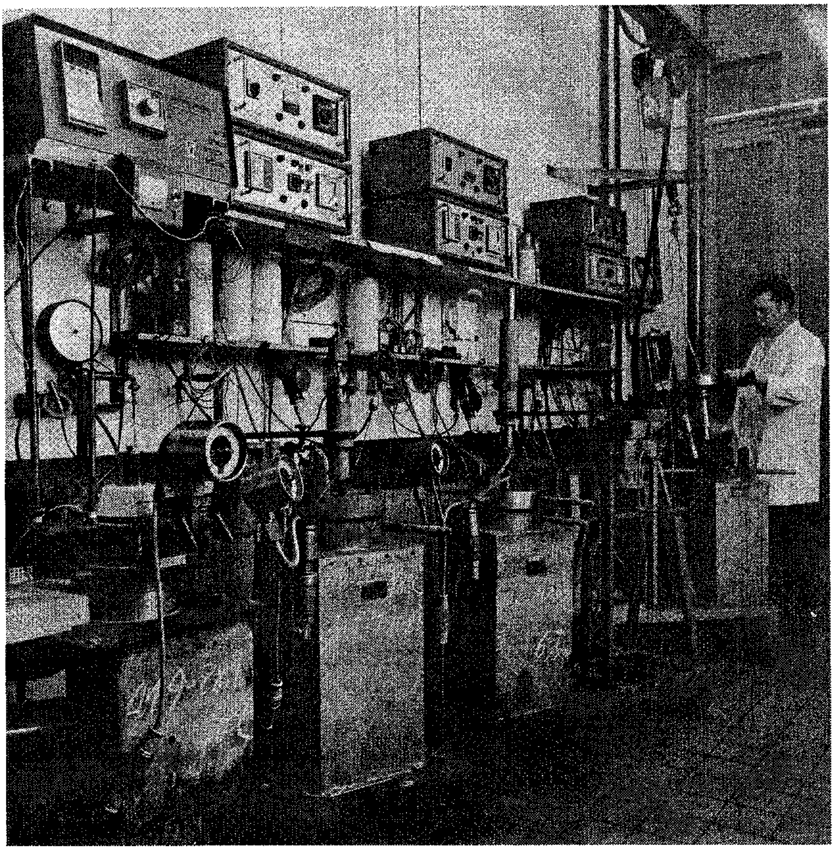




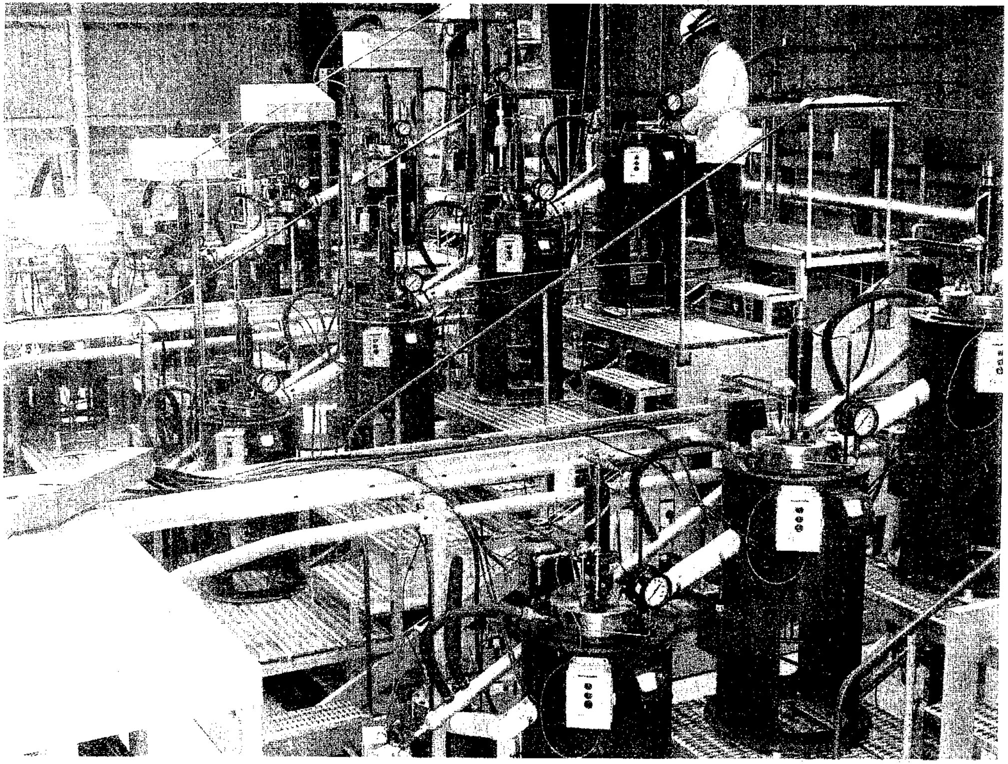
BERGHOF/AMERICA



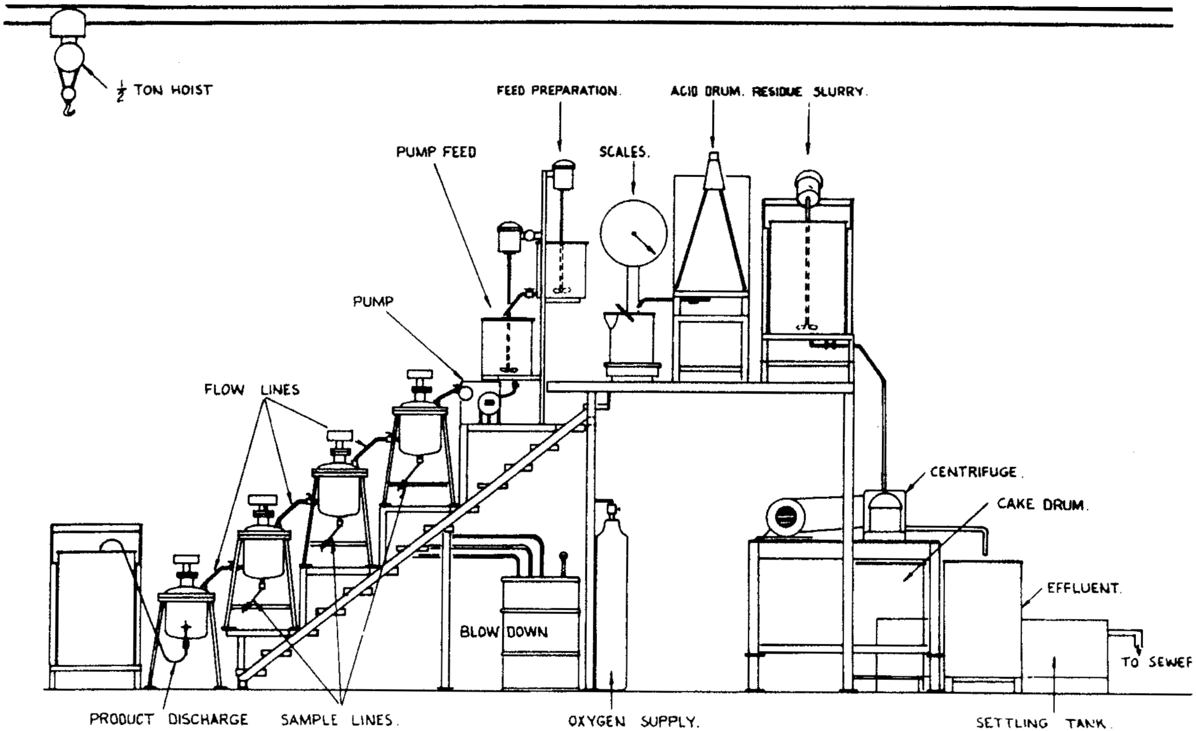
Autoclave assembly unit in operation.



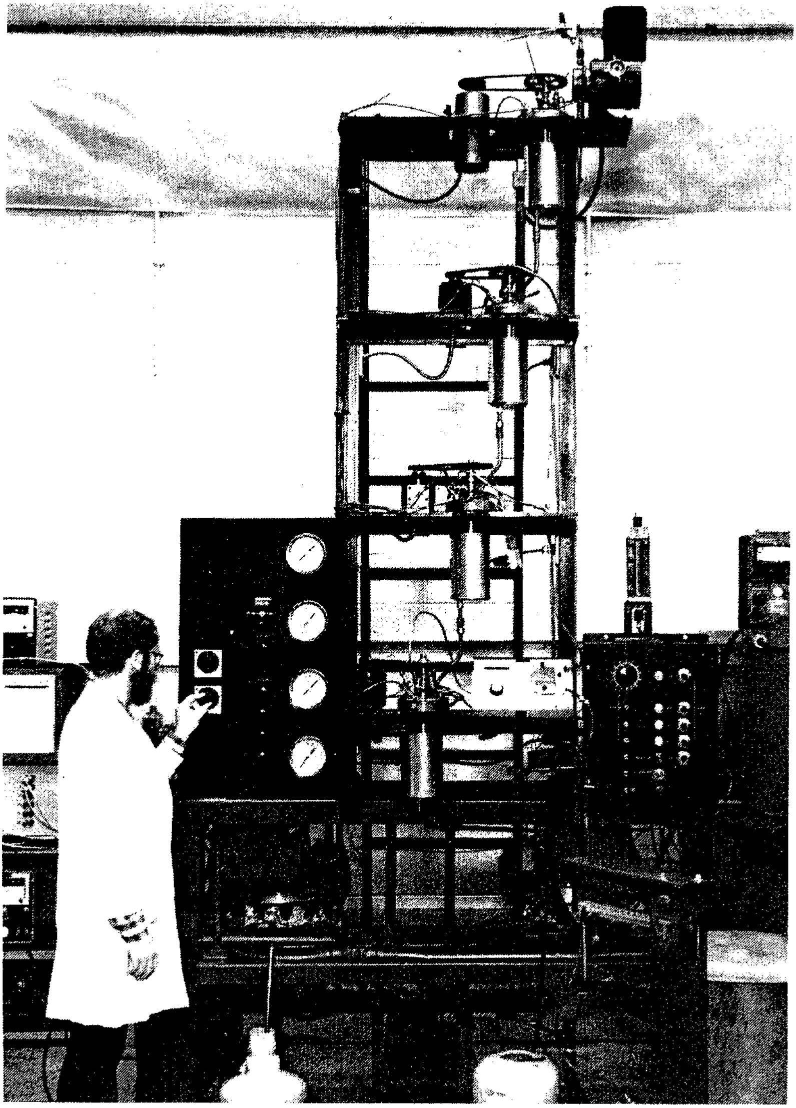
High-pressure hydrometallurgical laboratory.



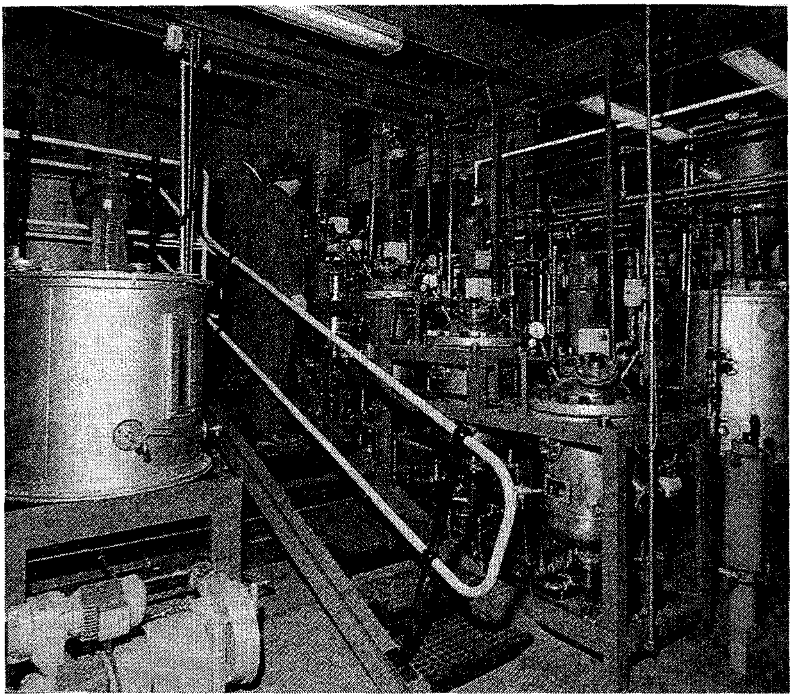
Titanium autoclaves in a hydrometallurgical pilot plant at Colorado School of Mines Research Institute, Golden, Colorado



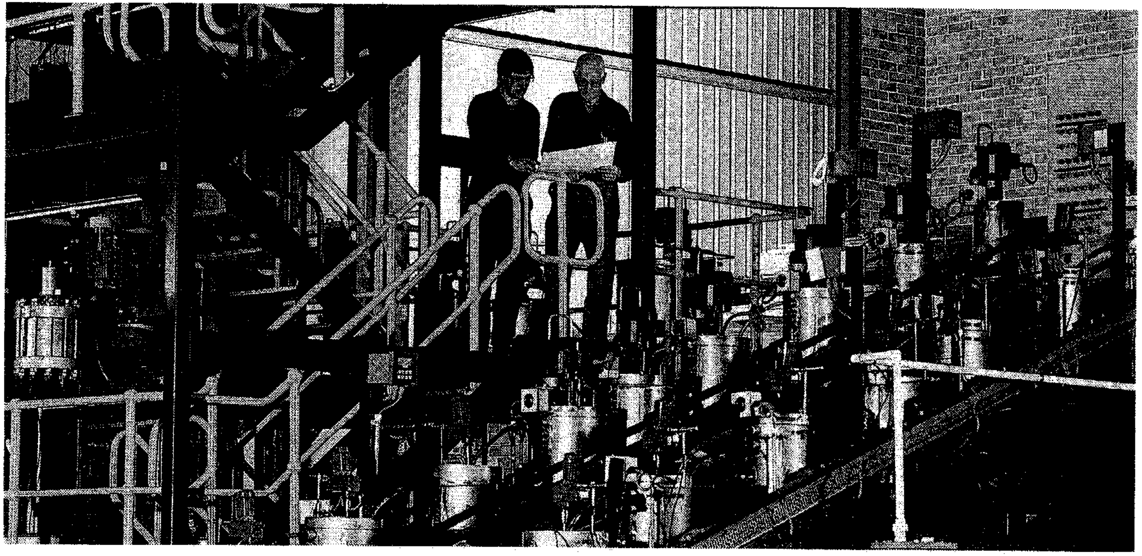
CSIRO MINI PLANT



INCO MINI PLANT



A miniplant with a total operating volume of about 100 litres in four stages, and can operate at pressures up to 18 bar and temperatures of 180 °C. The capacity is *40–60* L/h of feed, or about 7–10 kg/h of sulfide concentrate. Both oxidative and non-oxidative leaching can be performed. [MINTEK, South Africa]



Ortest Metallurgical Research Perth, Australia

Questions and Problems

1. General aspects

1.1 What are the advantages and disadvantages of hydrometallurgy in comparison to pyrometallurgy?

1.2 Write balanced equations showing:

- *a*) The hydrolysis of ferric ion
- 6) The reaction of limestone with sulfuric acid
- c) The oxidation of ferrous ion with oxygen
- *d*) The reaction of H_2S with CuSO4 solution
- e) The dissolution of a sulfide mineral in ferric chloride solution
- *f*) The reaction of hydrochloric acid with a solution of silver nitrate
- g) The formation of a complex ion between CuSO4 solution and ammonia.

2. Leaching

2.1 Discuss the mechanism of the following reactions:

- *a*) Covellite (CuS) with ferric chloride solution
- 6) Aluminum hydroxide with NaOH solution
- c) Zinc sulfide in dilute H_2SO_4 in presence of oxygen
- *d*) The aqueous oxidation of pyrrhotite (FeS) in presence and in absence of oxygen
- *e)* The dissolution of gold in cyanide solution.

2.2 What are the factors that influence leaching in general and in what way?

2.3 Discuss the reasons for which one is obliged to conduct certain leaching operations under pressure.

2.4 Make a diagram for a pressure-leaching plant. Show the essential equipment.

2.5 Describe how certain ores can be leached without their transportation from the mine.

2.6 Write some notes on the utilization of flash tanks in hydrometallurgy and make a sketch of a typical equipment.

2.7 While sulfuric acid is the least expensive leaching agent, one is obliged to use other more expensive reagents;

a) Explain why.

6) Give two examples to illustrate your answer.

2.8 Make a diagram showing an industrial process for the recovery of gold from its ores.

2.9 Describe an experiment showing the electrochemical nature of the dissolution of gold in cyanide solution and give the reactions involved.

2.10 Discuss the action of the following reagents on pyrrhotite (FeS):

a) Water saturated with oxygen

b) Dilute H_2SO_4

c) Dilute H_2SO_4 and oxygen under pressure in 110 °C.

2.11 Discuss the utilization of NH_3 in hydrometallurgy.

2.12 *a)* What are the industrial processes used for treating uranium ores?

b) What are the environmental problems involved?

c) How can such problems be solved?

2.13 *a)* What are the manganese nodules?

b) Discuss two methods for the selective recovery of nickel, cobalt, and copper from these nodules.

2.14 *a)* What is “synthetic rutile” and how can it be produced in industry?

6) Why is it necessary sometimes to produce this material?

2.15 **A** pyrrhotite ore analyzes 57% Fe, 37% S, 0.8% Ni, and the rest is gangue. Propose an economic method for the recovery of nickel.

2.16 Explain how elemental sulfur can be produced from pyrrhotite.

2.17 Discuss the action of H_2SO_4 on CuS under the following conditions:

a) Dilute, in absence of oxygen
b) Dilute, in presence of oxygen
c) Concentrated, at room temperature
d) Concentrated, at 150 °C
e) Concentrated, at 280 °C.

3. Applications

3.1 Discuss the recent tendency in the hydrometallurgy of zinc sulfide concentrated to liberate the zinc industry from the production of fertilizers.

3.2 What are the actual problems today in the zinc industry and how can hydrometallurgy contribute towards a solution?

3.3 Describe an industrial hydrometallurgical process for the treatment of a nickel sulfide concentrate.

3.4 Discuss the role of the following leaching agents:

a) NaOH
6) Na_2CO_3
c) Dilute H_2SO_4.

3.5 *a)* What are the most favorable conditions leading to the formation of elemental sulfur during the leaching of sulfides?

b) Give an industrial example in which these conditions are applied.

c) What are the advantages of this technology?

3.6 Describe an industrial hydrometallurgical process for:

a) The recovery of nickel from laterites,
6) The separation of nickel from copper from a mixture of their sulfides.

3.7 Write short notes on:

a) Leaching under pressure
6) Leaching in situ
c) Leaching in vats
d) Autotrophic bacteria

- e) The role of $Ca(OH)_2$ in cyanidation
- *f*) Leaching of copper with ammonia
- g) Red mud
- *h*) Gallium
- *i*) Gibbsite
- *j*) The synthesis of nitric acid
- *k*) The Pachuca tank
- *l*) Aqua regia
- *m*) The production of NaOH from sodium carbonate
- *n*) The precipitation of aluminum hydroxide.

3.8 Discuss how tungsten minerals can be treated for tungsten recovery.

3.9 North America is one of the largest producers of aluminum, although the raw material is nearly all imported. What do you think of this problem and what is the possibility of becoming independent of importation?

3.10 What is monazite sand and how is it beneficiated and treated industrially?

3.11 Explain why there is interest recently in the treatment of:

- *a*) Clays
- *b*) Asbestos tailings.

How can these materials be processed for recovering valuable products?

3.12 Pyrite is used extensively in the chemical industry. Explain how it can be treated to recover completely all its components.

3.13 The residues accumulating from the recovery of asbestos fibers represent a health hazard. Expose the problem and propose a solution.

3.14 Phosphate rock is an important source of uranium. Explain in what form it is present, how it can be determined, and how it can be recovered.

3.15 ***a)*** Explain the distribution of uranium, radium, and fluorine during the treatment of phosphate rock by different acids.

b) How can the uranium and fluorine be recovered without disturbing the process for fertilizer production?

4. Concentration/Purification

4.1 What is activated charcoal? How is it produced industrially? What is its main application in hydrometallurgy?

4.2 What are the different methods practiced today in gold recovery plants using activated charcoal?

4.3 What is the mechanism by which gold is recovered from cyanide leach solutions using activated charcoal?

4.4 What equipment are used industrially for extracting metal ions from leach solutions by organic solvents?

4.5 Make a schematic diagram for the process of solvent extraction in hydrometallurgy.

4.6 How can de-ionized water be prepared?

4.7 Discuss the concentration/purification of uranium from its leach solutions.

4.8 Compare ion exchange with solvent extraction with respect to:

a) Equipment
b) Mechanism.

4.9 What are the principal materials used in ion exchange processes?

4.10 Write short notes on:

a) Diluents and their role in solvent extraction
b) Swelling of ion exchange resins
c) Activated charcoal as compared to graphite
d) Synergism in solvent extraction
e) Third phase formation in solvent extraction
f) Mixer-settler
g) Pulse column
h) Purification of mineral acids by organic solvents.

5. Precipitation

5.1 Describe the following recovery processes:

  a) Magnesium from the sea

  b) Selenium from aqueous solutions of selenious acid

  c) Uranium from a uranyl sulfate solution

  d) Lithium from LiCl solution

  e) Cadmium present in a zinc sulfate solution

  f) Gold from cyanide solution

  g) Copper from H_2SO_4 leach solution.

5.2 In the precipitation of certain hydroxides, it is important to obtain crystalline products.

  a) Explain why.

  b) What are the conditions necessary for achieving this goal?

  c) Give two examples in which these conditions are applied industrially.

5.3 Describe three possible methods for separating Cu^{2+} and Fe^{2+} from an acidic solution containing both. Write balanced equations.

5.4 Write some notes on the use of hydrogen in hydrometallurgy.

5.5 Compare the behavior of activated charcoal towards gold from chloride and from cyanide media.

5.6 Compare the recovery of copper from sulfuric acid and leaching solution by cementation with iron versus solvent extraction-electrowinning.

6. Problems

6.1 The pH scale is widely used to indicate acidity or basicity of a solution. What is the pH of a 0.05 M HCl solution?

Solution:

$$\begin{aligned} \text{pH} &= -\log[H^+] = -\log(5 \times 10^{-2}) \\ &= -\log 5 - \log 10^{-2} = -0.7 + 2 = 1.3 \end{aligned}$$

6.2 Calculate the pH of a solution containing 0.2 M KCN given that $K_{HCN} = 4 \times 10^{-10}$.

Solution:

$$HCN \rightarrow H^+ + CN^- \qquad K_{HCN} = \frac{[H^+][CN^-]}{[HCN]} = 4 \times 10^{-10}$$

$$H_2O \rightarrow H^+ + OH- \qquad K_{H_2O} = [H^+][OH^-] = 10^{-14}$$

$$\begin{array}{lccc} CN^- + H_2O \rightarrow & HCN & + & OH- \\ (0.2 - x) & x & & x \end{array}$$

$$K = \frac{[HCN][OH^-]}{[CN^-]} = \frac{K_{H_2O}}{K_{HCN}} = \frac{10^{-14}}{4 \times 10^{-10}} = 0.25 \times 10^{-4}$$

$$K = \frac{x^2}{0,2 - x} = 0.25 \times 10^{-4}$$

Therefore:

$$x^2 = 5 \times 10^{-6} \qquad x = 2.236 \times 10^{-3}$$

i.e.: $[OH-] = 2.236 \times 10^{-3}$

Therefore:

$$[H^+] \times 2.236 \times 10^{-3} = 10^{-14}$$

$$[H^+] = 4.47 \times 10^{-12}$$

$$pH = -\log[H^+] = -\log(4.47 \times 10^{-12}) = 11.3$$

6.3 Commercial chemically pure hydrochloric acid contains 37% HCl by weight. If the density of the acid is 1.2 g/mL, what will be the concentration expressed in g/L?

Solution:

Weight of one liter acie = 1000 mL x 1.2 g/mL

Weight of HCl of 1 liter = $1000\,\text{mL} \times 1.2\,\text{g/mL} \times \frac{37}{100}$

Concentration = 444 g/L

6.4 Calculate the volume of H_2 gas generated during the dissolution of zinc in 25 mL of 44% H_2SO_4 solution. Density of acid used = 1.343.

Solution

Weight of acid = 25 mL x 1.343 g/mL x 0.44 = 14.8 g

$$\mathrm{Zn} + \mathrm{H_2SO_4} \rightarrow \mathrm{ZnSO_4} + \mathrm{H_2}$$

1 mole 22.4 L

$\frac{14.8}{98}$ moles x

$$x = \frac{14.8}{98} \times 22.4 = 3.38 \text{ L}$$

6.5 In the first step in the production of aluminum, bauxite is leached with NaOH solution at 180 °C. The aluminum mineral in bauxite is $Al(OH)_3$. Calculate:

a) The solubility of $Al(OH)_3$ in water

b) The solubility of $Al(OH)_3$ in a 1 M NaOH given that the solubility product of $Al(OH)_3$ is 1.9×10^{-33} and the instability constant of aluminate ion is 4.75×10^{-35}. Note: Aluminate ion may be represented as $[Al(OH)_4]^-$ or $[AlO(OH)_2]^-$.

Solution

a) The solubility of aluminum hydroxide in water can be calculated from the solubility product:

$$\underset{}{Al(OH)_{3(s)}} \rightleftarrows \underset{x}{Al^{3+}} + \underset{3x}{3OH^-}$$

At equilibrium, x grams of Al^{3+} ion and $3x$ grams of OH– ion are present.

The solubility product:

$$K = [Al^{3+}][OH^-]^3 = x \times (3x)^3 = 1.9 \times 10^{-33}$$

i.e.: $27x^4 = 1.9 \times 10^{-33}$

$$\begin{aligned} x &= 2.9 \times 10^{-9}\ \text{mol/L} \\ &= 2.9 \times 10^{-9} \times \text{molecular weight of } Al(OH)_3 \\ &= 2.9 \times 10^{-9} \times 78 \\ &= 2.2 \times 10^{-7}\ \text{g/L} \end{aligned}$$

The solubility of aluminum hydroxide in water is very low.

b) Aluminum hydroxide forms a stable aluminate ion in NaOH solution:

$$Al(OH)_{3(s)} \rightleftharpoons Al^{3+} + 3OH^-$$

$$K_1 = [Al^{3+}][OH^-]^3 = 1.9 \times 10^{-33}$$

$$Al(OH)_4^- \rightleftharpoons Al^{3+} + 4OH^-$$

$$K_2 = \frac{[Al^{3+}][OH^-]^4}{[Al(OH)_4^-]} = 4.75 \times 10^{-35}$$

$$Al(OH)_{3(s)} + OH^- \rightarrow Al(OH)_4^-$$

At start	1.0	0
At equilibrium	$1-x$	x

$$\begin{aligned} K &= \frac{[Al(OH)_4^-]}{[OH^-]} = \frac{K_1}{K_2} \\ &= \frac{1.9 \times 10^{-33}}{4.75 \times 10^{-35}} \\ &= 40 \end{aligned}$$

Substituting the concentrations of OH– and $Al(OH)_4^-$ into the equation:

$$K = \frac{[Al(OH)_4^-]}{[OH^-]} = \frac{x}{1-x} = 40$$

gives $x = \frac{40}{41} = 0.98$ mol/L

$$= 0.98 \times 78 = 76.4\ \text{g/L}$$

where 78 is the molecular weight of $Al(OH)_3$. Aluminum hydroxide has a high solubility in 1 M NaOH.

The same result could be obtained in another way. Aluminum hydroxide in an amphoteric hydroxide that gives aluminate ion according to:

$$Al(OH)_{3(s)} \rightleftharpoons AlO(OH)_2^- + 3H^+$$

$$K_1 = [AlO(OH)_2^-][H^+] = 4 \times 10^{-33}$$

$$H^+ + OH^- \rightarrow H_2O$$

$$K_2 = [H^+][OH^-] = 10^{-14}$$

$$Al(OH)_{3(s)} + OH^- \rightarrow AlO(OH)_2^-$$

At start	1.0	0
At equilibrium	$1 - x$	x

$$K = \frac{[AlO(OH)_2^-]}{[OH^-]} = \frac{K_1}{K_2}$$

$$= \frac{4 \times 10^{-13}}{10^{-14}} = 40$$

Substituting into the equation for K:

$$\frac{x}{1-x} = 40 = 40$$

$$x = \frac{40}{41} = 0.98 \text{ M}$$

$$= 0.98 \times \text{molecular weight of } Al(OH)_3$$

$$= 0.98 \times 78 = 76.4 \text{ g/L}$$

6.6 Some hydrometallurgical reactions are conducted at high temperature and pressure in closed reactors (autoclaves). It would therefore be necessary to determine the vapor pressure of water at high temperature. If the vapor pressure of water at 100 "C is one atmosphere, and the molar heat of vaporization is 9720 cal/mol for the temperature range 100–120 °C, what will the vapor pressure of water be at 120 "C?

Solution:

The variation of vapor pressure with temperature is governed by the relation:

$$\log\frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\times\frac{T_2 - T_1}{T_1 T_2}$$

$$\log\frac{P_2}{1} = \frac{9.720\times(393 - 373)}{2.303 \times 1.987 \times 393 \times 373} = 1.95 \text{ atm.}$$

6.7 Calculate the pH at which:

a) Ferric hydroxide precipitates from a 0.1 M ferric sulfate solution.

6) Magnesium hydroxide precipitates from a 0.1 M magnesium chloride solution.

Solution

The dissolution of a hydroxide in water (the reverse process of precipitation) is determined by the solubility product equation.

a) For ferric hydroxide:

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$$

$$K = [Fe^{3+}][OH^-]^3 = 1.5 \times 10^{-36}$$

Substituting 0.1 for the concentration of ferric ion gives:

$$0.1 \times [OH^-]^3 = 1.5 \times 10^{-36}$$

$$[OH-] = 2.5 \times 10^{-12}$$

$$pH = 2.4$$

6) For magnesium hydroxide:

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

$$K = [Mg^{2+}][OH^-]^2 = 1.5 \times 10^{-11}$$

Substituting 0.1 for the concentration of magnesium ion gives:

$$0.1 \times [OH^-]^2 = 1.5 \times 10^{-11}$$

$$[OH-] = 1.2 \times 10^{-5}$$

$$pH = 9.1$$

Note the great difference in the pHs necessary for precipitating these ions.

6.8 From conductivity measurements, the ionization constant of pure water was found to be 1.008×10^{-14} at 25 °C and 0.69×10^{-14} at 20 °C. Calculate the heat of neutralization of a strong acid with a strong base.

Solution

The neutralization of an acid with a base is the reverse of the reaction for the ionization of water. The ionization of water is represented by the equation:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K = [H^+][OH^-]$$

The neutralization of an acid with a base is the reverse process:

$$H^+ + OH^- \rightarrow H_2O$$

The equilibrium constant of this reaction is the inverse of that for the ionization of water. The heat of a reaction is related to the change in equilibrium constant of that reaction as a function of temperature by the Van't Hoff equation:

$$\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \times \frac{T_2 - T_1}{T_1 T_2}$$

Therefore:

$$\log\frac{0.69 \times 10^{-14}}{1.008 \times 10^{-14}} = \frac{\Delta H}{2.303 \times 1.987} \times \frac{298 - 293}{293 \times 298}$$

$$\Delta H = -13\,750 \text{ calories}$$

This is an excellent agreement with the directly determined value.

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Index

A

Acetyl acetone *455,460, 490*
Acid digestion *283*
Acid esters *476*
Acid-consuming gangue *68, 233,253*
Acid-insoluble sulfides *114*
Acid-resistant brick *153*
Acids *45, 71*
Acid-soluble sulfides *298*
Acorga *465*
  P50 *467*
Activated charcoal *190, 205, 385, 534,650*
Addition mechanism *493*
Adsorption *392, 538*
  isotherms *392*
  on activated charcoal *381*
Adsorption on gangue material *216*
Aerobic bacteria *195*
Agar-agar *419*
Agglomeration phenomenon *292*
Aging *535*
Agitated tanks *253*
Agitation *169*
  leaching, see ***Pulp** leaching*
Alamine *336* *481,484*
Albite *361, 368*
Alcan *601*
Alcohols *458,459,489, 509*
Aldehydes *459*
Aliphatic hydrocarbons *454*
Aliquate *336* *484*
Alizarin *488*
Alkali carbonate *616*
  process *265*
Alkaline earth nitrates *508*
Alkali-soluble sulfides *299*
Alkyl amines *491*
Alkyl sulfides *487*
Alluvial deposits *204*
Alpha-substituted acids *471*
Alumina from clays *364*
Aluminate ion *616*
Alumino silicates *107*
Aluminosilicates *248, 411*
Aluminum alums *282,566*
Aluminum fluoride *368*
Aluminum fluorosilicate *368*
Aluminum from clay *587*
Aluminum hydroxide *601*
  precipitation *603*
Aluminum silicates *364*
Aluminum sulfate *587*
Alums *373,566*
Alunite *364, 609*
Amalgamation *205*
Amberlite IRA *400* *415*
Amex process *518*
Amine *9D-178* *483*
Amine oxides *481,482*
Amine *S-24* *483,499*
Amines *481,482,501,507, 513, 521*
Ammine complexes *232, 260*
Ammonia *8, 88*
  leaching *254*
Ammoniacal ammonium carbonate *649*
Ammoniated triple superphosphates *345*
Ammonium carbonate *265*
Ammonium chloroplatinate *229*
Ammonium copper sulfites *625*
Ammonium cyanate *552*
Ammonium fluoroberyllate *588*
Ammonium hexachloroplatinate *621*
Ammonium hydrogen sulfide *625*
Ammonium hydroxide *88*
Ammonium ion *89*
Ammonium jarosite *271*
Ammonium molybdate *648*
Ammonium phosphomolybdate *610*
Ammonium polyacrylate *642, 647*
Ammonium polysulfide *205*

Ammonium sulfate *303, 633, 644, 646, 647*
Ammonium sulfide *623*
Ammonium sulfite *94, 252, 625, 633*
Ammonium thiocyanate *504*
Ammonium vanadate *611*
Ammonium wolframate *284*
Amphoteric hydroxide *103*
Amphoteric substances *45*
Anaconda *662*
Anaconda Company *409*
Anaerobic bacteria *195*
Analite *411*
Anatase *599*
Andalusite *360*
Anhydrite *575*
Anhydrous silicates *362, 363*
Animal charcoal *387*
Anion exchange *490*
Anion exchanger *406*
Anionic complexes *429*
Anodic slimes *229, 330, 333, 634*
Anodic zone *110*
Anorthite *361, 365, 368*
Anorthosite *362, 363, 364, 368*
Antagonistic effect *494*
Anthetite *249*
Anthraquinone *642*
Anti-agglomeration additives *642*
Antimony *666*
Antimony thiocomplex *300*
Anti-pollution automobile catalysts *232*
Antisynergism *494*
Apatite *247, 341, 364*
Aphthitalite *70*
Aqua regia *4, 85, 224, 228*
Aqueous chlorine *296, 316*
Aqueous oxidation of SO_2 *72*
Aqueous phase *502*
Arabicgum *642*
Aragonite *536*
Armeen 212 *483*
Aromatic hydrocarbons *454*
Arsenates *340, 594*
Arsenic acid *321*
Arsenic removal *440*
Arsenic sulfides *335*
Arsenides *335*
Arsenopyrite *212, 287, 317, 321, 323, 335*
Arsine *336, 656*
Asbestos *617*
  tailings *368*
Association of ionogenic groups *417*
Astrakhanite *566*
Atacamite *249*
Aurous sulfide film *216*
Autocatalytic precipitation *641*
Autoclave interior *153*
Autoclaves *146, 330, 626, 638, 647, 648*
Auto-oxidation *290, 323*
Autotrophic bacteria *195*
Azeotropic mixture *76, 83*
Azurite *249, 273*

B

Bacteria *195*
Baking *276, 280, 314*
Baking process *157*
Barrick Goldstrike *221, 222*
Bases *45*
Basic salts *608*
Bastnasite *351, 353, 523, 589*
Batch leaching *166*
Bauxite *86, 241, 273, 365, 600*
  leaching *148*
Bayer process *3, 7, 242, 243, 273, 364, 519, 601*
Bayer, Karl Josef *6, 7, 243*
Beach sand *352*
Belt filter *184*
Bentonite *361*
Benzene *454, 499, 501*
α-Benzoinoxime *464*
Bertrandite *360, 362, 370, 372*
Beryl *108, 360, 362, 363, 370, 371, 372*
Beryllate solution *603*
Beryllium *440, 513*
Beryllium fluoride *588*

Beryllium hydroxide *536*
Beta diketone *460*
Binary mixture crystallization *560*
Biotite *361*
Biringuccio, Vannoccio *4*
Bischofite *577, 580, 581*
Black acid *344*
Blast furnace *270*
Bleaching powder *96,204*
Bleed solution *188*
Bloedite *70*
Body-centered cubic system *545*
Bohmite *242*
Bone-char *387*
Boracite *70*
Borate *610*
Borax *585*
Boric acid *585*
Boron *440, 514, 574*
Boundary layer *117*
Brimstone *72*
Brochantite *249*
Bromine *581*
α-Bromo lauric acid *473*
Buffer solutions *46*
Bunker Hill process *303*
Butyl alcohol *457, 525*
Butyl dibutyl phosphinate *492*
4-*sec*-Butyl-2(α-methyl benzyl)
  phenol *474,507,515*

C

Cadmium *268,472,666*
  from zinc sulfate solution *661*
Calamine *360*
Calcines *268*
Calcite *536*
Calcium arsenate *594*
Calcium peroxide *210, 216*
Calcium sulfate *323*
Caledonite *249*
Calera process *337*
Caliche *586*
  deposits *575*
Calorimetric measurements *497*
Cameco Corporation *267*
Canadian Copper Refiners *330*
Carat *224*
Carbamide *552*
Carbitols *456*
Carbon black *386*
Carbon disulfide *293, 296,454*
Carbon monoxide *533,637,649*
Carbon tetrachloride *454,497,499*
Carbonaceous matter *212*
Carbonates *40,616, 629*
Carbonatoapatite *342*
Carbon-in-leach process *400*
Carbon-in-pulp process *400*
Carbonization *387*
Carboxylic acids *489, 520*
Carnallite *70,575, 578, 579, 580, 587*
Carnotite *261*
Caron process *234*
Carrier *537*
Cassiterite *342*
Catalysis *624*
Catalyst *641*
Catalytic action *198*
Catalyzed reduction *642*
Cathodic zone *110*
Cation exchange *489*
Cation exchanger *406*
Cationic resins *421*
Cement copper *643,656,659*
Cementation *515, 605, 651*
  of copper *658*
  process *4*
Cerium *482, 523*
Cesium *515*
Cesium aluminum silicate *373*
CESL process *307*
Chabazite *361, 411*
Chalcanthite *249*
Chalcopyrite 82, *115, 116,212,251, 307,311,314*
Chalcosiderite *249*
Charcoal *386*
Chelates *59*
Chelation *490*

Chemical adsorption 395
Chemical beneficiation 15
Chemical plating 635
Chemical processes 102,301
Chemically controlled processes 119
Chemisorption 391,395
Chevreul's salt 625, 626
Chlorides 40,618,629
Chlorinated ethers 456
Chlorination 276
Chlorine 85, 86,218,222,259
Chlorine water 94,204, 292
4-Chloro-2-phenyl phenol 474
Chloroform 454,497,499
Chromate 610
Chromatographic elution 432
Chrome alum 587
Chromite 276,280, 281, 282,285
Chromium 666
Chromium alum 280, 282, 566
Chromium(III) chloride 553
Chromium(III) sulfate 553
Chrysocolla 108, 249,273, 360, 362
Chrysotile 358
Chuquicamata 139
Cigar Lake 263
Cis-isomer 552
Citrate-soluble fertilizer 349
Clay 247,364, 365
  leaching 525
Co^{2+} oxidation 539
Coagulating agents 180
Coal 258
Cobalt 459,462,482,520,589,605, 638,644,647,666
  extraction 440
  from cinder 376
  precipitation 639, 646
Cobalt(III) ammine complexes 553
Cobalt hexammine complex 303
Cobalt oxidation 645
Cobalt(III) pentammine complex 589
Cobalt sulfide 624
Cobaltiferrous copper ores 605
Cobaltite 335
Co-ions 406
Colemanite 70
Collector 537, 595
Colophanite 342, 343
Color change of resins 427
Columbite 276, 281, 285, 521
Cominco 308
Cominco Engineering 307
Common ion effect 42
Complex fluorides 622
Complex formation 42, 104, 111, 503
Complex ore treatment 18
Complex oxides 275, 285
Complexes 58
Complex-forming sulfides 299
Complexing ion 538
Concentrated acid leaching 270
Concentrated H_2SO_4 296, 312
Concentration cells 111
Condensation 536
Condensing tower 574
Cone precipitator 663
Consumption of free cyanide 215
Consumption of oxygen from solution 215
Contact catalysis 641
Continuous ion exchange 409
Continuous leaching 166
Conversion reactions 567
Coordination compounds 58
Coordination number 548
Copper 515,638,643,647,666
  cementation 658
  from $[Cu(NH_3)_4]^{2+}$ 649
  ores 137
  precipitation 632, 639
  recovery 619
    by cementation 654
    by solvent extraction 440
Copper ammine solution 625
Copper ammine sulfite solution 633
Copper–cobalt ore 252
Copper hydroxysulfate 307, 610
Copper oxide ores 248,254, 273
Copper precipitate morphology 657

Copper sulfate *588*
  solubility *560*
Copper sulfides *311*
Copper sulfites *625*
Coprecipitation *537, 551*
Counter-current extraction *450*
Counter-current regeneration *427*
Counter-current washing *177*
Counter-ions *406*
Covalent bond *32*
Covalent solids *107*
Covellite *288, 322, 323*
Crandallite *342*
Cross-linking *412*
  degree *420*
Crown ethers *456,458*
Cryolite *349*
Crysotile asbestos *361*
Crystal form *536*
Crystal growth *537*
Crystal habit *546*
Crystal lattice *544*
Crystal systems *545*
Crystallization *282, 301, 313, 339, 371,531,540,544*
  by cooling *558*
  by evaporation *558*
  of a binary mixture *560*
  of a quaternary mixture *566*
Crystallization ponds *571*
Crystallization products *564*
Crystals *544*
Cube *547*
Cubic system *545*
Cupferrons *488,491*
Cuprite *249, 253*
Cuprous ammonium sulfite *626, 627*
Cuprous chloride
  precipitation *619, 620*
  solubility *618*
Cuprous cyanide *622*
Cuprous ion disproportionation *639*
Cuprous oxide *599*
Cyanamid *478*
Cyanate *93*
Cyanate ion *218*
Cyanex 272 *475,477*
Cyanex 471X *478*
Cyanex 921 *476*
Cyanidation *222, 307*
Cyanidation process *3, 5, 93,205*
Cyanidation stoichiometry *207*
Cyanidation under pressure *223*
Cyanides *622,629*
  destruction *218*
Cyclohexane *454,455, 501*
Cyclopentane *455*

D

D2EHPA, see *Di (2-ethylhexyl) phosphoric acid*
Dapex process *518*
Davidite *262*
Dawsonite *364*
DDPA process *518*
Dead Sea *575,576,579,616*
Deaeration *654*
Decane *497*
n-Decanol *501*
Decomposition
  of sulfurous acid *633*
Degree of cross-linking *420*
Dehydration *550*
Dehydroxylation *363, 371*
Deliquescence *549*
Deposition
  potentials *665*
Desorption *396, 399*
Destruction of cyanide *218*
Dextrin *642*
Dextrose *642*
Di (2-ethylhexyl) phosphoric acid *475,477,495, 515, 518, 523, 525*
Dialkyl phosphoric acids *489*
Dialkylphosphinic acids *497*
Dialkylphosphoric acids *497*
Dialuminate ion *616*
Dialuminates *629*
Diammonium phosphate *345*
Diarsenide ion *287, 321, 323*

Diaspore *242*
Dibutyl butyl phosphonate *492*
Dibutyl ether *493*
Dicalcium phosphate *349*
β,β'-Dichlorodiethyl ether *457,493*
Dichromate *610*
Dielectricconstant *37,396,399,419, 425,454,498,499*
Diethyl ether *456,457*
Diethylene glycol dibutyl ether *457*
Dietzeite *575*
Diffusion coefficient *118*
Diffusion-controlled processes *119*
Digesters *157,328*
Digestion *276, 283, 354*
Dihydrate process *344*
Diisobutyl ketone *461*
Diketones *491*
Diluents *454,455,497, 509*
Dimethyl glyoxime *465*
Dioctylphenyl phosphoric acid *519*
Dioptase *249, 360*
Dioximes *465*
Diphenyls *455*
Dipicrylamine *416*
Disilicate ion *357*
Disilicates *361*
Displacement *104, 111*
  by hydrogen *651*
  by metals *651*
Disposal pond *178,266*
Disproportionation *253, 539, 626, 633*
  of cuprous ion *639*
Dissolution reactions *121*
Distribution coefficient *442*
Distribution isotherm *384, 452*
Distribution ratio *384, 446,499*
Disulfate *610*
Disulfide ion *34, 287*
Disulfides *317*
Dithionite *295, 636*
Dithizone *488, 491*
Diuranates *610,613*
Divanadate *611*
Divinyl benzene *413*
DK process *376*
p-Dodecyl phenol *474*
Dodecyl phosphoric acid *475, 524*
Dolomite *574*
Doré furnace *329*
Doré metal *331,332*
Dorr agitators *5*
Dorr, John *5*
Double fluoride *283, 591*
Double salt *565, 626, 634*
Duisburger Kupferhutte *619, 660*
Dump leaching *4, 128, 130, 197, 253,515*
Dust formation *18*
Dynatec *307,308*

E

Eau de Javel *96*
Eau régale, see *Aqua regia*
EDTA, see *Ethylene diamine tetraacetic acid*
Effect of common ion *559*
Effect of complexing agents *423*
Efflorescence *549*
Electrochemical mechanism *208*
Electrochemical precipitation *651*
Electrochemical processes *108, 301, 534*
Electrochemical reduction *541, 650*
Electrochemical series *50*
Electrode potential *48*
Electroless electroplating *635*
Electrolysis *270, 401*
  of NaCl *86*
Electrolytic processes *54, 116, 534*
Electrolytic reduction *541, 664, 666*
Electrolytic refining *327*
Electrolytic zinc *9*
Electromotive series *651*
Electron exchangers *417*
Electron transfer *533*
Electro-oxidation process *96*
Electrostatic separation *352*
Electrowinning *665*
  of metals *642*

Elemental sulfur *290,306,309*
  viscosity *294*
Elovich equation *398*
Elution *382,386,399,426*
  of uranium sulfate *431*
Enargite *335*
Energy consumption *18*
Engineering aspects *163*
Enrichment factor *445*
Enstatite *360*
Enzymic processes *196*
Equilibrium constant *41*
Esters *474*
Ethers *455,489,491,502*
Ethylene diamine tetraacetic acid *59, 503, 514,605*
2-Ethylhexanol *457,499*
Evaporating sea water *570*
Evaporation *314, 603*
Exchange capacity *418,420*
Extractant polymerization *498*
Extractants *453*
Extracted species *496,498*
Extraction by chelation *455*
Extraction isotherms *449*
Extraction mechanism *489*
Extraction of inorganic acids *508*
Extraction of lanthanides *507*
Extraction of water *511*

F

Face-centered cubic system *545*
Falconbridge process *299*
Faraday's laws *54*
Fatty acids *469,642*
Fayalite *360*
Feldspars *358*
Ferric arsenate *321*
Ferric chloride *98, 311*
Ferric ion *98*
Ferric sulfate *98, 311*
Ferrihydroxy sulfate *608, 610*
Ferrite problem *269*
Ferrites *269*
Ferrochromium *280*
Ferrous ion *533*
Ferrous sulfate *258, 588*
Fertilizers *341, 633*
Fick's law *118*
Filter press *184*
Filtration *176, 181*
Fineness of gold *224*
Fission products *522*
Flash evaporators *174, 175*
Flash tank *297*
Flotation *580*
  of metal ions *595*
  of precipitates *624*
Fluorescence of resins *427*
Fluorides *40, 621, 629*
Fluorine *341*
Fluoroapatite *342*
Fluorosilicate ion *349*
Fluorosilicic acid *82, 107, 368*
Fluosilicic acid *349*
Fly ash *364, 365*
Foaming *68*
Foote Mineral Company *578*
Formaldehyde *533,637,649*
Formaldehyde sodium sulfoxylate *649*
Formation of a lead–gold alloy *214*
Formation of calcium peroxide *216*
Formation of solid solution *538*
Formation of thiocyanate *216*
Formation of toxic gases *656*
Forsterite *358, 360*
Fractional crystallization *570, 588, 590*
Framework structure *358*
Frankolite *342, 343*
Free energy change *56*
Fresenius, Carl Remigius *62*
Freundlich adsorption isotherm *393*
Fullerene *386*
Fuming *270*
Furaldehyde *459*
Furfural *459*
Fused salt electrolysis *313*

G

Galena 212
Gallium 248, 666
Galvani, Luigi 52
Galvanic cells 117
Galvanic processes 52
Gamma activity 348
Garnierite 361, 362
Gelatin 642
Geometrical isomerism 552
Geometrical orientation 552
Geothermal brines 577
Germanium 268
  extraction 440
Gibbsite 242
Glauber's salt 570, 581, 586
Glauberite 70
Glockerite 610
Goethite 271, 610
  process 271
Gold 85, 111, 204, 481, 666
  fineness 224
  ores 137
  precipitation 636
  recovery 654
  refining 224, 225
Gold bead 112
Gold electrode 213
Gold leaf test 212, 217
Gold oxide 217
Gold xanthate film 217
Graphite 386
Gravity concentration 352
Great Salt Lake 575, 576, 577, 581, 582, 585
Green acid 344
Green salt 614
Gypsum 575, 577

H

Haber, Fritz 8
Hafnium 462, 504, 521, 591
Halex process 308
Halides 618
Halite 70, 575
Hall, Charles Martin 8
Harvesters 571
Hayyan, Jabir Ibn 4
HCI recovery 56
HCN recovery 218
Heap leaching 349
Heap leaching, see *Dump leaching*
Heat economy 170
Heat exchangers 171, 573
Heat transfer 170
Heavy lanthanides 435
Hematite 271, 610
  process 271
Hemihydrate process 344
Hemihydrate–dihydrate process 344
Hemimorphite 360, 362, 374
Henglein, Friedrich August 9
Henkel Corporation 464, 477, 481, 484
Heptane 497
Héroult, Paul 8
Heterogeneous crystals 564
Heterogeneous reduction 534
Heteropoly ion 610
Heterotrophic bacteria 195
Hexaammonium molybdates 612
Hexagonal system 546
Hexane 454, 501
Hexatungstic acid 613
Hexavalent uranium 430
Hexone 460, 461, 504, 521
High-gold alloys 227
High-grade bullions 224
High-pressure membrane pumps 168
History of solvent extraction 440
Homogeneous reduction 533
Hot filtration 297, 313
Huanu 586
Hydrargillite 242
Hydrated ionic volumes 420
Hydrated metal ions 548
Hydrated oxides 600, 629
Hydrated silicates 362, 363
Hydrated tungsten oxide 613
Hydration 43
  of ions 39

Hydrazine *533, 637, 650*
Hydroaromatics *454*
Hydrochloric acid *75, 259, 345, 370*
Hydrochloric acid regeneration *279*
Hydrocyanic acid *92*
Hydrocyclone *178*
Hydrofluoric acid *82, 107, 282, 521, 591, 600, 621*
Hydrofluosilicic acid, see *Fluosilicic acid*
Hydrogen *533, 535, 637, 638*
  under pressure *9, 235, 658*
Hydrogen bond *494*
Hydrogen chloride *75*
Hydrogen cyanide *93, 209*
Hydrogen ion concentration *45*
Hydrogen peroxide *98, 207, 618*
Hydrogen sulfide *251, 623*
Hydrolysis *43, 55, 280, 532, 540, 596*
Hydrolytic products *656*
Hydronium ion *35*
Hydronium jarosire *609, 610*
Hydrothermal methods *411*
Hydroxides *40, 598, 600, 629*
Hydroxy copper sulfate *608*
Hydroxy iron sulfates *271, 608*
Hydroxysalts *608, 610, 629*
Hydroxyapatite *342*
Hydroxybenzophenone oximes *465, 466*
Hydroxyoximes *464*
8-Hydroxyquinoline *468*
Hydroxyquinoline–kerosene *648*
Hydrozincite *268*
Hygroscopy *549*
Hypochlorite *94*
Hypophosphite *634*
  ion *533*

I

Ignition temperature *454*
Ilmenite *276, 279, 285, 352*
  leaching *588*
Ilmenite leaching *76*
Imperial Chemical Industries *465*
In situ leaching *265*
Indanes *455*
Indian Rare Earths *279*
Indium *268, 515*
Information sources *19*
Infrared magnetic resonance *496*
Infrared spectra of resins *428*
Injection technique *127*
Inorganic acid extraction *508*
In-situ leaching *129, 349, 583*
Intec Copper *308*
Interatomic forces *392*
Intermediate-control processes *119*
Inverted cones *662*
Iodine *341, 575, 587*
Ion exchange *9, 190, 381, 570, 615*
Ion exchange columns *435*
Ion exchange membrane *415*
Ion exchange system *94*
Ion exclusion *429*
Ion flotation *595*
Ion hydration *507*
Ion pair transfer *489*
Ionic bond *32*
Ionic crystals *38*
Ionic precipitation *533, 540, 593*
Ionic radius *421*
Ionic reducing agents *533*
Ionic reduction *540*
Ionic–covalent solids *102*
Ionization *35*
  inside the resin *420*
Ionization constant *37*
Ipatieff, Vladimir *9*
Iron *525*
Iron arsenate *594*
Iron–nickel alloy *369*
Isobutyl alcohol *457*
Isomerism *552*
Isometric system *545*
Isomorphism *551*
Isomorphous substitution *551*
Isopentane *501*
Isopropyl carbinol *457*
Isopropyl ether *457*

J

Jarosite *271, 609*
Johnson Matthey Refinery *230, 231*

K

Kainite *70, 583*
Kaolinite *247, 358, 361, 362, 364*
Karl-Fischer reagent 511
Keelex-100 *469*
Keelex-*120* 469
Kennecott *663, 664*
Kernite *70*
Kerosene *454, 455, 499*
Ketakaolin *364*
Ketones *460, 461, 491, 493*
Key Lake *263*
Kowa-Seiko process *376*
Kunskite *342, 343*

L

Laboratory autoclaves *667*
Langbeinite *70, 575*
Langmuir adsorption isotherm 394
Lanthanides *341, 521, 523, 588, 618*
  extraction 507
Laterites *149, 236, 254, 257, 273*
Launders 661
Lautarite *575*
Le Chatelier, Louis *8*
Leach pad 135
Leach residues *266*
Leaching agents *69*
Leaching bauxite *148*
Leaching clays *525*
Leaching equipment 161
Leaching in a reducing atmosphere *260*
Leaching in place *123, 253*
Leaching in situ *123*
Leaching methods *161*
Leaching of ilmenite 76
Leaching of pyrite 198
Leaching pyrite *318*
Leaching–precipitation–flotation *249*
Leach–precipitate–float *658*
Lead membrane *153*
Lead salts in cyanide solutions *213*
Lead sulfide concentrates *312*
Les Beaux *241*
Létrange, L. 9
Leucite *361*
Liberate gold prior to cyanidation 152
Libethenite 249
Light lanthanides *435*
Lignosol *292*
Limonite *254*
Linarite *249*
Liquid sulfur *293*
Liroconite *249*
Lithium *574, 577*
Lithium aluminum silicate 373
Lithium carbonate *616*
Lithium carbonate solubility *616*
Lithium chloride 575
Lithium dialuminate *616*
Lithium recovery *616, 617*
LIX-63 *464*
LIX-64 465, 466, *515*
LIX-64N *464, 465, 466*
LIX-65N *465, 466, 468*
LIX-70 *465, 466*
LIX-71 *466*
LIX-73 *466*
LIX-860 *467*
Loeweite *70*
Low-gold bullion *225*
Low-grade ore treatment 19
LPF process *249*
Lurgi *155, 157, 159, 175*

M

MacArthur, John Stewart *5, 6*
Magnesite *358*
Magnesium *574*
  from sea water *604, 606*
Magnesium carbonate *617*
Magnesium chloride *575, 578, 582*
Magnesium diuranate *613*
Magnesium hydroxide *605*

Magnetic separation *352, 371*
Magnetite *352*
Malachite *249, 273*
Malzac, M. *8*
Manganese *666*
  nodules *236, 257, 259, 273*
  ores *257*
Manganese carbonate *260*
Manganese dioxide *97, 113, 648*
Manhattan project 3, 9
Mantos Blancos *619, 620*
Marcasite *288*
Material handling *17, 135*
Materials of construction *68, 168*
Maximum loading 495
Maximum selectivity *420*
McArther River *263*
McCabe–Thiele diagram *450, 452*
Mechanism of extraction *489*
Melting *363*
Membrane piston pump *169, 170*
Mercury *659*
Metal electrowinning *642*
Metal ion flotation *595*
Metal powders *535, 644*
Metallic bond *32*
Metallic chromium *282*
Metasilicates *360*
Methyl isoamyl ketone *461*
Methyl isobutyl ketone *460, 461, 462*
Methylethylcarbinol *457*
Methylnaphthalenes *455*
Mica group *361*
Michigan Chemical Corporation 435
Microorganisms *195*
Mindigite *252*
Mineral structure *32*
Mineral wool *369*
Minimum viscosity *296*
Mirabilite *70*
Mixer settlers *439*
Mixing *169*
Moa Plant *624*
Mobile positive ions *411*
Molybdates *611, 629*
Molybdenite 302, 306, *311, 316, 611*
Molybdenum *251, 482*
  recovery *612*
  removal *440*
Molybdenum dioxide *648*
Molybdenum sulfide *302*
Molybdic acid *316*
Molycorp Process *523*
Monazite *341, 352, 589, 618*
Monazite sand *86*
Monoalkylphosphinic acids *497*
Monoalkylphosphoric acid *489*
Monoalkylphosphoric acids *497*
Monoammonium phosphate *344*
Monocalcium phosphate *349*
Monoclinic system *545*
Monohydrate process *585*
Monohydric alcohols *458*
Montmorillonite *361, 362, 365*
Morin *488*
Morphology of copper
    precipitate *657*
Mountain Pass, California *524*
Multicrystal growth *546*
Multiple extractions *447*
Multiple-effect evaporator *173, 571*
Muscovite *361*

N

Nahcolite *70*
Naphtha *454*
Naphthenes *455*
Naphthenic acids *472, 473, 489*
Naphthenic compounds *455*
β-Naphthol *272*
Native copper ore *236*
Native platinum *228*
Natron 70
Natural gums 419
Nepheline *361, 362, 364, 365*
Nernst, Walther *117*
Nernst's equation *49, 52*
Neutral esters *478*
Neutral phosphoric acid esters *489*
Neutralization *103*
Niccolite *335*

Nickel *459, 520, 589, 638, 644, 647, 666*
  in asbestos tailings *369*
  powder *635*
  precipitation *638–640*
  recovery *440, 645*
Nickel ammine complex *646*
Nickel ammonium sulfate *589, 645, 646*
Nickel phosphide *635*
Nickel precipitation *646*
Nickel sulfate *587*
Nickel sulfide *309, 624*
  precipitation *624*
Niobium *521, 591*
Niobium–tantalum *462*
Niter *70*
Nitrate fertilizers *586*
Nitrates *40*
Nitric acid 8, 78, 265, 296, 316, 345, *518*
  manufacture *79*
Nitric oxide *78*
Nitrobenzene *501*
Nitrogen oxide *81*
Nitrophosphate *345*
Nitrosonaphthols *488, 491*
Nitrosyl chloride *85*
Nitrous acid *522*
Nonane *497*
Non-bauxitic sources *364*
Non-catalyzed reduction *641*
Nonenzymic processes *196*
Non-ionic crystals *38*
Non-ionic reducing agents *533, 636*
Non-ionic reduction *540*
Non-oxidizing acids *71*
Nonpolar molecules *38*
Nuclear magnetic resonance *497*
Nucleating agent *651*
Nucleation *537, 641*

O

Occlusion *537*
Octahedral complexes *553*
Octahedron *547*
1-Octanol *457*
n-Octyl alcohol *458*
Octyl pyrophosphoric acid *475, 518*
Oil well brines *575*
Olivenite *249*
Olivines *357*
Olympic Dam *263*
Opal *361*
Operating line *452*
OPPA, see *Octyl pyrophosphoric acid*
Orange cake *518*
Ore stock-piling *135*
Organic exchangers *412*
Organic matter *247, 400*
Organic phase *495*
Organic phosphorus compounds *348, 475*
Organic sulfides *487*
Organic sulfoxides *487*
Organic sulfur *323*
Organometallic complex *438*
Organophosphorus compounds *513*
Orpiment *335*
Orthoclase *358, 361*
Orthorhombic system *545*
Orthosilicates *360*
Osmosis *419, 425*
Overvoltage *665*
Oxalate ion *113*
Oxalates *618, 629*
Oxalic acid *258, 524, 636*
Oxidation *47, 105*
  of a divalent metal ion *55*
  of Co^{2+} *539*
  pond *654*
Oxidation–reduction *258, 533*
Oxides 113, 598, *629*
  precipitation *648*
Oxides and hydroxides *273*
Oxidizing acids *71*
Oxidizing agent *97*
Oxidizing agents *97*
Oximes *463, 491*
Oxine *468, 491*
Oxygen *97*
Oxyhydrolysis 55, 78, *189, 279, 304,*

550
Ozone *97,217*

P

Pachuca tanks *144, 145,253*
Packed column *439*
Palladium *481*
Palmitic acid *469*
Paradise Peak mine *219*
Partial leaching *276*
Parting alloy *225*
Patera process *205*
Pedro Sotto Alba *255*
Péligot *440*
Pentane *501*
2,4-Pentanedione *461*
Pentavalent arsenic *336*
Pentlandite *369*
Percent extraction *445,446*
Perchloroethylene *292*
Percolation leaching, see *Vatleaching*
Percolation tanks *253*
Peroxide ion *290*
Peroxides *618,629*
Pervanadyl ion *611*
Phase diagram *555*
Phase ratio *444*
Phase transformation 373, 599
Phenol formaldehyde resins 4*12*
Phenols *473*
o-Phenyl phenol *474*
Phosphate rock *82,341*
Phosphates *40, 594*
Phosphine *656*
Phosphine sulfides *478*
Phosphogypsurn *348*
Phosphomolybdate *610*
Phosphoric acid *509, 518, 525*
Phosphorus *343, 525*
Physical adsorption *395*
Physical processes 101
Pickling of steel *76*
Pirotechnia *4*
Pirssonite *70*
Pisanite *249*
Pitchblende 261, 262
Placer deposits *204,228*
Platinum *481, 621*
Platinum metals *228*
  precipitation *636*
Platinum sponge *229*
Plattner process *205*
Plutonium *462,482, 522*
  separation *440*
Plutonium peroxide *618*
Plutonium trifluoride *621*
Poisoning *427*
Polar molecules *35, 38*
Polarity *425*
  of water *36*
Pollucite *361, 362, 373, 515*
Polyacids *610, 629*
Polyhalite *70*
Polyions *610, 611, 613*
Polymerization of extractant 497, *498*
Polymorphic precipitates *624*
Polymorphism *536, 55*1
Polyol *473,474, 514*
Polystyrene resins 413
Polysulfide *303*
Polythionate *295*
Ponds *571*
Porphyry copper ores *250, 251*
Porphyry ores *248*
Portlant cement *364*
Potash 5, 70, 124, 583, 584
Potassium *574*
Potassium chloride *579*
Potassium iron jarosite *609*
Potassium manganate *648*
Potential–pH *29*1
  diagram *51*
Pourbaix diagrams *50*
Powellite *276*
Precipitants *538, 594*
Precipitate flotation *624*
Precipitating tanks *602*
Precipitation *62, 537*
  by ionic reduction *632*
  by non-ionic reduction *637*
  by reduction *533, 631*

- by substitution *647*
- methods *531, 540*
- of $Al(OH)_3$ *603*
- of cobalt *639,646*
- of copper *632,639*
- of cuprous chloride *619*
- of metals from aqueous medium *638*
- of metals from non-aqueous medium *647*
- of nickel *638–640,646*
- of nickel sulfide *624*
- of oxides *648*
- of selenium *634*
- with hydrogen *645*
- with oxalic acid *435*
- with zinc *654*

Pressure filters *183*
Pressure hydrometallurgy 9, *223*
Pressure leaching *144, 276, 329, 337*
Pressure reactors *624*
Primary amyl alcohol *457*
Primene JM *482,483*
Primene JM-T *486,499*
Products of crystallization *564*
Propylcarbinol *457*
Protonation *105*
Prussian blue *92*
Pugmills *157, 158*
Pulp density *165*
Pulp leaching *140*
Pulse column *441*
Pumping *168*
Pure TiO_2 *278,280*
Purex process *522*
Purple ore *376*
Pyridine oxides *487*
Pyrite *135, 212,287, 317, 323*
- leaching 198

Pyrite cinder *375, 619, 625*
Pyrochlore *276, 281, 285*
Pyrohydrolysis *550*
Pyrolusite *257, 273*
Pyrometallurgy 16
Pyrosilicates *360*
Pyrrhotite *212, 309, 323*

- concentrate *237*

Q

Quartz *247, 361*
Quaternary ammonium compounds *482*
Quaternary ammonium salt *484*
Quaternary mixture crystallization *566*
Quenching *363*
Quinolines *468*

R

Radioactive pollution *266*
Radioactivity-free gypsum *350*
Radium *266, 348, 538*
Radium sulfate *75*
Radon *75,266*
Raoult’s law *493*
Rare earths *281, 590*
- recovery *619*
- separation *440*

Rare-earth-conraining clays *94*
Rate *164*
Realgar *335*
Recovering HCI *56*
Recovery *163*
- ofcopper *619*
  - by cementation *654*
- of gold *654*
- of gold and platinum metals *440*
- of lithium *616, 617*
- of molybdenum 612
- of nickel *645*
- of rare earths *619*
- of thorium *619*
- of tungstic oxide *614*
- of uranium *429*

Recovery of HCN *2*18
Recrystallizations *535*
Recycle of leach solution 188
Red amorphous selenium *634*
Red cake *611*
Red mud *244,246*
Redox couple *417*
Redox process *522*

Reducing acids *71*
Reducing agent *97,258, 637*
Reducing agents *97*
Reducing ion *632*
Reduction *47, 533*
  of hydroxide slurries *640*
Refining of gold *224*
Reflux condenser *283*
Refractory gold ores *221, 222, 223, 317*
Refrigeration *570*
Regeneration of leach solution *188*
Removal of arsenic from solution *440*
Removal of molybdenum *440*
Reprocessing of spent nuclear fuel *522*
Residue disposal *187*
Resin-in-pulp process *408*
Rhenium *250,251,482, 516*
Rhenium in molybdenite *303*
Rhodonite *360, 362*
Role of additives *642*
Rongalit C *649*
Rotary drum vacuum filter *185*
Rotary kiln *157, 158, 160,270*
Rotary leaf filter *186*
Rotating autoclaves *154*
Rotating drums *661*
  for cementation *659*
  for copper precipitation *660*
Rotating-disk column *442*
Royal water, see *Aqua regia*
Rutile *276, 352, 599*

S

Salar de Atacama *576,577, 578, 585*
Salar de Uyuni *577*
Salicylaldoxime *464*
Saline brine *616*
Salt lakes *577*
Salting-out agents *502*
Saltpeter *4*
Sand filter *183*
Saturated solution *554*
Scandium *351,440, 524*
Scheelite *276, 283, 285*
  concentrates *613*
Schonite *70,583*
Seawater *576*
  evaporation *570*
Searles Lake *574, 576, 577, 585, 587*
Seaweeds *575*
Secondary butyl alcohol *457*
Sedimentary phosphate *347*
Seed *599,600*
Selective sorption *431*
Selectivity *421*
Selenides *327*
Selenium *327,628,629*
  precipitation *634*
  recovery *332*
Selenous acid *634*
Semipermeable membrane *415*
Separation factor *445*
Separation of hafnium and zirconium *433*
Separation of KCl from NaCl *563*
Separation of lanthanides *434*
Separation of niobium from tantalum *440*
Separation of plutonium *440*
Separation of rare earths *440*
Separation of transition metals *433*
Serpentine *108,358,361,362, 369*
Sesquicarbonate process *585*
Shale *364,365*
Shell Chemicals *472*
Sherritt Gordon *307*
Sherritt Gordon, see *Dynatec*
Sherritt-Gordon Mines *151*
Sherritt-Gordon Plant *644*
Sherritt-Gordon process *303, 305, 645*
Siderite *247*
Silica *358*
Silica gel *108*
Silicates *40, 107, 109*
Siliceous shale *374*
Silicon tetrafluoride *349*
Sill process *338*
Sillimanite *360*

Silver 204, 481, 666
  from $AgNO_3$ 649
Single crystals 546
Single-effect evaporator 172
Site sharing 423
Skutterudite 335
Slimes 178
Slimy ores 400
Smaltite 335
SME 529 467
Smithsonite 268
Soapstone 361
Soda ash 585
Soda niter 70
Sodalite 361
Sodium 574
Sodium aluminate 600
Sodium aluminosilicate 248
Sodium borate 575,585
Sodium carbonate 91, 574
Sodium chlorate 99
Sodium chloride 93, 575
  electrolysis 86
Sodium cyanide 252
Sodium formate 636
Sodium hydroxide 86
  process 355
Sodium hypochlorite 316
Sodium hypophosphite 635
Sodium jarosite 271
Sodium nitrate 99
Sodium nitrate industry 575
Sodium nitrire 522
Sodium paratungstate 613
Sodium selenosulfate 628
Sodium sulfate 581
Sodium sulfide 93, 623
  process 300
Sodium sulfite 628
Sodium tellurate 332
Sodium tetravanadate 611
Sodium thiosulfate 94, 205, 238
Sodium uranous fluoride 622
Sodium vanadate 261, 611
Sodium wolframate 284
Solar crystallizers 570
Solar evaporation 580
  ponds 616
Solar pond 577
Solar ponds 572
Solid oxidants 99
Solid solution 551, 565
  formation 538
Solubility 38
  data 40
  diagrams 554, 560
  of copper sulfate 560
  of cuprous chloride 618
  of lithium carbonate 616
  system $FeSO_4$–$CuSO_4$ 561
  system KCl–NaCl 561
  system $NiSO_4$–$ZnSO_4$ 562
Solubility product 41
  of sulfides 106
Solution mining 123, 581
Solvation 419
  mechanism 494
  of ions 425
Solvay process 92, 567, 574
Solvent extraction 9, 366, 381, 570, 614, 615, 618, 658
Solvent loading 450
Sorption of uranium 430
Sources of information 19
Soxhlet extractor 296, 297
Specific resins 416
Speiss 339, 606
Spent nuclear fuel reprocessing 522
Sphalerite 273
Spodumene 108, 360, 362, 363, 373, 574, 616
Sponge model of exchangers 407
Spray drying 573
Spraying technique 125
Square planer complexes 552
Stearic acid 469
Steel pickling 76
Steel wool cathodes 401
Steelmaking 272
Stibnite 212
Stockpiling crushed ore 135
Stoichiometry of cyanidation 207

Stripping *382, 438, 490*
Stripping coefficient *443*
Strong-acid cation exchangers *414*
Strong-base anion exchangers *415*
Structural isomerism *552*
Structure of minerals *32*
Submerged combustion *574*
Substituted hydrocarbons *454*
Substitution *535, 540*
  mechanism *494*
  reaction *647*
Subsurface brines *577*
Subterranean water *575, 617*
Sulfamates *647*
Sulfarsenides *335*
Sulfates *40, 610*
Sulfides *40, 114, 629*
Sulfite ion *533, 632*
Sulfites *625, 629*
Sulfohalite *70*
Sulfonated coals *386, 412*
Sulfones *487*
Sulfoxides *487*
Sulfoxylate *295*
Sulfur *292*
Sulfur dioxide *258*
  generation *17*
Sulfur pellets *297*
Sulfuric acid *72, 343*
  manufacture *72*
Sulfurous acid *83, 113, 252, 628*
Sulfurous acid decomposition *633*
Superphosphate *343*
Supersaturated solution *554*
Surface complexes *388*
Surface nucleation *546*
Surface oxides *389*
Surface waters *575*
Surface-active agent *595*
Swelling *419*
Sylvinite *70, 580*
Sylvite *70, 569, 575*
Synergic action *519*
Synergic effect *509*
Synergism *491*
Synthetic resins *412*
Synthetic rutile *277, 278, 279*
System Fe_2O_3–SO_3–H_2O *610*
System KCl–$MgCl_2$–H_2O *578, 579*
System KCl–$MgSO_4$ *567*
System NaCl–KCl *563*
System NaCl–$MgSO_4$ *567*
System $NaSO_4$–$MgSO_4$–H_2O *566*
System NH_4HCO_3–NaCl *567*

T

Talc *361, 617*
Tantalite *276, 281, 285*
Tantalum *521, 591*
TBP, see *Tributylphosphate*
Tectosilicates *361*
Tellurides *327*
Tellurium *327, 634, 666*
Tenorite *249*
Tertiary butyl alcohol *457*
Tetrachloroethene *292*
Tetragonal system *545*
Tetrahedron *547*
Tetralin *455*
Tetravalent uranium *430*
Tetravanadate *611*
Thenardite *70*
Thenoyl trifluoro acetone *460, 491, 522*
Theoretical stage *453*
Thermal decomposition *366*
Thermonatrite *70*
Thermophilic bacteria *197*
Thickening 180
Thin layer leaching *139*
Thiobacillus ferrooxidans 195
Thiobacillus thiooxidans *195*
Thiocyanate formation *216*
Thioethers *487*
Thionates *305*
Thiosulfate *295, 303, 305*
Thiosulfates in waste solutions *320*
Thiourea *205*
  process *218*
Third-phase formation 501
Thorite *360*

Thorium *341, 440, 482, 517, 521, 618*
  recovery *619*
Thucholite *262*
Tilting pan vacuum filter *187*
Tin slags *282*
Tincal *70*
Tincalconite *70*
Tioxide Canada *599*
Titanium dioxide *598*
Titanium slag *276, 280*
Titanium-lined autoclaves *256*
Toluene *454*
Top-blown rotary converter *331*
TOPO, see *Trioctyl phosphine* oxide
Torbenite *249*
Toxic gas formation *656*
Tragacanth *419*
Transfer of electrons *108*
Tranr-isomer *553*
Transition temperature *556*
Transmutation *3*
Treadwell process *314*
Treatment of complex ores *18*
Treatment of low-grade ores *19*
Tremolite *360*
Tributyl phosphate *440, 455, 476–??, 478, ??–480, 489, 492, 497, 504, 507*
Tributyl phosphine oxide *492*
Triclinic system *546*
Tricuite *252*
Triisooctylamine *484, 485, 491, 501, 520*
Trimethyl carbinol *457*
Tri-*n*-octylamine *484, 499*
Trioctyl phosphine oxide *476, 477, 518*
Triple-effect evaporators *585*
Tritiated water *129*
Trivalent arsenic *336*
Trona *70, 124, 585*
TTA process *522*
Tube autoclave *154, 157, 159*
Tungstates *613, 629*
Tungsten *440, 482, 517*
Tungstic acid *613*
Tungstic oxide recovery *614*
Turquoise *249*
Twinned crystal habits *547*

U

Ulexite *70*
Unit cell *544*
United McGill *156*
Uranates *610, 613, 629*
Uraninite *261*
Uranium *10, 250, 341, 451, 462, 482, 492, 499, 502, 504, 506, 517, 521, 522, 524*
  from wet process phosphoric acid *440*
  ores *137, 260, 273, 615*
  recovery *347, 429*
  sorption *430*
Uranium dioxide *113, 638, 648*
Uranium fluorides *621*
Uranium peroxide *618*
Uranium sulfate elution *431*
Uranyl ion *429*
Urea *552*
US Borax Mine *586*

V

Vacuum crystallization *585*
Vacuum crystallizers *571, 573*
Vacuum evaporators *172*
Vacuum filters *184*
Vanadates *611, 629*
Vanadium *248, 342, 451, 519*
  minerals *261*
  recovery *440*
Vanadium fluorocomplexes *519*
Vanadium pentoxide *611*
Vat leaching *138, 349*
Venturi *173*
Vereinigte Aluminium Werke *159*
Versatic acid *469*
Viscosity of elemental sulfur *294*
Vivianite *342*

W
Waelz process *269*
Washing *176*
Waste disposal *19*
Water as a leaching agent *69*
Water extraction *511*
Water jet venturi *173*
Water of crystallization *548*
Water of hydration *44*
Water treatment *189, 587*
Water-soluble minerals *70*
Wavellite *342*
Weak-acid cation exchangers *413*
Weak-base anion exchangers *414*
Willemite *362, 374*
Wolframite *86,276, 283, 285*
Wolframite concentrates *613*

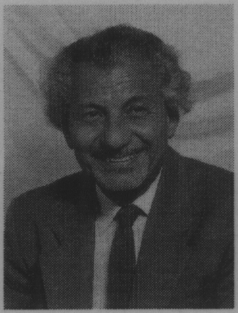
X
Xenotime *341,351, 589,618*
X-ray diffraction of resins *428*
Xylene *454,485,486*

Y
Yellow cake *518,614, 615*

Z
Zeolites *411,419*
Zinc *472,647, 666*
  dust *661*
  from pyrite cinder *440*
Zinc blend *212*
Zinc hydroxy carbonate *647*
Zinc oxide ores *268*
Zinc sulfide *306, 315*
  concentrate *268*
Zincite *268*
Zircon *352,360,362*
Zirconium *462,482, 504, 521, 522, 591*

The Book

Textbook of Hydrometallurgy covers the general principles of solution chemistry, engineering aspects, and detailed studies of hydrometallurgical processes in 750 pages fully illustrated with drawings and photographs. It contains a selected list of over 250 review articles, proceedings volumes, and books directly related to the subject. Emphasis is laid on chemical reactions, equipment used, and flowsheets.



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