

# **Extraction of Nonferrous Metals**

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# **EXTRACTION OF NONFERROUS METALS**

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# Contents

## Preface

xi

## 1 Early Developments in Metal Extraction

1

1.0	Introduction	1
1.1	Discovery of Metals	1
1.2	Landmarks	3
1.3	Uses of Metals	4
1.4	Substitution of Scarce Nonferrous Metals	4
	Suggested Reading	4

## 2 Principles of Metal Extraction

6

2.0	Introduction	6
2.1	Thermodynamic Principles	6
2.2	First Law of Thermodynamics: Concept of Internal Energy	7
2.3	Second Law of Thermodynamics: Concept of Entropy	10
2.4	Entropy Criteria for Spontaneous Processes	12
2.5	Variation of Free Energy with Pressure and Temperature	13
2.6	Standard Free Energy and Equilibrium Constant	14
2.7	Compilation of Free Energy Data	17
2.8	Thermodynamics of Solutions	27
2.9	Gibbs-Duhem Equation	29
2.10	Activity	31
2.11	Excess Thermodynamic Quantities	34
2.12	Regular Solutions	36
2.13	Thermodynamics of Dilute Metallic Solutions	37
2.14	Interaction Parameters in Multicomponent Solutions	40
2.15	Kinetic Principles: Reaction Rate	41
2.16	Theory of Absolute Reaction Rates	45
2.17	Homogeneous and Heterogeneous Reactions	47
2.18	Laws of Diffusion	47
2.19	Mass Transfer between a Fluid and a Solid	48
2.20	Gas-Solid Reactions	54
2.21	Electrochemistry	59
2.22	Cells and Thermodynamic Relations	62
2.23	Arbitrary Potential Zero: The Hydrogen Scale	64
2.24	Kinetics of Electrode Processes	67

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Problems	71
References	72
Suggested Reading	72

**3 Minerals, Ores, and Methods of Beneficiation****PART I MINERALS AND ORES**

3.0 Introduction	74
3.1 Reactivities of Metals	76
3.2 Relative Reactivities and Modes of Occurrence of Metals in Nature	80
3.3 Nature of Atomic Bonding in Compounds	82
3.4 Exploration for Mineral Deposits	82
3.5 Sources of Metals	85
3.6 Sea as Source of Metals	87
3.7 Ocean-Floor Nodules	89
3.8 Mineral Resources of the World	90
3.9 Nonferrous Mineral Wealth of India	101

**PART II METHODS OF BENEFICIATION**

3.10 Introduction	109
3.11 Comminution (Size Reduction)	111
3.12 Efficiency in Comminution	113
3.13 Size of a Particle	115
3.14 Sizing	117
3.15 Classification and Concentration	118
3.16 Sizing and Sorting Equipment	120
3.17 Magnetic Separation	121
3.18 Electrostatic Separation	123
3.19 Flotation	123
Questions	127
References	127
Suggested Reading	128

**4 General Methods of Extraction**

4.0 Introduction	129
4.1 Pyrometallurgy	129
4.2 Calcination	130
4.3 Roasting	131
4.4 Predominance Area Diagrams	133

74

4.5 Roasting Practice	137
4.6 Smelting	144
4.7 Metallothermic Reduction of Oxides	146
4.8 Smelting Furnaces	150
4.9 Matte Smelting	156
4.10 Reduction of Halide by Another Element	156
4.11 Halide Metallurgy and Halogenation	157
4.12 Pyrometallurgical Processes Using Vacuum	163
4.13 Hydrometallurgy	168
4.14 Leaching: Solution Preparation	171
4.15 Theory of Leaching	173
4.16 Role of Oxygen in Leaching Operations	181
4.17 Pressure Leaching	182
4.18 Bacterial or Microbial Leaching	186
4.19 Contact Reduction of Metals in Aqueous Solutions (Cementation)	189
4.20 Gaseous Reduction of Metals in Aqueous Solutions	194
4.21 Kinetic Aspects of Gaseous Reduction	201
4.22 Recovery of Metal Values from Leach Liquor by Ion Exchange, Solvent Extraction, and Electrolysis	205
4.23 Electrometallurgy	205
4.24 Structure of Solvent Media	207
4.25 Electrolysis of Aqueous Solutions	212
4.26 Electrolysis of Fused Salts	214
4.27 Electrolysis of Low-Temperature Nonaqueous Systems	220
4.28 Cell Design	221
4.29 Electroplating	223
4.30 Role of Energy in Metal Extraction	224
4.31 Environmental Problems	227
Questions	227
References	228
Suggested Reading	229

**5 General Methods of Refining**

5.0 Introduction	230
5.1 Basic Approaches to Refining	232
5.2 Preparation of Pure Compounds	232
5.3 Purification of Crude Metal Produced in Bulk	251
Problems	279
References	280
Suggested Reading	280

129

**6 Extraction of Metals from Oxides**

6.0 Introduction	282
------------------	-----

230

282

6.1	Magnesium	283
6.2	Magnesium Ores	284
6.3	Methods of Magnesium Extraction	284
6.4	Pidgeon Process	285
6.5	Magnesium Production in India	288
6.6	Aluminium	288
6.7	Extraction of Aluminium	290
6.8	Bayer Process for Alumina Production	291
6.9	Hall-Héroult Process	293
6.10	Methods of Treating Low-Grade Ores	302
6.11	Production of Aluminium in India	303
6.12	Environmental Considerations in Aluminium Production	307
6.13	Newer Processes for Aluminium Production	307
6.14	Tin	310
6.15	Concentration of Tin Ores	311
6.16	Smelting of Tin Concentrate	312
6.17	Refining of Tin	314
6.18	Ferroalloying Elements	316
6.19	Chromium	316
6.20	Manganese	318
6.21	Silicon	319
6.22	Tungsten	320
6.23	Vanadium	321
6.24	Niobium (Columbium) and Tantalum	323
6.25	Molybdenum	325
6.26	Ferroalloys	325
6.27	General Methods of Producing Ferroalloys	327
6.28	Production of Individual Ferroalloys	332
	Problems	335
	References	336
	Suggested Reading	336

**7 Extraction of Metals from Sulphide Ores**

7.0	Introduction	337
7.1	Winning of Metals from Sulphide Ores	338
7.2	Copper	341
7.3	Pyrometallurgical Extraction of Copper	343
7.4	Newer Processes for Copper Extraction	354
7.5	Energy Concepts in Copper Smelting	367
7.6	Hydrometallurgy of Copper	367
7.7	Production of Copper in India	371
7.8	Lead	373
7.9	Extraction of Lead	374
7.10	Modern Developments in Lead Smelting	379
7.11	Production of Lead in India	381

7.12	Zinc	382
7.13	Extraction of Zinc	383
7.14	Pyrometallurgical Extraction of Zinc	384
7.15	Hydrometallurgical Extraction of Zinc	387
7.16	Imperial Smelting Process (ISP)	389
7.17	Zinc from Lead Slags by Slag Fuming	393
7.18	Production of Zinc in India	394
7.19	Treatment of Complex Sulphides of Lead, Copper, and Zinc	397
7.20	Nickel	399
7.21	Extraction of Nickel by Pyrometallurgy	399
7.22	Extraction of Nickel from Oxide Ores	403
7.23	Hydrometallurgy of Nickel Sulphide Concentrates	410
7.24	Other Metals from Sulphide Ores	410
	Problems	416
	References	417
	Suggested Reading	417

**8 Extraction of Metals from Halides**

8.0	Introduction	419
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**PART I**

8.1	Extraction of Nuclear Reactor Metals	419
8.2	Beneficiation of Complex Ores	421
8.3	Reduction of Metal Halides	425
8.4	Extraction of Uranium	428
8.5	Production of Uranium in India	435
8.6	Properties and Production of Plutonium	438
8.7	Extraction of Thorium	442
8.8	Methods for Producing Thorium Metal	448
8.9	Extraction of Zirconium	451
8.10	Zirconium Production in India	455
8.11	Beryllium Extraction	462

**PART II**

8.12	Extraction of Other Metals from Chlorides	465
8.13	Magnesium	466
8.14	Alkali and Alkaline Earth Metals	467
8.15	The Alkaline Earth Metals	471
8.16	Rare-Earth Metals	472
8.17	Titanium	475
8.18	Treatment of Ilmenite for Upgradation	477
8.19	Chlorination of TiO <sub>2</sub>	480

## CONTENTS

8.20 Production of Metallic Titanium by Reduction of Titanium Tetrachloride	482
8.21 Production of Ductile Titanium	484
Problems	487
References	487
Suggested Reading	487
<b>9 Precious Metals</b>	
9.0 Introduction	489
9.1 Occurrence and Production	489
9.2 Extraction of Gold	492
9.3 Extraction of Silver	496
9.4 Extraction of Platinum Group Metals	498
Problems	500
Reference	501
Suggested Reading	501
<b>10 Secondary Metals and Utilization of Metallurgical Wastes</b>	
10.0 Introduction	502
10.1 Secondary Copper	502
10.2 Secondary Lead	504
10.3 Secondary Zinc	505
10.4 Secondary Aluminium	505
10.5 Aluminium from Non-scrap Sources	506
10.6 Secondary Tin	507
10.7 Recovery of Vanadium from Bayer Plant Liquors and Red Mud	508
10.8 Utilization of Metallurgical Wastes	508
Reference	509
Suggested Reading	509
Appendix 1 Some minerals and their formulae	510
Appendix 2 Selected physical properties of metals	514
Appendix 3 Physical properties of metals	517
Appendix 4 Thermal conductivity of metals	520
Appendix 5 Electrical resistivity of metals	521
Appendix 6 Thermal neutron absorption cross-sections of possible structural materials in ascending order of absorption cross-section (for 2200 m/sec neutron velocity)	523
Appendix 7 Vapour pressures of some metals and corresponding temperatures (temperature in K for various partial pressures in atmosphere)	524
Index	

489

## Preface

502

This text is based on the experience gained by us over several years of teaching and research (H.S. Ray and K.P. Abraham) and of industrial and process development work (R. Sridhar) in extraction metallurgy. It is designed to meet the needs of the undergraduate student and practising metallurgist. There are not many books with adequate information on the state of Indian technology in this area and we hope this volume will fill the gap.

The theoretical framework of studies to which the present-day students are exposed does not justify piecemeal instruction on industrial processes. This text provides a modern integrated course on the principles of extraction and refining of nonferrous metals and also the details of some of the important extraction and refining processes. Moreover, in keeping with the existing trends, it emphasizes the energy and environmental aspects of the extraction processes, in addition to the current developments in the technology.

We are aware that a logical treatment of the extraction of metals should also cover ferrous metallurgy. In terms of the principles involved, the ferrous extraction metallurgy is no different. However, in view of the fact that ferrous metallurgy finds a prominent place and is treated as a separate subject in the undergraduate and graduate curricula, the treatment here is confined to the extraction metallurgy of nonferrous metals.

In preparing a work such as this, it is natural to use information from several sources. We are indebted to all the authors, too numerous to list, from whose knowledge we have benefited. We also wish to acknowledge the valuable discussions we had with Mr. C.V. Sundaram and the advice on some topics we received from friends and colleagues, including Professors A. Ghosh and A.K. Biswas and Dr. G.N.K. Iyengar. We record too our appreciation of the financial assistance granted by the Educational Development Centre (at the Indian Institute of Technology, Kanpur) and the Curriculum Development Cell (at the Indian Institute of Science, Bangalore), established by the Ministry of Education and Culture, for the preparation of the manuscript.

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526

# 1 Early Developments in Metal Extraction

## 1.0 INTRODUCTION

The history of man can be broadly classified into three divisions, namely, the stone age, the bronze age, and the iron age. The transition from the stone age to the metal age—brought about by the discovery of copper in its native form around 8000 B.C.—can be considered one of the most significant phases of human history. The period, when man employed both stone and metal, is known as the *chalcolithic* period (GK. *chalcos*, copper; *lithos*, stone). As is evident from the name, during this period, copper was the chief metal, although man must have located sizeable natural deposits of native metals such as gold and silver. Also, iron and nickel may have been found in the remnants of meteorites that occasionally fall onto the earth's surface from outer space. Copper found ready application in the manufacture of tools and weapons whereas gold and silver served adornment purposes. As time passed, deposits of native copper must have diminished, compelling man to devise new methods for extracting the metal from its ores or to produce its alloy.

The common method for extracting copper from its ores was smelting, i.e., melting or fusing of an ore to separate and refine the metal. Around 1300 B.C., ore was first subjected to smelting along with a fuel followed by a second smelting, using charcoal together with an air blast, to attain a high temperature needed for the process. Although copper had many useful functional properties, man sought an even harder material for fashioning tools and weapons. He eventually discovered an alloy, namely, bronze, by mixing copper and tin. Thus began the bronze age. Since, as compared with copper, bronze is harder, has a lower melting point, and can be more easily shaped into implements and utensils, it replaced copper. But the bronze age was not to last long; it ended when a new metal—iron—replaced bronze. Since then, man has constantly experimented with metals and has developed, through empirical methods, many standard processes for metal extraction.

## 1.1 DISCOVERY OF METALS

Although man has been using metals since around 8000 B.C., till about the fifteenth century A.D., only a handful of metals was known (e.g., gold, silver, mercury, copper, tin, lead, zinc, and iron); also, some alloys were considered metallic elements. Further developments in alchemy and the subsequent scientific renaissance accelerated the rate of discovery of metals. The metals known and used by the Mesopotamians, Egyptians, Greeks, and Romans were copper, tin, gold, silver, mercury, and lead. In addition to these metals, iron was known and used widely in India as early as 2000 B.C. Of all the metals currently known, nearly three-fourths have been discovered since the beginning of the nineteenth century.

## 2 EXTRATION OF NONFERROUS METALS

The following factors contributed to the widespread use of the metals.

- (1) Metals such as Au, Ag, Cu, and Hg occur in the natural state. Iron sometimes occurs in meteorites.
- (2) Oxides of copper, iron, tin, and lead are readily reduced at or below 800°C. Such temperatures are attained easily by burning a carbonaceous material.
- (3) Pb, Sn, and Hg have a low melting point and are easy to recover. Such metals sometimes form low melting alloys, e.g., Cu-Sn alloys.

It is interesting to note that till about the twelfth or thirteenth century zinc was unknown in the West although it had perhaps been isolated in India around the ninth or tenth century.

The years/periods now listed are considered significant in the history of extractive metallurgy:

8000 B.C.	Earliest (neolithic) peasant communities of Western Asia start using metallic objects
4000 B.C.	Egyptians learn to extract copper from its ores Chinese start employing flame techniques for producing bronze and iron
2000-1000 B.C.	Indians learn to extract copper from its ores; they also learn to make bronze with varying tin content Chinese and Indian artisans master art of casting, riveting, brazing, and forging of copper-tin alloys Indians and Egyptians learn to wash gold containing sand or crushed and ground rocks; they also learn amalgamation process Chinese and Indians master iron production by charcoal reduction of iron ores
1500-0 B.C.	West Asians and Indians learn to reduce lead ores by charcoal; also, cinnabar is reduced to produce mercury and purified by squeezing through leather Silver is produced from impure lead, and tin from its ores
300 B.C.	Aristotle describes winning of silver from its ores by flame technique
79 B.C.	Pliny describes preparation of lead by electrochemical displacement and by retort distillation; he also purifies gold by amalgamation
700-800 A.D.	In Europe, copper is precipitated from acid solution with metallic iron
1100-1300 A.D.	Alchemists develop inorganic acids for treating ores and metals Arsenic and antimony are discovered
1550 A.D.	Handbooks on metallurgy begin to appear
1700-1800 A.D.	Large number of metals are discovered, namely, Co, Pt, Zn, Ni, Bi, Mn, Mo, Te, W, U, Zr, Ti, Y, Be, and Cr Coke is produced extensively from coal for use in blast furnaces
1800-1900 A.D.	More metals are discovered, namely, Ta, Ir, Os, Pa, Rh, K, Na, B, Ba, Ca, Mg, Sr, Ce, Li, Cd, Se, Si, Al, Th, V, La, Ru, Rb, In, Ga, rare earths, Ra, Ac, and Po

## EARLY DEVELOPMENTS IN METAL EXTRACTION 3

From prehistoric times up to about 1860, almost all metals were produced by the fire assay techniques. During 1860-1940, the principles of inorganic and physical chemistry were applied, on an organized basis, to metal extraction. The pyrometallurgical reduction techniques under controlled conditions using carbonaceous materials and metals were developed and improved upon continuously. In addition, the electrochemical decomposition techniques in aqueous and nonaqueous media were developed.

### 1.2 LANDMARKS

The landmarks in the development of modern extractive metallurgy must be examined with respect to the scientific innovations. Some important landmarks are:

Dudley, 1620	Introduces coke to replace charcoal in England
Lavoisier, 1772	Proves invalidity of phlogiston theory and shows that oxides are compounds of metals and oxygen
Wöhler, Berzelius, Bergman, 1783	Demonstrate hydrogen reduction of $WO_3$ and establish use of hydrogen as reducing agent
Oersted, 1825	Discovers aluminium and shows that alumina is not an element
Nielson, 1828	Uses hot blast to attain high temperatures in blast furnaces
Faraday, 1831	Explains phenomenon of electrolysis and proposes what are today known as Faraday's laws
Bessemer, Kelly, 1856	Introduce pneumatic steel
Woehler, St. Claire Deville, 1850*	Reduce aluminium salts to metal
Galvani, Volta, Grothans, Faraday, Davy, 1850*	Develop electrochemistry
Clausius, 1857	Explains origin of ions in electrolytes
Cowper, 1857	Proposes stoves for regeneration of heat
Siemens, Martin, 1868*	Develop open-hearth furnace for steel-making
Mendeleev, 1869	Proposes periodic table
Castner, 1886	Demonstrates electrolysis of sodium hydroxide
Hall, Héroult, 1886	Produce aluminium by electrolysis of alumina dissolved in cryolite
Bayer, 1887	Patents Bayer process for alkali leaching of alumina that marks beginning of modern hydrometallurgy
McArthur, Forests, 1887	Introduce cyanidation process for gold extraction
Goldschmidt, 1894	Demonstrates aluminothermal reduction of metal oxides
Becquerel, 1897	Discovers radioactivity
Hahn, Strassmann, 1938	Demonstrate uranium fission

a, approximate date.

**1.3 USES OF METALS**

A metal usually reaches commercial status mainly because of its ability to meet certain requirements more economically than any other material. Metals such as gold and silver, when used for adornment, must, however, be treated as exceptions to this rule.

The properties of metals vary widely from one metal to the other even in the case of pure metals. For example, mercury is a liquid at room temperature whereas tungsten melts only at 3410°C. The other nonferrous metals melt at varying temperatures between these extremes. Similarly, the other properties, e.g., the boiling point, strength, hardness, ductility, expansivity, conductivity, and corrosion resistance, also vary within wide limits. Of these, some properties can be further varied by thermal and mechanical treatment, by modifying the characteristics of the surfaces, and by alloying. If we take into account alloy systems, we find that the diversity of properties that may be achieved increases manifold. There are several thousand industrial alloys each of which may be subjected to mechanical and thermal treatment and special processing. The range of properties available today is therefore very wide.

We shall discuss the uses and applications of individual metals in the chapters that follow.

**PRODUCTION OF UTENSILS: MAJOR NONFERROUS INDUSTRY IN INDIA**

Aluminium and brass domestic utensils are the major products of the Indian nonferrous industry and account for over 50 per cent of the total consumption of these metals in India. The utensils industry is thus a much more significant part of the nonferrous metal industry in India than anywhere else in the world. The annual production of brass utensils is over 40,000 tons of which only about 6000 tons are produced in factories, the balance being manufactured by the cottage industries. Aluminium utensils, on the other hand, are mostly manufactured in factories, the annual production being over 20,000 tons. India exports aluminium and brass wares and utensils mostly to the East African, Middle Eastern, and South Asian countries.

**1.4 SUBSTITUTION OF SCARCE NONFERROUS METALS**

India has poor reserves of common metals, notably, zinc, lead, copper, and tin. Also, various measures have been considered to reduce, as far as possible, India's imports of these metals, taking into account the inadequate reserves of such metals and the availability of adequate to abundant resources of aluminium, manganese, and chromium.

Fortunately, it is today possible to develop entirely different alloys with similar properties. Thus, if economic necessity demands, substitutes can be made available for certain metals and alloys in some traditional applications. Therefore, in recent years, substitution technology has assumed considerable importance.

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## 2 Principles of Metal Extraction

### 2.0 INTRODUCTION

In this chapter, we shall discuss the principles of chemical thermodynamics, reaction kinetics, and electrochemistry, which are fundamental to the understanding of many extraction and refining processes. Chemical thermodynamics tries to explain why a chemical reaction occurs and serves as a guide to what is theoretically feasible and what is not. On the other hand, kinetics determines the rate at which a reaction may occur. The theoretical treatment of a process involving a large departure from equilibrium conditions cannot be complete without considering the accompanying kinetics. The thermodynamic treatment gives an idea of the equilibrium state that can ultimately be reached.

The rate of a metallurgical reaction is controlled by the kinetics of mass transfer as well as by chemical and electrode kinetics. Therefore, the methods of speeding up a process can be ascertained only if the reaction mechanism and the kinetic principles involved are fully understood. Electrolytic extraction and refining processes can be considered to be the logical application of basic facts about electrode potentials and stabilities of ions which are generally covered under electrochemistry.

### 2.1 THERMODYNAMIC PRINCIPLES

The tendency of an element to pass from one combined state to another can be predicted by applying thermodynamic principles. Hence, thermodynamics can indicate the feasibility of various chemical reactions associated with possible extraction processes.

Many of the well-known extraction processes have been evolved over a period of time by empirical methods. The task of the extraction metallurgist is becoming more and more difficult because he is being called upon to produce metals from increasingly leaner ores and refine them to a much higher degree of purity than stipulated hitherto. So, wasteful empirical methods have to be replaced by theoretically sound ones. The strategy should be to make use of all the available thermodynamic data in order to produce a material of the required specification. Fortunately, much thermodynamic data have accumulated over the years, and these enable us to calculate the equilibria of various chemical reactions.

In this chapter, we do not attempt a comprehensive treatment of chemical thermodynamics, but emphasize the main concepts and their applications to practical problems and highlight the limitations in their use.

The concepts of energy and entropy, which provide the framework for thermodynamics, are derived from the first and second laws of thermodynamics, respectively.

### 2.2 FIRST LAW OF THERMODYNAMICS: CONCEPT OF INTERNAL ENERGY

#### DEFINITIONS

A *system* in thermodynamics is a portion of matter under study and consists of a definite amount of a specific substance or substances. A system is separated from its surroundings consisting of the rest of the universe. An *open system* can exchange energy and matter with its surroundings. A *closed system* cannot exchange matter, but can exchange energy with its surroundings. A system along with its surroundings is called an *isolated system* and an isolated system cannot exchange energy or matter with any other system.

The law of conservation of energy is based purely on human experience. The first law of thermodynamics is an extension of this law necessitated by the realization that work could be converted into heat and the expenditure of a fixed amount of work always resulted in the production of the same amount of heat. Therefore, it is possible to define a new function called *internal energy* ( $E$ ) such that the change in the internal energy  $\Delta E (=E_2 - E_1)$ , considering a system going from State 1 to State 2, is always given by

$$\Delta E = q - w. \quad (2.1)$$

From eq. (2.1), we see that the change in the internal energy  $\Delta E$  is equal to the sum of the heat  $q$  absorbed by the system and the work done on the system  $-w$ . The values of both  $q$  and  $w$  depend on the path taken, but the difference in their values is independent of the path. By convention,  $q$  is positive if the system gains energy in the form of heat and  $w$  is positive if the work is done by the system, i.e., when the system loses energy as a result of doing some form of work. The work  $w$  may be of different kinds. It includes the volume work, i.e., the work done against an external pressure and all other forms of work such as work against external electrical and magnetic fields and surface work. That is,

$$w = w_{\text{volume}} + w_{\text{electrical}} + w_{\text{magnetic}} + w_{\text{surface}} + \dots$$

It is usual for systems to do only volume work of expansion against pressure. This work is  $p dv$ , where  $p$  denotes pressure and  $v$  volume. In our discussion, the work of expansion alone is taken into account, and unless otherwise stated, all other forms of work are not considered. Hence, for an infinitesimal change,

$$dE = q - p dv. \quad (2.2)$$

Equation (2.1) is the mathematical formulation of the first law of thermodynamics. Since the internal energy is independent of the path, it is a state property and a complete differential.

#### NATURE OF INTERNAL ENERGY

A piece of matter is composed of smaller fundamental particles possessing energy in several forms, for example, energy due to molecular translation, rotation and vibration, electron translation and spin, nuclear spin, nuclear binding, molecular binding, coulomb binding, and also due to magnetic and electric dipole moments. The internal energy represents all the energies associated with the aforesaid microscopic modes. Because of the complex nature of internal energy, it is difficult to determine its absolute value even in the case of simple elements.

#### HEAT CONTENT OR ENTHALPY $H$

For a process occurring at constant volume,  $dv = 0$ ,  $w = 0$ . Hence, from eq. (2.1), we get  $\Delta E = q$ ,

where  $q_v$  is the heat absorbed at constant volume. However, for a process occurring at constant pressure  $p$ ,

$$\Delta E = E_2 - E_1 = q_p - w = q_p - p(v_2 - v_1)$$

or

$$q_p = (E_2 + pv_2) - (E_1 + pv_1),$$

where  $q_p$  is the heat absorbed at constant pressure.

A new function, called *enthalpy* or heat content, denoted by  $H$ , can be defined as

$$H = E + Pv, \quad (2.3)$$

$$\Delta H = H_2 - H_1 = q_p. \quad (2.4)$$

Since  $p$  and  $v$  are state properties of the system, it follows that  $H$ , like internal energy  $E$ , is a state function of the system and is independent of the path by which the state is reached. The concept of heat content is important because many chemical and metallurgical processes are carried out at constant pressure.

When reactions occur between condensed phases, the volume change is small, so the difference between  $\Delta E$  and  $\Delta H$  is also negligibly small. As in the case of  $E$ , the absolute value of  $H$  is difficult to determine.

#### HEAT CAPACITY AND CHANGE OF ENTHALPY WITH TEMPERATURE

Heat capacity may be measured at constant volume or at constant pressure. The molar heat capacities, denoted by  $C_v$  (at constant volume) and  $C_p$  (at constant pressure), are defined as

$$C_v = \frac{dq_v}{dT} = \left(\frac{\partial E}{\partial T}\right)_v, \quad (2.5)$$

$$C_p = \frac{dq_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p. \quad (2.6)$$

The variation of heat capacity with temperature is expressed by empirical expressions of the type  $C_p = a + bT + cT^2 + \dots$ , where  $a, b, c, \dots$  are constants. The temperature variation of the heat of reaction can be determined with the help of eqs. (2.5) and (2.6).

The enthalpy change of a chemical reaction can be written as

$$\begin{aligned} \Delta H &= H_{\text{product}} - H_{\text{reactant}}, \\ \left(\frac{\partial \Delta H}{\partial T}\right) &= \left(\frac{\partial H}{\partial T}\right)_{\text{product}} - \left(\frac{\partial H}{\partial T}\right)_{\text{reactant}} \\ &= C_p(\text{product}) - C_p(\text{reactant}) = \Delta C_p. \end{aligned} \quad (2.7)$$

By integrating eq. (2.8) at a constant pressure of 1 atm, we obtain the value of  $\Delta H$  at a higher temperature  $T_2$  from its value at a lower temperature  $T_1$  by the relationship

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_p \, dT. \quad (2.9)$$

This is one of Kirchhoff's equations. Using eq. (2.9), we can calculate high-temperature values of  $\Delta H$  from available  $C_p$  data and from the low-temperature value of  $\Delta H$ .

#### HEATS OF FORMATION

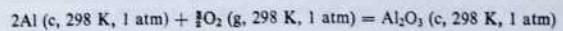
Although the absolute values of thermodynamic quantities such as internal energy and enthalpy cannot be obtained, the difference in their relative values in two different states can always be determined. Hence, the common practice is to give the thermodynamic properties of substances with respect to a reference state or a standard state. The choice of the standard state is quite arbitrary, but a convenient standard state for a substance is taken as its most stable form at 1 atm at the temperature under consideration. Thus, we see that the standard state depends on temperature. For example, gray tin and white tin are allotropic forms of tin, the former being stable below 286 K and the latter above this temperature. Therefore, gray tin is the standard state for tin below 286 K and white tin above this temperature. Graphite is the most stable form of carbon and is to be taken as the standard state for carbon in all computations.

The standard heat of formation (or enthalpy of formation) of a compound is equal to the heat of reaction by which it is formed from its elements, all the reactants and the products being in their standard states. It is a common practice to list the enthalpies of formation at a standard temperature, say, 298 K. Table 2.1 gives the standard heats of formation of some substances.

Table 2.1 Standard Heats of Formation

Substance	$-\Delta H_{298}^0$ (kcal/mole)
$\text{H}_2\text{O}$ (g)	57.8
$\text{H}_2\text{O}$ (l)	68.32
Alumina (c)	400.0
Graphite	0.0
Diamond	-0.454
$\text{H}_2$ (g)	0.0
Silica (c) ( $\alpha$ -quartz)	217.0

When 1 gm mole of alumina is formed from its elements, the heat evolved is 400 kcal according to the reaction



for which  $\Delta H_{298}^0 = -400$  kcal. Here, the superscript zero indicates that this value is the standard heat of formation.

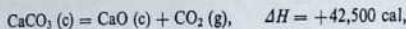
#### HESS'S LAW OF CONSTANT HEAT SUMMATION

The law of constant heat summation, established by G.H. Hess, states that the heat change in a

given reaction is the same whether it takes place in one step or in several steps. This law is an immediate consequence of the first law of thermodynamics. The enthalpy of a compound is a state property and is independent of the method by which the compound is produced. Therefore, the enthalpy change for any chemical reaction is independent of any intermediate steps, but depends only on the initial state of the reactants and the final state of the products. Consequently, the enthalpy change,  $\Delta H$ , of a reaction at a given temperature is the difference between the enthalpies of the reactants and products, all being at the same temperature and 1 atm.

#### CRITERIA FOR SPONTANEOUS PROCESSES

After the formulation of the first law of thermodynamics, it was suggested that the tendency of a chemical reaction to occur could be measured in terms of the heat evolved during the reaction. It was observed that spontaneous processes usually took place with the evolution of heat, and, consequently, the products always had a lower energy content than the reactants. Moreover, the more the heat evolved, the more stable the product seemed to be. However, this criterion was soon found unreliable, as many endothermic processes were found to be spontaneous. For example, calcium carbonate dissociates spontaneously into calcium oxide and carbon dioxide at about 900°C, i.e.,



although this reaction is known to occur with the absorption of heat.

At room temperature, gray tin has a lower energy content than white tin, but the latter is the more stable form. So, the sign of the enthalpy change of a reaction is not useful in predicting its feasibility. Thus, we may conclude that the first law of thermodynamics provides no clue to the feasibility of a reaction; it only specifies the equivalence between the various forms of energy. On the other hand, a satisfactory criterion for spontaneous processes and for chemical equilibrium can be derived from the second law of thermodynamics.

#### 2.3 SECOND LAW OF THERMODYNAMICS: CONCEPT OF ENTROPY

The second law of thermodynamics is useful to the process metallurgist because it provides a method of predicting the conditions under which a process is thermodynamically feasible. This law may be expressed in various equivalent forms, two of which are now given:

- (1) It is impossible to construct a machine which takes heat from a reservoir and converts it into work unless some heat is transferred from a hot to a cold reservoir.
- (2) It is impossible to transfer heat from a cold to a hot reservoir without, in the same process, converting a certain amount of work into heat.

These formulations have been useful in applying thermodynamics to mechanical processes. An important consequence of the second law of thermodynamics is the concept of a new function called *entropy* and denoted by  $S$ . Entropy, like energy, is a conceptual property and also an extensive property. For a reversible process, the entropy function is defined by

$$dS = \frac{dq_{rev}}{T}, \quad (2.10)$$

where  $dq_{rev}$  is the heat absorbed during the reversible process at temperature  $T$ . Although, in eq. (2.10),  $q_{rev}$  is not a complete differential,  $q_{rev}/T$  is. The postulate that the entropy of the isolated system (system plus surroundings) can never

decrease and always tends to a maximum value is one form of the second law of thermodynamics. Thus, any process that would increase the entropy of the isolated system is possible and any process that would decrease it is impossible. Further, any process that keeps the entropy of the isolated system constant is possible both in the forward and backward directions. The formulation of the second law in terms of entropy is of great interest to metallurgists and chemists.

#### VARIATION OF ENTROPY WITH TEMPERATURE

The variation of entropy with temperature can be calculated as follows. If the pressure is constant, then we have

$$dS = \frac{dq}{T} = \frac{dH}{T} = \frac{C_p}{T} dT, \quad (2.11a)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT. \quad (2.11b)$$

Similarly, at constant volume,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v}{T} dT. \quad (2.12)$$

Heat capacities are generally given as a function of temperature. So, the changes of entropy with temperature can be evaluated by integrating eqs. (2.11b) and (2.12).

#### STATISTICAL TREATMENT OF ENTROPY

The definition of entropy already given is according to classical thermodynamics. L. Boltzmann derived a relationship between the entropy of a system in a given state and the probability of existence of the given state. Boltzmann's relationship can be mathematically expressed as

$$S = K \ln W, \quad (2.13)$$

where  $K$  is Boltzmann's constant and  $W$  a measure of the probability that a given state will exist, i.e., the number of different microscopic states which give rise to one and the same macroscopic state.  $W$  can be calculated using statistical mechanics.

At this stage, we make a distinction between the configurational entropy  $S_c$  and vibrational entropy  $S_v$ , corresponding to the configurational states and vibrational states into which the microstates in a crystalline substance can be divided. In other words,

$$S_c = K \ln W_c, \quad (2.14)$$

$$S_v = K \ln W_v, \quad (2.15)$$

where  $W_c$  is the number of different ways in which the atoms or molecules may be arranged in the available lattice positions and  $W_v$  is the number of different ways in which the atoms or molecules can vibrate in their lattice positions. The total entropy is

$$S_{\text{total}} = S_c + S_v. \quad (2.16)$$

For a pure crystalline material, since all atoms are alike and indistinguishable, there is only one way of arranging them in the lattice sites. Hence,  $S_c = K \ln 1 = 0$ . In such cases, the entropy is solely vibrational.

According to the third law of thermodynamics, while the vibrational entropy of a pure crystalline substance is 0 at the absolute 0 of temperature (i.e.,  $S_v = 0$  at 0 K), at a higher temperature, it is

$$S_v = \int_0^T \frac{C_p}{T} dT. \quad (2.17)$$

If the frequency of an oscillator is changed from  $\nu$  to  $\nu'$ , it can also be shown that the change in its vibrational entropy is

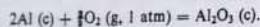
$$\Delta S_v = 3K \ln \frac{\nu'}{\nu}. \quad (2.18)$$

From eq. (2.18), we see that if the frequency is lowered, the entropy change is positive.

#### 2.4 ENTROPY CRITERIA FOR SPONTANEOUS PROCESSES

It has been stated in Section 2.3 that any spontaneously occurring change in an isolated system is accompanied by an increase in entropy. This is not a convenient criterion when studying spontaneous changes in a system in the laboratory, because, to test the feasibility of a process, we have to determine entropy changes in the said system as well as in the surroundings. The example that follows illustrates this point.

A freshly polished piece of aluminium when exposed to air is easily oxidized, the surface being coated by a thin film of oxide even at room temperature, that is,



For this reaction, the enthalpy change at 25°C is  $\Delta H_{298}^0 = -400,000 \text{ cal}$  and the entropy change is  $\Delta S_{298}^0 = -74.87 \text{ cal deg}^{-1}$ .

The preceding calculations show that the entropy change of the system on oxidation is negative but the reaction is still spontaneous. Now, the entropy change undergone by the surroundings during this oxidation can be calculated as follows. As a result of the oxidation of 2 gm atoms of aluminium, 400,000 cal of heat are given out to the surroundings by the system. Although this heat is given out irreversibly, it can be considered that this heat is absorbed by the surroundings reversibly, the heat capacity of the surroundings being infinitely large. Hence, the entropy change of the surroundings is equal to  $-\Delta H_{\text{system}}/T$ . Thus, the entropy change of the isolated system (system plus surroundings) is

$$\Delta S = \Delta S_{\text{system}} - \left( \frac{\Delta H_{\text{system}}}{T} \right). \quad (2.19)$$

From eq. (2.19), we deduce that if  $(\Delta S_{\text{system}}) - (\Delta H_{\text{system}}/T)$  is positive, the reaction is spontaneous, as stipulated by the second law of thermodynamics. The advantage of this criterion is that both  $\Delta S$  and  $\Delta H$  refer to the system under study and not to the surroundings. Since  $T$  is always positive, this criterion can also be written as follows.  $(\Delta H - T\Delta S)_{\text{system}}$  must be negative for all spontaneous processes because it ensures that the entropy of the isolated system increases. Therefore, each time a spontaneous reaction occurs,  $(\Delta H - T\Delta S)_{\text{system}}$  must be negative or less than zero. Similarly, for a reversible process or equilibrium process,  $(\Delta H - T\Delta S)_{\text{system}}$  is zero. For an impossible process,  $(\Delta H - T\Delta S)_{\text{system}}$  is greater than zero. The driving force for all chemical reactions can be expressed in terms of  $(\Delta H - T\Delta S)$  of the system. Since the expression

$(\Delta H - T\Delta S)$  has the dimensions of energy, it is convenient to define a new function called free energy  $G$  of the system given by

$$G = H - TS, \quad (2.20)$$

$$G = E + Pv - TS. \quad (2.21)$$

Also,

$$\Delta G = \Delta H - T\Delta S. \quad (2.22)$$

For spontaneous processes,  $\Delta G$  must be negative. So, as can be seen from eq. (2.22), the tendency of natural processes to occur is governed by two main directive influences which determine the state of an equilibrium system. One is the ordering influence which tends to minimize the potential energy. The other is the disordering influence which tends to maximize the entropy. At very low temperatures, the former is important, but, as the temperature increases, the latter becomes more important, and at high temperatures, the tendency towards disorder is supreme. At intermediate temperatures, there is an interplay between these opposing tendencies. The free energy  $G$ , as defined in eq. (2.20), tends to strike a balance between these influences. The loss of free energy  $-\Delta G$  measures the thermodynamic tendency of the process to occur. So,  $G$  can be viewed as the available energy,  $H$  as the total energy, and  $TS$  as the unavailable energy.

The driving force for all chemical reactions can now be expressed in terms of change in the free energy  $G$  of the system. In the example on the oxidation of aluminium given earlier,  $\Delta S = -74.87 \text{ cal deg}^{-1}$ ,  $\Delta H = -400,000 \text{ cal}$ , and  $\Delta G = -400,000 - (298 \times -74.87) = -377,689 \text{ cal}$ . Since  $\Delta G$  is negative, the oxidation is thermodynamically spontaneous. However, kinetic factors can still act as a barrier to this spontaneous oxidation, as explained in Section 2.15.

#### 2.5 VARIATION OF FREE ENERGY WITH PRESSURE AND TEMPERATURE

By definition,

$$G = E + Pv - TS.$$

Therefore,

$$dG = dE + P dv + v dp - T dS - S dT. \quad (2.23)$$

From the first law of thermodynamics, for a closed system at equilibrium, and in the absence of all other work except the work of expansion,

$$\begin{aligned} dE &= q_{\text{rev}} - P dv \\ &= T dS - P dv. \end{aligned} \quad (2.24)$$

Combining eqs. (2.23) and (2.24), we get

$$dG = v dp - S dT. \quad (2.25)$$

At constant temperature, the variation of  $G$  with pressure is given by

$$\left(\frac{\partial G}{\partial P}\right)_T = v. \quad (2.26)$$

At constant pressure, the variation of  $G$  with temperature is given by

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (2.27)$$

Also,

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \end{aligned} \quad (2.28)$$

This is the Gibbs-Helmholtz equation which can also be written as

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = -\frac{\Delta H}{T^2}, \quad (2.29)$$

$$\left[\frac{\partial(\Delta G/T)}{\partial(1/T)}\right]_P = \Delta H. \quad (2.30)$$

Since the free energy is related to enthalpy and entropy, the free energy changes of a reaction at a higher temperature ( $T_2$ ) can be expressed in terms of the enthalpy and entropy changes at a lower temperature ( $T_1$ ) as

$$\begin{aligned} \Delta G_{T_2} &= \Delta H_{T_1} - T_2 \Delta S_{T_1} \\ &= \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT - T_2 (\Delta S_{T_1} + \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT). \end{aligned} \quad (2.31)$$

Equation (2.31) is valid as long as either the reactants or the products do not undergo any phase transformation in the temperature range  $T_1-T_2$ .

#### FREE ENERGY CRITERION FOR EQUILIBRIUM AND SPONTANEOUS PROCESSES

The free energy criterion for spontaneous processes is a convenient one because any process for which  $\Delta G < 0$  is theoretically possible, and  $\Delta G$  is equal to zero for equilibrium.

#### SIGNIFICANCE OF EQUILIBRIUM

The two main factors that govern a chemical reaction are thermochemistry and kinetics. The former decides the final equilibrium under a given set of conditions, and the latter the rate at which a reaction proceeds towards equilibrium. The conditions of equilibrium determine the limits within which metallurgical processes can take place. It is obvious that no reversible reaction can proceed beyond equilibrium. Therefore, to determine whether a reaction takes place completely, we have to understand the factors that control equilibrium. Hence, process metallurgists have devoted much attention to the study of equilibrium.

#### 2.6 STANDARD FREE ENERGY AND EQUILIBRIUM CONSTANT

As in the cases of internal energy and enthalpy, there is no method of determining the absolute value of free energy. But this is not important, because, for most purposes, what we need to know are the values of the free energy changes from one state to another, preferably from a standard

or reference state. The standard or reference state taken is the most stable form of the pure substance at 1 atm and at the temperature under consideration. The standard free energy change  $\Delta G^\circ$  of a reaction is the free energy change when all the reactants and all the products are in their standard states. The free energies of all elements in their standard states are assumed to be zero at all temperatures. Thus, the standard free energy of a compound is equal to the standard free energy of formation.

The relationship between the standard free energy change of a reaction at a given temperature and its equilibrium constant at that temperature can be derived as follows. Consider a chemical reaction at a constant temperature and pressure:



The letters  $a$ ,  $b$ ,  $c$ , and  $d$  denote the number of atoms of the chemical elements or species A, B, C, and D, respectively, taking part in the reaction.

Under experimental conditions, the free energy change  $\Delta G$  of reaction (2.32) is given by

$$\Delta G = cG_C + dG_D - (aG_A + bG_B). \quad (2.33)$$

The standard free energy change  $\Delta G^\circ$  of reaction (2.32) is given by

$$\Delta G^\circ = cG_C^\circ + dG_D^\circ - (aG_A^\circ + bG_B^\circ). \quad (2.34)$$

Hence,

$$\Delta G - \Delta G^\circ = c(G_C - G_C^\circ) + d(G_D - G_D^\circ) - a(G_A - G_A^\circ) - b(G_B - G_B^\circ).$$

The difference in free energy between the given state and the standard state is related to the thermodynamic activity (see Section 2.10). For example,

$$G_A - G_A^\circ = RT \ln a_A.$$

Therefore,

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C^\circ \cdot a_D^\circ}{a_A^\circ \cdot a_B^\circ}, \quad (2.35)$$

where  $a_i$  is the activity of species  $i$ . Here, the activities of A, B, C, and D are under the experimental conditions represented by reaction (2.32) and are in relation to the same standard state as in this reaction. If the actual activities of the reactants and the products are known under the experimental conditions, then, with the help of eq. (2.35), we can calculate the driving force  $\Delta G$  of the forward reaction (2.32), provided  $\Delta G^\circ$  is known. Reaction (2.32) proceeds until equilibrium is attained. Under the equilibrium condition,  $\Delta G = 0$ , and the activity product on the right-hand side of eq. (2.35) becomes equal to the thermodynamic equilibrium constant  $K$ . The activities then refer to the value at equilibrium, that is,

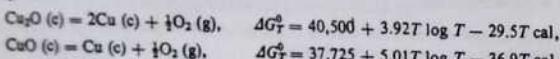
$$\begin{aligned} \Delta G^\circ &= -RT \ln \frac{a_C^\circ \cdot a_D^\circ}{a_A^\circ \cdot a_B^\circ} \\ &= -RT \ln K. \end{aligned} \quad (2.36)$$

Equation (2.37) gives the relationship between the standard free energy change  $\Delta G^\circ$  and the equilibrium constant  $K$ , and is one of the most important equations used in chemical equilibria

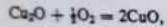
calculations. If the standard free energy change,  $\Delta G^\circ$ , of a reaction is negative at a given temperature, it indicates that the forward reaction is spontaneous, provided the reactants and the products are in their standard states at unit activity; also,  $K$  will have a value that favours the forward reaction. The more negative the value of  $\Delta G^\circ$ , the greater the value of  $K$ . Large positive values of  $\Delta G^\circ$  correspond to small values of  $K$ , indicating that the equilibrium favours the backward reaction. Equation (2.37) is remarkable, because, by knowing the standard free energy change, we can estimate the extent of reaction under equilibrium conditions.

We now give examples to illustrate the use of free energy data.

**Example 1** The standard free energies of formation of cuprous oxide and cupric oxide are given by the equations



To determine which oxide is formed when oxygen at 20 mm Hg pressure is passed over pure copper at 900°C, the given data can be used. The standard free energy change for the reaction



using the foregoing data, is

$$\Delta G_T^\circ = -34,950 - 6.17 \log T + 44.3T = -4948 \text{ cal at } 900^\circ\text{C}.$$

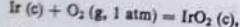
Therefore,  $-RT \ln K = -4948$ ,  $K = 8.356$ , where  $K$  is the equilibrium constant. Now  $K = 1/p_{\text{O}_2}^{1/2}$ , where  $p_{\text{O}_2}$  is the oxygen pressure in equilibrium with CuO and Cu<sub>2</sub>O at 900°C. The value of the activities in the condensed state is one (see Section 2.10). Therefore,  $p_{\text{O}_2} = 0.0143 \text{ atm} = 10.87 \text{ mm}$ . Since the oxygen is passed over copper at a pressure greater than 10.87 mm, the oxide formed is CuO.

**Example 2** The standard free energy change for the formation of iridium oxide is given by

$$\Delta G^\circ = -52,200 - 12.65T \log T + 77.25T \text{ cal}.$$

It is required to calculate the minimum temperature above which iridium oxide can be considered to decompose to the metal (a) in pure oxygen at 1 atm and (b) in air ( $p_{\text{O}_2} = 0.2 \text{ atm}$ ).

We have



$$\Delta G^\circ = -52,200 - 12.65T \log T + 77.25T.$$

(a) Iridium, iridium oxide, and oxygen at 1 atm will be in equilibrium when

$$\Delta G^\circ = -52,200 - 12.65T \log T + 77.25T = 0.$$

Solving for  $T$ , we get  $T = 1393 \text{ K}$ . Therefore, above 1393 K, the free energy change for the reaction is positive, and iridium oxide is unstable and decomposes. Below this temperature,  $\Delta G^\circ$  is negative and iridium oxide remains stable.

(b) Equation (2.35) can be used to calculate the free energy change  $\Delta G$  for the decomposition of iridium oxide in air. That is,

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{IrO}_2}}{a_{\text{Ir}} \cdot p_{\text{O}_2}},$$

where

$$a_{\text{IrO}_2} = 1, \quad a_{\text{Ir}} = 1, \quad p_{\text{O}_2} = 0.2.$$

At equilibrium,

$$\Delta G = -52,200 - 12.65T \log T + 77.25T + 4.575T \log 5 = 0.$$

Solving for  $T$ , we obtain  $T = 1267 \text{ K}$ . Therefore, above 1267 K, iridium oxide remains unstable in air.

## 2.7 COMPILATION OF FREE ENERGY DATA

The foregoing discussion shows that it is necessary for the process metallurgist to know the values of the standard free energy change of reactions and their variations with temperature. In thermodynamic tabulations, the standard free energy of formation of a compound from its elements is usually given as a function of temperature. It is derived from the results obtained by calorimetry, electrochemical measurements, the measurement of chemical equilibria, and also by spectroscopic measurements. The standard free energy change of a reaction involving many elements and compounds can then be obtained by suitable addition or subtraction according to Hess's law. The standard free energy changes of various reactions are available in standard reference books.

If  $\Delta G^\circ$  has not been tabulated for a particular reaction at a temperature  $T_2$ , it can be calculated from data available at a reference temperature  $T_1$  by using eq. (2.31). Thus,

$$\Delta G_{T_2}^\circ = \Delta H_{T_1}^\circ + \int_{T_1}^{T_2} \Delta C_p^\circ dT - T_2(\Delta S_{T_1}^\circ + \int_{T_1}^{T_2} \frac{\Delta C_p^\circ}{T} dT).$$

Therefore,

$$\Delta G_{T_2}^\circ = \Delta H_{T_1}^\circ + \int_{T_1}^{T_2} \Delta C_p^\circ dT - T_2(\Delta S_{T_1}^\circ + \int_{T_1}^{T_2} \frac{\Delta C_p^\circ}{T} dT). \quad (2.38)$$

The value of  $S_{T_1}^\circ$  can be obtained from the third law of thermodynamics, provided heat capacity data are available and assuming  $\Delta S_0^\circ$  to be zero at the absolute zero of temperature. Data on the heat of formation and heat capacity along with other thermodynamic data are given in the following standard publications:

O. Kubaschewski, E.L. Evans, and C.B. Alcock, Metallurgical Thermochemistry, Pergamon Press, Oxford, 1974.

National Bureau of Standards, JANAF Thermochemical Tables, Washington (1965). Bureau of Mines, Bulletin 605, Oregon, U.S.A. (1963).

J.F. Elliott and M. Gleiser, Thermochemistry for Steel Making, Vol. 1, Addison-Wesley, Reading, Mass. (1960).

A. Glassner, The Thermodynamic Properties of the Oxides, Fluorides and Chlorides up to 2500 K, Argonne National Laboratory, Argonne, Illinois.

I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, 1973; Supplement, 1977.

Free energy data are generally compiled using three convenient methods.

**Method 1**  
For accurate calculations, the variation of  $\Delta G^\circ$  (cal) with temperature can be represented by

$$\Delta G_T^\circ = A + BT \log T + CT, \quad (2.39)$$

where  $A$ ,  $B$ , and  $C$  are constants. Table 2.2 gives the values of the constants for a few typical reactions and also the temperature range over which the free energy data are valid.

Table 2.2 Standard Free Energy Changes for Some Reactions  
(Kubaschewski *et al.*, 1974)

Reaction	A	B	C	Temperature range (K)
$\text{Al}_2\text{O}_3(\text{c}) = 2\text{Al}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$	400,810	3.98	-87.64	298-925
$\text{C}(\text{c}) + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$	-94,200		-0.2	298-2000
$\text{C}(\text{c}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{CO}(\text{g})$	-26,700		-20.95	298-2500
$\text{CaCO}_3(\text{c}) = \text{CO}_2(\text{g}) + \text{CaO}(\text{c})$	40,250		-34.4	449-1150
$\text{MgCl}_2(\text{g}) = \text{Mg}(\text{g}) + \text{Cl}_2(\text{g})$	134,500	-2.29	-17.94	1691-2000
$2\text{Fe}(\text{c}) + \text{O}_2(\text{g}) + 2\text{TiO}_2(\text{c}) = 2\text{FeTiO}_3(\text{c})$	-129,200		+25.86	1173-1400

#### Method 2

Free energy data can be calculated using free energy functions. The relationship connecting free energy, enthalpy, and entropy can be written in the form

$$\frac{G_T^\circ - H_T^\circ}{T} = -S_T^\circ.$$

The free energy function (fef) is defined as

$$fef = \frac{G_T^\circ - H_{T_{ref}}^\circ}{T} = -S_T^\circ + \frac{H_T^\circ - H_{T_{ref}}^\circ}{T}, \quad (2.40)$$

where  $T_{ref}$  is the reference temperature, usually 298.15 K, and the superscript zero indicates the standard state. From eq. (2.40), it is evident that fef can be calculated from heat capacity data. We also have

$$\Delta fef = \frac{\Delta G_T^\circ - \Delta H_{T_{ref}}^\circ}{T}.$$

Since  $\Delta G_T^\circ = -RT \ln K$ , we have

$$-R \ln K = \frac{\Delta H_{T_{ref}}^\circ}{T} + \Delta fef. \quad (2.41)$$

Thus, by knowing the free energy function data and the standard heats of formation, we can calculate the equilibrium constant at any particular temperature. (The values of the free energy function and of the heats of formation, for various temperatures, can be obtained from reference books.)

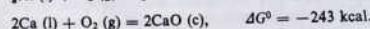
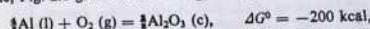
#### Method 3 (Ellingham Diagrams)

The simplest method of representing free energy data is to graphically plot  $\Delta G^\circ$  versus temperature for compounds such as oxides and sulphides. Such plots are named after Ellingham who originally drew them in 1944. Subsequently, they have been modified by others, notably by Richardson and Jeffes (1952) and Kellogg (1950, 1951).

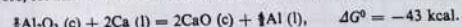
An accurate evaluation of  $\Delta G^\circ$  at a given temperature from  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and heat capacity data involves tedious work and, as already pointed out, the resulting expression for  $\Delta G^\circ$  is a complicated multitemperature function of temperature. Richardson and Jeffes (1952) have pointed out that the temperature variations in  $\Delta H^\circ$  and  $\Delta S^\circ$  tend to counterbalance one another, as shown in eq. (2.38). Therefore, it is possible to express  $\Delta G^\circ$  in the form of a simple equation

$$\Delta G^\circ = a - bT,$$

where  $a$  and  $b$  are mean values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the temperature range under consideration. The free energies of formation of a large number of compounds such as oxides and sulphides can now be represented in the form of linear plots without much loss of accuracy over wide ranges of temperature. The linear equation just given for  $\Delta G^\circ$  is the basis for the Ellingham diagrams shown in Fig. 2.1. For oxides, the free energy change  $\Delta G^\circ$ , when one mole of gaseous oxygen at 1 atm combines with a pure element to form an oxide, is plotted against temperature for various elements. Since all the curves are drawn with one mole of oxygen as the basis, it is possible to compare the relative reducing or oxidizing tendencies of oxides and elements. For example, Fig. 2.1 gives the free energy changes at 1000°C for the reactions



Therefore, for the reduction of alumina by calcium, we have



Since  $\Delta G^\circ$  is negative, calcium can reduce alumina at 1000°C to aluminium.

We may generalize that, in the Ellingham diagram, highly stable oxides are found at the bottom and the less stable oxides occupy higher positions. Therefore, an element occupying a lower position in the diagram can always reduce the oxide of another metal lying above it, when all the reactants and products are in their standard states.

In the regions, where phase transformation does not occur, for the reasons already mentioned, the plots are almost straight lines. Since  $d\Delta G^\circ/dT = -\Delta S^\circ$ , the slope of the line gives  $-\Delta S^\circ$  and the intercept of the line, extrapolated to absolute zero, gives  $\Delta H^\circ$  on the free energy axis. At the temperature of transformation of the metal or the oxide, the curves show a change of slope due to the changed value of  $\Delta S^\circ$ . An increase in the slope corresponds to the reactant undergoing phase transformation, whereas a decrease corresponds to the product undergoing phase transformation. It is evident that the change in slope is related to the entropy of transformation of the reactant or the product. A large change in slope suggests the transformation from a condensed

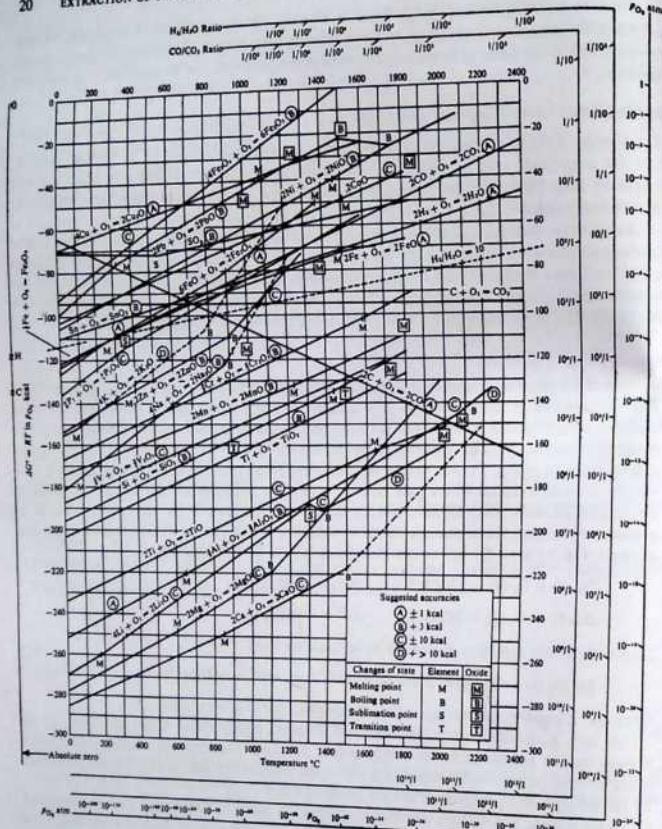
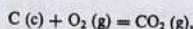


Fig. 2.1 Standard Free Energy Diagram for Oxides.

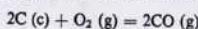
phase to a gaseous state, or vice versa, as a result of large entropy changes. A small change in slope is expected for a melting process or for a transformation from one solid phase to another.

Most lines in  $\Delta G^\circ$ -versus- $T$  plots are roughly parallel to each other, i.e., their slopes are almost the same. Hence, they indicate reactions in which the value of  $\Delta S^\circ$  remains the same as

long as both the metal and the oxide are condensed phases. The entropy decreases by about 45 cal gm mole<sup>-1</sup> K<sup>-1</sup> (henceforth called entropy units or e.u.), when the metal reacts with one mole of gaseous oxygen to form the solid oxide. This entropy decrease corresponds to the disappearance of 1 gm mole of gaseous material into the condensed state and explains why the lines should have the same slope. The line for CO<sub>2</sub> would be almost parallel to the temperature axis, indicating the value for  $\Delta S^\circ$  is almost zero. This is to be expected because, for the reaction



there is no change in the number of gas molecules and the entropy change ( $\Delta S = 0.7$  e.u.) is negligibly small. The upward slopes of most of the lines indicate that the oxides become less stable as the temperature increases. The line for the reaction

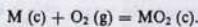


is extremely important. It has a downward slope cutting across the free energy diagram. The slope indicates that  $\Delta S$  has a positive value of about 43 e.u. in conformity with the generation of 1 gm mole of gaseous material from the condensed phase. This is in agreement with the fact that, in the presence of carbon, carbon monoxide becomes more stable as the temperature increases. The downward slope also explains why carbon can reduce any metal oxide to the metal, provided the temperature is high enough. Consequently, carbon is commonly used as a reducing agent in pyrometallurgical processes. On the other hand, the upward slope of the free energy line for H<sub>2</sub>O explains why H<sub>2</sub> is a poor reducing agent at high temperatures. We now discuss some uses of the Ellingham diagrams.

#### Calculation of oxygen pressures in equilibrium with a metal and its oxide at a given temperature

The standard dissociation temperature of an oxide is the temperature at which the oxide is in equilibrium with the element and oxygen gas at 1 atm. At this temperature,  $\Delta G^\circ = 0$ . When a metal oxide is heated to this temperature, it dissociates to give the metal.

Consider the formation of a metal oxide MO from a metal M and 1 gm mole of oxygen, both the metal and oxide being in the condensed state. The reaction is



The equilibrium constant  $K$  is given by

$$K = \frac{a_{MO_2}}{a_M \cdot a_{O_2}}. \quad (2.42)$$

The activities of M and MO<sub>2</sub> are equal to one (see Section 2.10) and the activity of oxygen is taken to be its partial pressure, assuming ideal behaviour of the gas. Therefore,

$$K = \frac{1}{P_{O_2}}, \quad (2.43)$$

$$\Delta G^\circ = -RT \ln K = RT \ln P_{O_2}. \quad (2.44)$$

$RT \ln P_{O_2}$  is sometimes referred to as the oxygen potential of the oxide-metal system. The more negative this potential, the more tightly is oxygen bound to the metal and oxygen moves from other less tightly bound systems to this one. For example, at 800°C,  $\Delta G^\circ$  for the formation of

nickel oxide is approximately  $-69$  kcal, as read off from Fig. 2.1. Using eq. (2.44), we calculate the oxygen pressure in equilibrium with nickel and nickel oxide as approximately  $10^{-14}$  atm. This value can be also read off from the oxygen scale on the extreme right of Fig. 2.1 as now explained.

#### Use of oxygen scale

The point at the upper left-hand corner of Fig. 2.1 corresponding to  $-273^\circ\text{C}$  and  $0$  kcal is marked  $O$ . The imaginary lines radiating from  $O$  and passing through the points marked on the  $p_{\text{O}_2}$  scale represent the free energy change that results when  $1$  gm mole of oxygen expands from  $1$  atm to the pressure indicated on the oxygen scale. For instance, each point on the line connecting  $O$  and the point marked  $10^{-14}$  on the oxygen scale, at different temperatures, gives the free energy change for the process, i.e.,



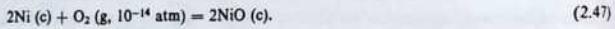
Also,

$$\Delta G_T = RT \ln p_{\text{O}_2}$$

The imaginary line—a plot of  $\Delta G$  versus  $T$  for a constant pressure of  $10^{-14}$  atm—cuts the free energy line for the reaction



at  $800^\circ\text{C}$ ;  $\Delta G^0$  for reaction (2.46) at  $800^\circ\text{C}$  is approximately  $-69$  kcal. Therefore,  $\Delta G = 0$  for the reaction

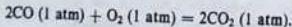


The metal and oxide are therefore in equilibrium at an oxygen pressure of  $10^{-14}$  atm.

From the foregoing discussion, we see that the oxygen pressure in equilibrium with a metal and its oxide at any particular temperature can be read off, using the point  $O$  and the graduations on the oxygen scale. If the line radiating from  $O$  and passing through the point under consideration on the free energy line at the desired temperature cuts the oxygen scale in between two graduations on the scale, the oxygen pressure should be read by logarithmic interpolation between the graduations.

#### Use of CO/CO<sub>2</sub> scale

Consider the line drawn for the reaction



The equilibrium constant  $K$  for this reaction is given by

$$K = \left( \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \right)^2 \cdot \frac{1}{p_{\text{O}_2}} \quad (2.48)$$

Since both CO and CO<sub>2</sub> are gases,  $\Delta G^0$  for the foregoing reaction does not directly give the equilibrium  $p_{\text{O}_2}$  as in the case of those reactions in which the metal and oxide are at unit activity, both being in the condensed state. From eq. (2.48), it is seen that at a given temperature, a definite CO/CO<sub>2</sub> ratio corresponds to a fixed oxygen pressure in equilibrium with a metal and

its oxide in the condensed state. Since a CO-CO<sub>2</sub> gas mixture is frequently used for reducing metal oxides, the common practice is to link the equilibrium  $p_{\text{O}_2}$  with the associated CO/CO<sub>2</sub> ratio. If this ratio is higher than the equilibrium value, the metal oxide is reduced and, if lower, the metal is oxidized. The CO/CO<sub>2</sub> ratio in a gas, in equilibrium with a metal and its oxide in the condensed state can be directly read off from the CO/CO<sub>2</sub> scale in Fig. 2.1.

The line drawn for CO<sub>2</sub> represents the free energy of formation,  $\Delta G^0$ , of  $2$  moles of CO<sub>2</sub> from  $2$  moles of CO and  $1$  mole of O<sub>2</sub>; all three being at  $1$  atm. As pointed out under Method 3, such a plot would be linear because  $\Delta H^0$  and  $\Delta S^0$  are constants in the temperature range considered. In Fig. 2.1, the line cuts the  $\Delta G^0$  axis at  $-273^\circ\text{C}$  at the point  $C$ . This line is redrawn in Fig. 2.2

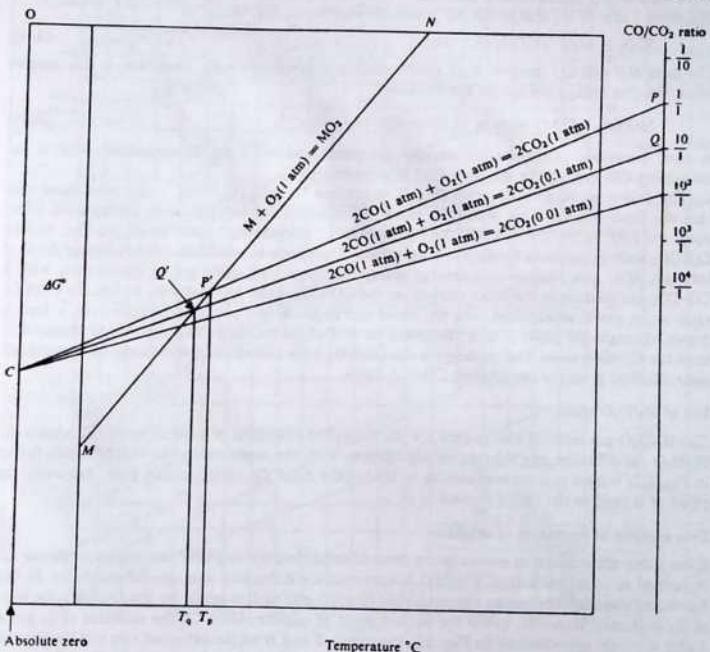
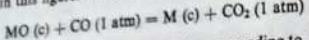


Fig. 2.2 CO/CO<sub>2</sub> Scale.

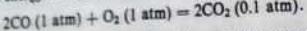
as  $CP$ , where  $P$  is the point  $1/1$  on the CO/CO<sub>2</sub> scale. A typical line  $MN$  that gives the free energy of formation of a metal oxide MO<sub>2</sub>(c) from a metal M(c) and oxygen (1 atm) is also

At the point  $P'$ , where  $MN$  and  $CP$  intersect,  $\Delta G^\circ$  for the reaction shown in this figure. At the point  $P'$ , where  $MN$  and  $CP$  intersect,  $\Delta G^\circ$  for the reaction

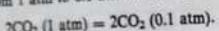
(2.49)



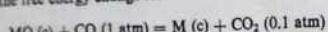
is zero. Therefore, at temperature  $T_p$  (corresponding to  $P'$ ), the metal and its oxide are in equilibrium with a gas phase containing  $CO$  and  $CO_2$  in the ratio 1/1. The line  $CQ$  (Fig. 2.2) represents the free energy change for the formation of  $CO_2$  at 0.1 atm, i.e.,



Now, the line  $CQ$  is obtained by adding the free energy change for the expansion of 2 moles of  $CO_2$  from 1 atm to 0.1 atm to the  $\Delta G^\circ$  value for reaction (2.49), i.e.,



The lines  $MN$  and  $CQ$  intersect at  $Q'$  corresponding to temperature  $T_q$ . Therefore, at this temperature, the free energy change for the reaction



is zero. From eq. (2.51), we deduce that the metal and oxide are in equilibrium with a gas containing  $CO$  and  $CO_2$  in the ratio 10/1 at temperature  $T_q$ .

The points on the  $CO/CO_2$  scale (Fig. 2.2), marked  $10/1, 10^2/1, 10^3/1, \dots$  are positioned such that the lines joining them with  $C$  lie below the standard free energy line by amounts  $\Delta G$  being equal to  $2RT \ln 10, 2RT \ln 100, 2RT \ln 1000, \dots$  respectively. Each point marked on the  $CO/CO_2$  scale is obtained by similar calculations. The points at which the lines radiating from  $C$  intersect  $MN$ , give the temperatures at which the metal and oxide are in equilibrium with a  $CO-CO_2$  gas mixture in the ratio marked on the  $CO/CO_2$  scale. Alternatively, to find the  $CO/CO_2$  ratio in the gas in equilibrium with the metal and its oxide at a particular temperature, a line is drawn through the point  $C$  and the point on  $MN$  at the required temperature and extended to meet the  $CO/CO_2$  scale. The reading on the  $CO/CO_2$  scale (obtained, if necessary, by logarithmic interpolation) gives the equilibrium  $CO/CO_2$  ratio.

#### Use of $H_2-H_2O$ scale

The  $H_2-H_2O$  gas mixture also is used for the controlled reduction of a metal oxide. To obtain the  $H_2-H_2O$  ratio in the gas mixture in equilibrium with the metal oxide, the  $H_2-H_2O$  scale (given in Fig. 2.1) is used in a manner similar to that of the  $CO/CO_2$  scale. In this case, however, the point  $H$  is used as the origin instead of  $C$ .

#### Free energies of formation of sulphides

Since many metals exist in nature in the form of sulphides, the sulphide free energy diagrams are important in metal extraction. Figure 2.3 represents the Ellingham diagram for sulphides. In this figure, the standard free energy change for the formation of each sulphide by consuming 1 gm mole of  $S_2$  is shown. However, below the boiling point of sulphur (444.6°C), the existence of  $S_2$  gas at 1 atm is purely hypothetical. In Fig. 2.3, the points  $S$  and  $H$  on the left-hand side and the gradations on the right-hand side can be used to calculate the sulphur pressure and the  $H_2S/H_2$  ratio of the gas mixture in equilibrium with the metal and its sulphide. (The method is similar to that described for an oxide.) Further, the position of the line for the reaction  $2Ca + S_2 = 2CaS$  (at the bottom of Fig. 2.3) shows that calcium sulphide is highly stable. Therefore, calcium's marked affinity for sulphur makes it an effective desulphurizer. Hydrogen cannot be a very efficient reducing

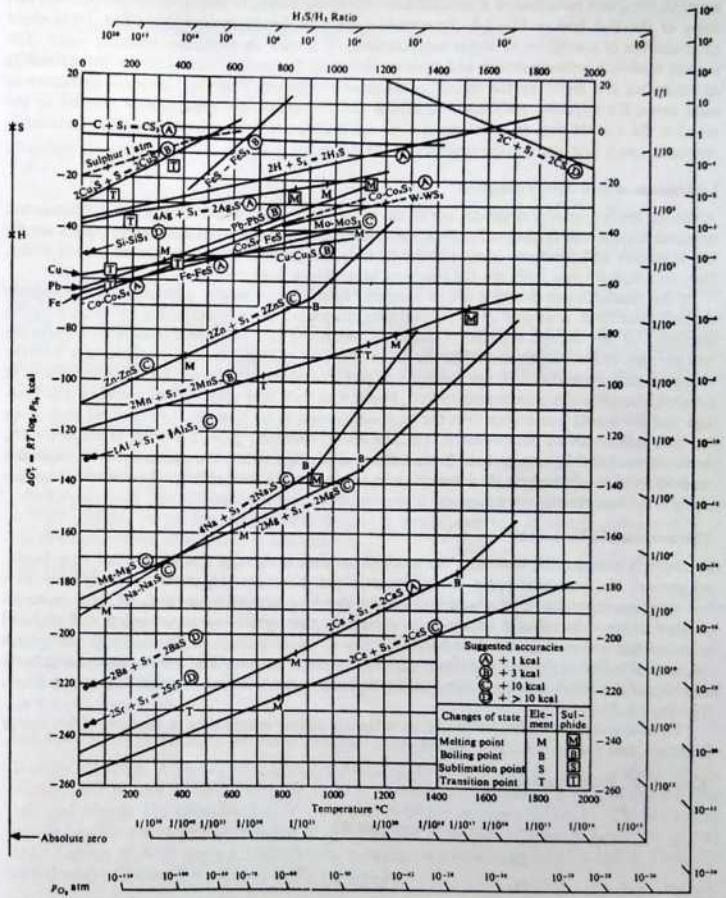


Fig. 2.3 Free Energy Diagram for Metal Sulphides.

agent in the direct reduction of a metallic sulphide to the metal, as indicated by the position and slope of the  $H_2S$  line in Fig. 2.3. Since carbon has no sulphide analogous to CO to bring about the reduction of a sulphide at higher temperatures, it is also an inefficient reducing agent. The mutual solubility between metals and their sulphides, in the molten state adds to the difficulties of extracting the metal by the direct reduction of a sulphide. Therefore, for metal extraction in some cases, the sulphides are roasted to oxides and the oxides are subsequently reduced to the metal in the normal way. In other cases, a special smelting technique known as matte smelting is resorted to as a first step for the recovery of the metal.

#### Limitations of free energy diagrams

Although the free energy diagrams are useful in estimating the theoretical minimum temperature required for reduction, they suffer from certain severe limitations. The free energy values are for the reactants and products when present in their standard state, i.e., pure substances at 1 atm. Only in relatively rare cases are the reactants present in a pure state.

If the reactants and products are in solution, then experimentally measured thermodynamic activity data (not available in the Ellingham diagrams) are a prerequisite for estimating the feasibility of the desired reaction. Compound formation in a solution considerably reduces the free energies of the constituents. The reactions given in the free energy diagrams are between stoichiometric proportions of the elements to give stoichiometric compounds. The composition of nonstoichiometric compounds such as  $FeO$ ,  $Fe_2O_3$ , and  $TiO_2$  may vary with temperature and pressure and the actual free energy lines for such compounds differ from the hypothetical lines given for their stoichiometric compositions. The free energy diagrams give no account of reaction rates, which are essential for any process. Temperatures much higher than the thermodynamic minimum read off from the Ellingham diagrams may be needed for a reasonably good reaction rate, especially if the temperatures are low.

#### Thermochemical Data Bank

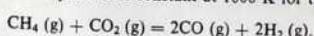
A relatively new method of storing thermochemical data is through thermochemical data banks. At present, the computer-based thermodynamic data bank not only stores thermodynamic data but organizes them into a structural body which can be consulted to get updated data or manipulated to provide reliable solutions to problems that practising metallurgists and material scientists encounter. A computer is handy for this purpose because of its ability to store large amounts of mixed alphabetic and numerical data, to scan them rapidly, and to perform accurately complex arithmetical operations. One such data bank is the National Physical Laboratory Bank, Teddington, England.

We now give a few examples to illustrate the use of free energy data in the form of free energy functions, free energy equations, and plots.

**Example 1** From the data

	$\Delta f_{\text{ref}}^{\circ}$ at 1000 K (cal/mole/K)	$H_{\text{ref}}^{\circ}$ (kcal/mole)
CO	-48.77	-27.202
$H_2$	-32.74	0
$CH_4$	-47.65	-15.99
$CO_2$	-54.11	-93.969

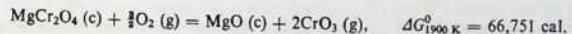
calculate the equilibrium constant at 1000 K for the reaction



[Hint

$$\frac{\Delta G^{\circ}}{T} = -R \ln K = \frac{\Delta H_{\text{ref}}^{\circ}}{T} + \Delta f_{\text{ref}}^{\circ} \quad [1]$$

**Example 2** Can a chrome magnesite refractory be used in an oxidizing atmosphere at 1900 K?  
[Hint



In an atmosphere of almost pure oxygen,  $p_{CrO_3}$  is more than 0.1 mm Hg and deterioration can occur.]

**Example 3** Manganese oxide ( $MnO$ ) dissolved in a liquid silicate slag at 1600°C at a concentration of 10 wt % has an activity of 0.04 relative to pure  $MnO$ . What is the highest value of  $p_{O_2}$  below which  $MnO$  in the slag gets reduced to free manganese metal? What is the corresponding value of  $p_{O_2}$  if the reduced manganese forms an alloy with iron at an activity of 0.04 relative to pure manganese metal? To what  $CO/CO_2$  ratio does the  $p_{O_2}$  value correspond in both cases? (All data can be obtained from Fig. 2.1.)

#### 2.8 THERMODYNAMICS OF SOLUTIONS

The extraction metallurgist is concerned with molten metal and slag systems, the latter being composed mainly of oxides. Both these molten phases play an important role in extraction and refining processes. The driving force for the movement of chemical elements from one phase to another depends on the free energy difference in the two phases, so a thorough understanding of the thermodynamics of solutions is essential.

#### SOLUTION

A solution is any single homogeneous phase that contains more than one component, and may be gaseous, liquid, or solid. When two components are mixed to form a binary solution, a free energy change results, and the free energy of each component in the solution is different from that of the pure substance. One of the important problems in the theory of solutions is to understand how properties such as free energy, entropy, and enthalpy depend on the concentration of the various components.

#### PARTIAL AND INTEGRAL MOLAR PROPERTIES

Consider a solution consisting of  $n_A$  moles of A and  $n_B$  moles of B. Let  $V'$  be the volume of this solution. We assume  $V'$  to be so large that the addition of one mole of A or B to this solution does not change the concentration of the solution to any appreciable extent. The change in volume brought about by the addition of one mole of A to this solution is called the partial molar volume of A at a given temperature, pressure, and concentration of A and B. Thus, the partial molar volume of A denoted by  $\bar{V}_A$  is given by

$$\bar{V}_A = \left( \frac{\partial V'}{\partial n_A} \right)_{T, P, n_B} \quad (2.52)$$

Similarly,

$$\bar{V}_B = \left( \frac{\partial V'}{\partial n_B} \right) T, P, n_A \quad (2.53)$$

According to this definition of partial molar volume, if  $d n_A$  moles of A and  $d n_B$  moles of B are added to the solution, then the change in volume  $dV$  is given by

$$dV = \left( \frac{\partial V'}{\partial n_A} \right) d n_A + \left( \frac{\partial V'}{\partial n_B} \right) d n_B, \quad (2.54)$$

i.e.,

$$dV = \bar{V}_A \cdot d n_A + \bar{V}_B \cdot d n_B. \quad (2.55)$$

By integrating eq. (2.58) under conditions of constant composition such that  $\bar{V}_A$  and  $\bar{V}_B$  are constants, we obtain the equation for the volume  $V'$  of the solution containing  $n_A$  moles of A and  $n_B$  moles of B as

$$V' = \bar{V}_A \cdot n_A + \bar{V}_B \cdot n_B. \quad (2.56)$$

If  $V$  is the volume of 1 gm mole of the solution of A and B, then

$$V = \frac{V'}{n_A + n_B} = \bar{V}_A X_A + \bar{V}_B X_B. \quad (2.57)$$

where  $X_A$  and  $X_B$  are the atom fractions of A and B, respectively, and  $V$  is known as the integral molar volume of the solution.

For a multicomponent solution containing  $n_1$  moles of component 1,  $n_2$  moles of component 2,  $n_3$  moles of component 3, ...,  $n_n$  moles of component  $n$ , the value of the total property  $G'$ , taking free energy as an example, is given by

$$G' = n_1 \bar{G}_1 + n_2 \bar{G}_2 + n_3 \bar{G}_3 + \dots + n_n \bar{G}_n. \quad (2.58)$$

Dividing both sides by the total number of moles, the integral molar free energy  $G$  is given by

$$G = X_1 \bar{G}_1 + X_2 \bar{G}_2 + X_3 \bar{G}_3 + \dots + X_n \bar{G}_n, \quad (2.59)$$

where  $X_1, X_2, X_3, \dots, X_n$  are mole fractions of 1, 2, 3, ...,  $n$  and  $\bar{G}_1, \bar{G}_2, \bar{G}_3, \dots, \bar{G}_n$  the partial molar free energies. We see that the total property ( $G'$ ) is an extensive property that depends on the number of moles present in the solution whereas the partial molar free energy ( $\bar{G}$ ) is an intensive property and is a function of the composition of the solution.

#### INTEGRAL AND PARTIAL MOLAR FUNCTIONS OF MIXING

Consider the formation of 1 gm mole of a solution AB by mixing  $n_A$  moles of A and  $n_B$  moles of B. Let  $X_A$  and  $X_B$  be the atom fractions of A and B, respectively, given by

$$X_A = \frac{n_A}{n_A + n_B}, \quad X_B = \frac{n_B}{n_A + n_B}.$$

The mixing process when one mole of alloy is formed can be represented by

$$X_A \cdot A + X_B \cdot B = AB_{\text{solution}}$$

Taking free energy of mixing ( $\Delta G_M$ ) as an example, the change in the thermodynamic property brought about by this mixing process in the formation of 1 gm mole of the solution is given by the expression

$$\begin{aligned} \Delta G_M &= G_{AB} - (X_A G_A^0 + X_B G_B^0) \\ &= X_A \bar{G}_A + X_B \bar{G}_B - (X_A G_A^0 + X_B G_B^0) \\ &= X_A (\bar{G}_A - G_A^0) + X_B (\bar{G}_B - G_B^0) \\ &= X_A \Delta \bar{G}_A + X_B \Delta \bar{G}_B. \end{aligned} \quad (2.60)$$

Here,  $\Delta G_M$  is the integral molar free energy of mixing,  $\bar{G}_A$  and  $\bar{G}_B$  are the partial molar properties of A and B, respectively, and  $G_A^0$  and  $G_B^0$  the molar free energies of A and B in their pure states, respectively. In general, for a solution containing several components, namely, 1, 2, 3, ...,  $n$ ,

$$\Delta G_M = X_1 \Delta \bar{G}_1 + X_2 \Delta \bar{G}_2 + X_3 \Delta \bar{G}_3 + \dots + X_n \Delta \bar{G}_n. \quad (2.61)$$

Using either eq. (2.60) or eq. (2.61), we can calculate the integral molar properties of a solution if the partial molar properties are known.

#### 2.9 GIBBS-DUHEM EQUATION

Equation (2.58) has been obtained on the assumption that  $G'$  is an extensive property. Subjecting  $G'$  to complete differentiation at a constant temperature and pressure, we have

$$dG' = n_1 d\bar{G}_1 + n_2 d\bar{G}_2 + \dots + \bar{G}_1 dn_1 + \bar{G}_2 dn_2. \quad (2.62)$$

At a constant temperature and pressure,  $G'$  is a function of  $n_1, n_2, n_3, \dots$ . Hence,  $dG'$  is also given by [see eq. (2.55)]

$$dG' = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \bar{G}_3 dn_3 + \dots + \bar{G}_n dn_n. \quad (2.63)$$

Subtracting eq. (2.63) from eq. (2.62), we get

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 + n_3 d\bar{G}_3 + \dots + n_n d\bar{G}_n = 0. \quad (2.64)$$

Dividing both sides of eq. (2.64) by the total number of moles, we obtain

$$X_1 d\bar{G}_1 + X_2 d\bar{G}_2 + X_3 d\bar{G}_3 + \dots + X_n d\bar{G}_n = 0. \quad (2.65)$$

Equations (2.64) and (2.65) are different forms of the Gibbs-Duhem equation which is important in the thermodynamics of solutions because, by using it, we can evaluate the partial molar property of a particular component if the partial molar properties of the other components in the solution are known. For example, for a binary solution of A and B, it follows from eq. (2.65) that

$$\bar{G}_A = - \int \frac{X_B}{X_A} d\bar{G}_B. \quad (2.66)$$

Thus, by knowing the partial molar free energy of B over a range of composition of the solution, we can evaluate  $\bar{G}_A$  from the relationship (2.66). The integral property is then calculated from the equation

$$G = X_A \bar{G}_A + X_B \bar{G}_B.$$

### TANGENT INTERCEPT METHOD FOR OBTAINING PARTIAL MOLAR PROPERTY

For a multicomponent solution having the elements 1, 2, 3, ..., we can show that

$$(2.67)$$

$$G_i = G + (1 - X_i) \left( \frac{\partial G}{\partial X_i} \right)_{X_1, X_2, \dots, X_n}$$

Therefore, for a binary solution of A and B, we have

$$(2.68)$$

$$G_A = G + (1 - X_A) \left( \frac{\partial G}{\partial X_A} \right)$$

From eq. (2.68), we can calculate  $\bar{G}_A$  and  $\bar{G}_B$  if  $G$  is known. For this, we use the tangent intercept method which is a graphical method of evaluating the partial molar properties from the integral method. As depicted in Fig. 2.4, the integral molar property is plotted as a function of molar properties. The intercepts of the tangents drawn at the point  $P$  on the free energy curve give the  $X_A$  or  $X_B$ . The intercepts of the tangents drawn at the point  $P$  on the free energy curve give the partial molar properties  $\bar{G}_A$  and  $\bar{G}_B$  corresponding to the composition represented by the point  $P$ .

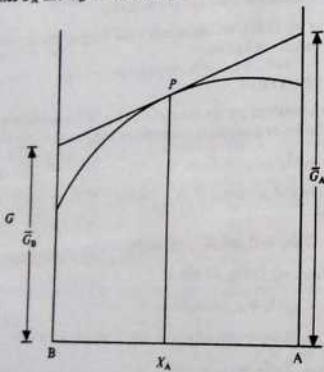


Fig. 2.4 Intercept Method for Obtaining  $\bar{G}_B$  and  $\bar{G}_A$  from  $G$ .

By applying the methods just outlined, we can determine  $\bar{G}_A$  and  $\bar{G}_B$  from  $G$ . Equation (2.59) permits the calculation of  $G$  from  $\bar{G}_A$  and  $\bar{G}_B$ . The reader should bear in mind that eqs. (2.58)-(2.68) are also valid for other thermodynamic properties such as enthalpy and entropy.

#### PARTIAL MOLAR FREE ENERGY: CHEMICAL POTENTIAL

The partial molar free energy of an element A in solution is the same as its chemical potential  $\mu_A$ , i.e.,

$$\left( \frac{\partial G}{\partial n_A} \right)_{T, P, n_B} = \bar{G}_A = \mu_A$$

$$(2.69)$$

The partial molar free energy of an element (or its chemical potential) is the free energy of the element in solution. (It should be noted that the chemical potential of a *pure* element can be equated to its molar free energy.) In our discussion, 'chemical potential' is used in a manner analogous to the gravitational potential and electric potential. To exemplify, a body falls from a high to low gravitational potential region, and the electrical potential difference gives the direction and intensity with which electrons tend to go into motion. Similarly, the chemical potential  $\mu$  of a particular element in two states decides the direction and tendency for the element to go into motion. An element moves from a high to a low chemical potential state according to the criterion that in all spontaneous processes the free energy change in the system is negative. As in the case of free energy and enthalpy, the absolute value of partial molar free energy cannot be determined. It is, therefore, expressed in terms of a difference between the value for a particular state and that for the standard state. For a binary solution of A and B, such a difference is given by

$$\Delta G_A = \bar{G}_A - G_A^0$$

In this equation, the superscript zero indicates the standard state, which is usually the most stable form of the pure element at 1 atm and at the temperature under consideration. It should be noted that  $G_A^0$  is the same as  $\mu_A^0$ , the chemical potential of A in the standard state.

#### 2.10 ACTIVITY

The activity  $a_A$  of the component A in solution is defined as

$$a_A = \frac{p_A}{p_A^0}, \quad (2.70)$$

where  $p_A$  is the partial pressure of A in the vapour in equilibrium with A in the solution and  $p_A^0$  is the vapour pressure of A in the vapour in equilibrium with A in the standard state. In a more rigorous treatment than the present one, the vapour pressures used in eq. (2.70) would be the corrected vapour pressures or fugacities.

The relationship between the activity of A in solution and the chemical potential is given by

$$\mu_A - \mu_A^0 = RT \ln \frac{p_A}{p_A^0} = RT \ln a_A, \quad (2.71)$$

i.e.,

$$G_A - G_A^0 = \Delta G_A = RT \ln a_A.$$

It is evident that the activity of any element in the standard state is always equal to one and that in the given state depends on the chosen standard state. The effect of external pressure on the vapour pressure of a pure element or compound in the solid or liquid state is negligible at a given temperature. Hence, the activity of a pure element or compound in the condensed state is taken as one.

#### IDEAL SOLUTIONS

When the components of an ideal solution are mixed, no heat of mixing results, nor is there any change in the volume. The partial pressure of each component obeys Raoult's law expressed as

$$X_n = \frac{p_n}{p_n^0},$$

where  $X_n$  is the mole fraction of  $n$ ,  $p_n$  the partial vapour pressure of the component  $n$  over the solution, and  $p_n^0$  the vapour pressure of the pure component  $n$ . If the pure component is taken as the standard state, then, for an ideal solution, we have

(2.72)

$a_n = X_n$ .

The activity in an ideal solution, at all temperatures, is always equal to the mole fraction. From eq. (2.72), it follows that the partial heats and volumes must also be zero. Now, we know that

$dG_n = dH_n - TdS_n$ .

For an ideal solution,

$$dS_n = -\frac{dG_n}{T} = \frac{RT \ln a_n}{T} = -R \ln X_n$$

It follows that

$$dS_M = -R(X_1 \ln X_1 + X_2 \ln X_2 + \dots + X_n \ln X_n)$$

(2.73)

Equation (2.73) is the expression for  $dS_M$  (integral molar entropy of mixing) which can be derived from statistical mechanics for a solution whose components are mixed completely at random. Since the enthalpy of mixing is zero, no interaction between the component species, both like and unlike is expected, and hence a random mixing is possible.

#### NONIDEAL SOLUTIONS

In reality, very few solutions behave ideally; most solutions exhibit a departure from ideal behaviour on account of the attractive or repulsive interactions between unlike atoms. In a binary solution of A and B, if the attractive interaction between A and B is strong compared with that between like atoms, then, the tendency for A and B to escape from the solution is lowered and the vapour pressures of A and B over the solution are lower than those over an ideal solution. This leads to activities lower than the corresponding ideal activities, and the solution is said to exhibit a negative deviation from ideality. On the other hand, a strong repulsive interaction between unlike atoms results in the activities being higher than the ideal activities, and the solution is said to exhibit a positive deviation from ideality. Such a deviation from ideality is expressed in terms of an activity coefficient  $\gamma$ , defined as

$$\gamma_A = \frac{a_A}{X_A}, \quad \gamma_B = \frac{a_B}{X_B}$$

(2.74)

It should be noted that for an ideal solution  $\gamma = 1$ , for a positive deviation  $\gamma > 1$ , and for a negative deviation  $\gamma < 1$ .

#### NONIDEAL DILUTE SOLUTIONS

In a binary solution of A and B, as the atom fraction of A, namely,  $X_A$  tends to zero, the distance between two atoms of A in solution increases to such an extent that we can assume very little zero, the vapour pressure of A is proportional to its concentration, i.e.,  $p_A = kX_A$ , where  $k$  is a constant depending on the nature of the interaction between the solute and the solvent. Again, over this range, a particular atom of A is always surrounded by atoms of B, and as the concen-

tration of A increases, its vapour pressure also proportionately increases. It follows that

$$a_A = \frac{p_A}{p_A^0} = \left( \frac{kX_A}{p_A^0} \right) = \gamma_A^0 X_A$$

where  $\gamma_A^0 = k/p_A^0 = \text{constant}$ . This relationship is known as Henry's law, and  $\gamma_A^0$ , referred to as Henry's law constant, is the activity coefficient in Henry's law range. It can be shown that in the range over which the solute obeys Henry's law, the solvent obeys Raoult's law. Now, applying the Gibbs-Duhem equation to a binary solution, we get

$$X_A dG_A + X_B dG_B = 0, \\ dG_A = RT d \ln a_A, \quad dG_B = RT d \ln a_B.$$

Therefore,

$$d \ln a_B = -\frac{X_A}{X_B} d \ln a_A. \quad (2.76)$$

Since  $a_A = X_A \cdot \gamma_A^0$  over Henry's law range, for solute A, we have

$$d \ln a_A = d \ln X_A,$$

$\gamma_A^0$  being a constant. Therefore,

$$d \ln a_B = -\frac{X_A}{1-X_A} d \ln X_A = -\frac{dX_A}{1-X_A}. \quad (2.77)$$

Integrating eq. (2.77) (the left-hand side between the limits  $a_B = 1$  and  $a_B = a_B$  and the right-hand side between the limits  $X_A = 0$  and  $X_A = X_A$ ), we obtain

$$\int_{a_B=1}^{a_B=a_B} d \ln a_B = - \int_{X_A=0}^{X_A=X_A} \frac{dX_A}{1-X_A}.$$

Therefore,

$$\ln a_B = \ln X_B$$

or

$$a_B = X_B. \quad (2.78)$$

By a similar treatment, it can be shown that at the other extremity of composition, where B is the solute, A obeys Raoult's law.

At intermediate compositions, the type of deviation from ideality would depend on the nature of the concerned binary solution. Figure 2.5 depicts a typical activity composition diagram for a binary solution exhibiting a positive deviation from ideality. The straight line ending at the lower extremities of the two curves indicates Henry's law range.

The range of composition over which the solute obeys Henry's law depends on the interaction between the two component species of the binary solution. The greater the deviation of the activity coefficient  $\gamma$  from unity, the more restricted is Henry's law range. The properties that hold good for the range over which solute A obeys Henry's law are

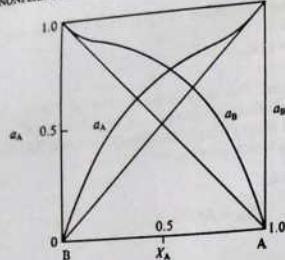


Fig. 2.5 Activity Composition Diagram.

(2.79)

$a_A = kX_A$ ,  
 $\Delta\bar{H}_A$  (partial molar enthalpy of mixing) and  $\Delta\bar{V}_A$  (partial molar volume of mixing) are constants independent of composition,

$$a_B = X_B, \quad \Delta\bar{S}_B = -R \ln X_B, \quad \Delta\bar{H}_B = 0, \quad \Delta\bar{V}_B = 0, \quad (2.80)$$

where  $\Delta\bar{S}_B$  is the partial molar entropy of mixing. Moreover, in the dilute solutions considered,

$$\Delta G_M = X_A RT \ln kX_A + (1 - X_A)RT \ln (1 - X_A). \quad (2.81)$$

Therefore,

$$\frac{d}{dX_A} \Delta G_M = RT \left( \ln \frac{X_A}{X_B} + \ln k \right).$$

Hence, as  $X_A \rightarrow 0$ ,

$$\frac{d}{dX_A} \Delta G_M \rightarrow -\infty. \quad (2.82)$$

Similarly, as  $X_B \rightarrow 0$ ,

$$\frac{d}{dX_B} \Delta G_M \rightarrow -\infty. \quad (2.83)$$

Thus, a plot of  $\Delta G_M$  versus  $X_A$  has vertical tangents at the two extremities where  $X_A = 0$  and  $X_B = 0$ . Similarly, it can be proved that the  $\Delta S_M$  curve also has vertical tangents at the two extremes. However,  $(d/dX_A)\Delta H_M$  approaches limiting values as  $X_A \rightarrow 0$ . Figure 2.6 shows the plots of the typical values of  $\Delta G_M$ ,  $T\Delta S_M$ , and  $\Delta H_M$  as functions of the composition of the solution and Fig. 2.7 shows the plots of the corresponding partial functions.

### 2.11 EXCESS THERMODYNAMIC QUANTITIES

The deviation of the thermodynamic properties of a solution from those of an ideal solution is of

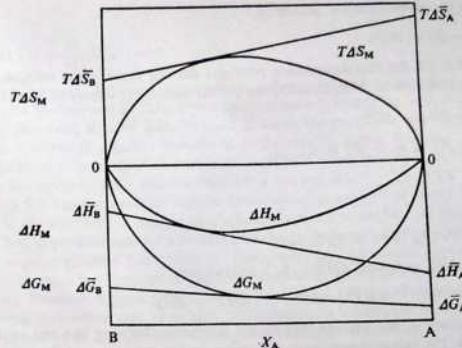


Fig. 2.6 Integral Molar Properties of Mixing.

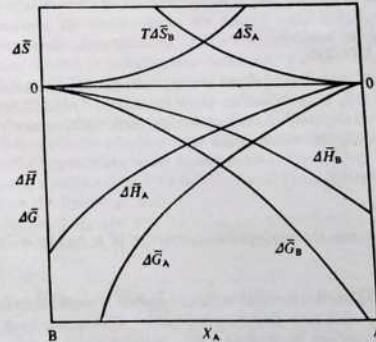


Fig. 2.7 Partial Molar Properties of Mixing.

interest because it leads to an understanding of the interactions between the components. If  $G$  is the value of the thermodynamic function in a given solution, the excess thermodynamic property  $G^{xs}$  is given by

$$G^{xs} = G - G^{id}, \quad (2.84)$$

where  $G^{id}$  is the corresponding thermodynamic property in an ideal solution having the same

composition as the given solution. Similarly,

$$\Delta G_A^{xs} = \Delta G - \Delta G_A^{\text{id}}. \quad (2.85)$$

It is evident that all the thermodynamic relations derived for a given solution apply to excess thermodynamic functions as well. Considering partial molar free energy as an example, we have

$$\begin{aligned} \Delta G_A^{xs} &= \Delta G_A - \Delta G_A^{\text{id}} \\ &= RT \ln a_A - RT \ln X_A \\ &= RT \ln \gamma_A. \end{aligned} \quad (2.86)$$

Further,

$$\Delta G_M^{xs} = RT(X_A \ln \gamma_A + X_B \ln \gamma_B). \quad (2.87)$$

Since  $\Delta H_M^{\text{id}} = 0$ ,  $\Delta B_A^{\text{id}} = 0$ , and  $\Delta B_B^{\text{id}} = 0$ , it follows that

$$\Delta H_M^{xs} = \Delta H_M, \quad \Delta B_A^{xs} = \Delta B_A, \quad \Delta B_B^{xs} = \Delta B_B. \quad (2.88)$$

In an ideal solution, we assume that no net interaction between like and unlike atoms takes place and, as such, the excess thermodynamic properties are a measure of the interaction between the constituents of the solution. Further, in an ideal solution, since the atoms are randomly mixed, the excess entropies reflect a measure of the deviations from a random distribution and also of any contribution to entropy due to nonconfigurational factors such as vibrational entropy changes.

## 2.12 REGULAR SOLUTIONS

In certain solutions, the distribution of atoms is completely random and hence statistical mechanics requires that  $\Delta S_M$  and  $\Delta S_B$  have values as given by eqs. (2.73) and (2.80). These solutions can have a nonzero heat of mixing despite random mixing. Such solutions are referred to as regular solutions. For a regular solution, we can show that

$$\Delta B_A = RT \ln \gamma_A, \quad (2.89)$$

$$\Delta B_B = RT \ln \gamma_B. \quad (2.90)$$

We now calculate the excess thermodynamic properties of a regular solution. For a regular solution, we know

$$\Delta S_M^{xs} = 0, \quad \Delta S_A^{xs} = 0, \quad \Delta S_B^{xs} = 0, \quad \frac{\partial}{\partial T} \Delta G_M^{xs} = -\Delta S_M^{xs} = 0.$$

Similarly,

$$\frac{\partial \Delta S_A^{xs}}{\partial T} = 0.$$

Moreover,

$$\begin{aligned} \Delta G_A^{xs} &= \Delta B_A^{xs} - T \Delta S_A^{xs} = \Delta B_A^{xs} \\ &= RT \ln \gamma_A. \end{aligned} \quad (2.91)$$

Therefore,

$$\frac{\partial}{\partial T} (RT \ln \gamma_A) = \frac{\partial}{\partial T} (\Delta G_A^{xs}) = 0. \quad (2.92)$$

Thus, for a regular solution,  $RT \ln \gamma_A$  is a constant, independent of temperature. For a regular solution, it can also be shown that  $\Delta H_M$  obeys the parabolic relationship  $\Delta H_M = bX_AX_B$ , where  $b$  is a constant. However, if both  $\Delta H_M$  and  $\Delta G_M^{xs}$  obey the parabolic relationship, it does not follow that the solution is regular, because it is frequently found that  $\Delta H_M = bX_AX_B$  and  $\Delta G_M^{xs} = b'X_AX_B$ , where  $b'$  is another constant not equal to  $b$ . Since  $b$  is not equal to  $b'$ , consequently,  $\Delta S_M$  is not equal to  $\Delta S_M^{\text{id}}$ , and the solution is not regular.

Although very few solutions exhibit regular behaviour, the concept of a regular solution has proved useful. If the entropies of mixing of a solution are not available, we may assume regular behaviour as a first approximation for a solution whose components are not too dissimilar. The definition of a regular solution has a built-in incongruity, i.e., a nonzero heat of mixing implies a net interaction between the components, and this cannot be reconciled with a random distribution of the atoms. However, a regular solution is formed by those constituents having a weak interaction among themselves and at a high temperature, at which, the contribution of entropy ( $T\Delta S$ ) to the free energy of mixing is large compared with that of enthalpy.

## 2.13 THERMODYNAMICS OF DILUTE METALLIC SOLUTIONS

### CHANGE OF STANDARD STATE

In many refining operations, the impurities in the molten metal solution that is to be refined may be present in very small concentrations. The thermodynamic properties of such a dilute solution are of particular interest to metallurgists. As already pointed out, in such a dilute solution, the solute obeys Henry's law, i.e., the activity coefficient of a solute  $i$ , i.e.,  $\gamma_i$ , approaches a finite value  $\gamma_i^0$ , which is Henry's law constant and is independent of the composition in Henry's law range. It should be noted that the solute obeys Henry's law only if it is present in the dilute solution in the same form as in the standard state. Here, the standard state is taken as the pure substance at 1 atm at the temperature under consideration. The activity on a scale with the pure substance as the standard state is referred to as the Raoultian activity and  $\gamma_i^0$  is referred to as Henry's law constant on the Raoultian scale.

As mentioned in Section 2.10, the activity  $a_i$  of the component  $i$  on the foregoing scale is related to the chemical potential  $\mu_i$  in the given state and  $\mu_i^0$  in the standard state by the equation

$$\mu_i - \mu_i^0 = RT \ln a_i.$$

The activity in the standard state is always equal to one, but the choice of the standard state is purely arbitrary; it need not always be the pure substance at 1 atm. Other standard states can also be used, for instance, a dilute solution with 1 atom % of the component  $i$  can be taken as the standard state with unit activity. In such a case,

$$\mu_i - \mu_i^0 = RT \ln a_{(1 \text{ atom } \%)} \quad (2.93)$$

The activity given by eq. (2.93) is with respect to the new standard state. If the solution is ideal throughout the range of composition, then it is evident that the activity on the new scale (i.e., with 1 atom % solute as the standard state) is always proportional to the atom fraction. Further, if the activity of a 1 atom % solution is unity, then the activity of an  $x$  atom % solution is  $x$ .

that of the pure component  $i$  is 100. Even if the solution is not ideal, the activity on this new scale, over Henry's law range, again, is proportional to the atom fraction. Therefore, in the dilute solution range over which Henry's law is valid, activity is equal to atom %.

In industrial practice, concentration is generally expressed as wt % instead of atom %. Therefore, a common practice is to consider a 1 wt % solution of a solute  $i$  as the standard state with unit activity. Such a standard state would be hypothetical because many solutes may not dissolve in a metal up to a concentration of 1 wt %, and even if they did, they may not obey Henry's law up to 1 wt %.

Activity on a scale with 1 wt % solution as the standard state is called Henrian activity denoted by  $h$  and given by

$$\mu_i - \mu_{i(1\text{ wt }%)} = RT \ln h_i. \quad (2.94)$$

In a dilute solution, it can be shown that the atom % is proportional to the wt % concentration. For example, if  $w$  wt % of a component  $i$ , whose atomic weight is  $M_i$ , is dissolved in a metal whose atomic weight is  $M$ , then the atom fraction of  $i$ ,  $X_i$ , is given by

$$X_i = \frac{w/M_i}{[(100-w)/M] + (w/M_i)} = \frac{w}{M/100} \quad \text{as } w \rightarrow 0, \quad (2.95)$$

i.e.,  $X_i$  is proportional to  $w$ , as  $w \rightarrow 0$ . This implies that the Henrian activity  $h$  is proportional to the wt % in the Henry's law range. Therefore, if a 1 wt % solution has an activity 1, a  $\frac{1}{2}$  wt % solution has an activity  $\frac{1}{2}$  and a  $w$  wt % solution an activity  $w$ . On such a scale, if the solute obeys Henry's law throughout the composition range, the activity of the pure component is 100.

A Henrian activity coefficient  $f_i$  for the component  $i$  can now be defined as

$$f_i = \frac{h_i}{wt\% i}. \quad (2.96)$$

It may be noted that as the concentration approaches zero,  $f_i$  approaches unity. For many solutes, since Henry's law is valid only at extremely low concentrations, it is practicable to consider the standard state as the solution in which the activity becomes equal to the wt % of the solute at infinite dilution. The hypothetical 1 wt % solution then has a unit activity as defined by eq. (2.94). At concentrations beyond Henry's law range,  $f_i$  becomes more than or less than unity.

#### CONVERSION FROM ONE STANDARD STATE TO ANOTHER

The chief advantage in using Henrian activity is that the activities of the solute can be replaced by wt % in calculations involving equilibria. In order to do these calculations, it is sometimes necessary to convert the activities from one standard state to another.

Consider the reaction



If the standard state of the reactants and the products are the pure substances at 1 atm,  $\Delta G_1^0$  the standard free energy change, and  $K_1$  the equilibrium constant, then

$$\Delta G_1^0 = -RT \ln K_1,$$

(2.97)

where the activities are expressed on the Raoultian scale.

Now, suppose  $\underline{A}$  is an element dissolved in a metal to form a dilute solution at a concentration of  $w$  wt %, and the standard state of  $A$  is a 1 wt % solution with unit activity. The reaction is represented by



where  $\underline{A}$  represents a solution of  $A$  in the metal.

The standard free energy change  $\Delta G_2^0$  for reaction (2.99) differs from  $\Delta G_1^0$  because the standard state of  $A$  is now different.  $\Delta G_2^0$  can be obtained from standard reference books whereas  $\Delta G_2^0$  is not readily available. Now,  $\Delta G_2^0 = -RT \ln K_2$ , where  $K_2$  the equilibrium constant is given by

$$K_2 = \frac{a_C \cdot a_D}{a_B \cdot h_A}, \quad (2.100)$$

$h_A$  being the Henrian activity of  $A$  on the Henrian scale. Moreover,  $h_A = wt\% A = w$ , if Henry's law is obeyed by solute  $A$  in the metal in the dilute solution. Therefore,

$$K_2 = \frac{a_C \cdot a_D}{a_B \cdot w}, \quad (2.101)$$

i.e.,  $h_A$  in eq. (2.100) is replaced by  $w$ . This is the advantage in using the new standard state. In this case, however,  $\Delta G_2^0$  has to be evaluated in order to calculate  $K_2$ . This can be done as follows. Consider the reaction representing the transfer of 1 gm atom of a pure element  $A$  at 1 atm to the metal in order to form a 1 wt % solution (i.e., from the old standard state to the new standard state)



Reaction (2.102) represents the transfer of 1 gm atom of  $A$  from the old standard state to the new standard state. The free energy change  $\Delta G_3$  for this reaction is given by

$$\Delta G_3 = RT \ln \left[ \frac{a_{\underline{A}}(1\text{ wt }%)}{a_A (\text{pure, 1 atm})} \right]. \quad (2.103)$$

$\Delta G_3$  can be evaluated by expressing both the activities on the Raoultian scale, that is,

$$a_A (\text{pure, 1 atm}) = 1, \quad a_{\underline{A}} (1\text{ wt }%) = \gamma_A \cdot X_A,$$

where  $\gamma_A$  is the activity coefficient of  $A$  on the Raoultian scale and  $X_A$  the atom fraction of  $A$  in the 1 wt % solution. Therefore,

$$\begin{aligned} \Delta G_3 &= RT \ln \left( \frac{\gamma_A \cdot X_A}{1} \right) \\ &= RT \ln (\gamma_A \cdot \frac{1M}{M_i 100}), \end{aligned} \quad (2.104)$$

where  $M$  is the atomic weight of the solvent metal and  $M_i$  is the atomic weight of solute  $A$ . Thus,  $\Delta G_3$  is estimated if  $\gamma_A$  is determined experimentally or obtained by other methods.

By combining  $\Delta G_3$  and  $\Delta G_1^0$ , we can evaluate  $\Delta G_2^0$  and hence  $K_2$ . To illustrate, we now give a simple example.

**Example** At 1200°C, the Raoultian activity coefficient of zinc in a dilute solution of copper is 0.23. Hence, the free energy change when 1 gm atom of zinc dissolves in copper to form a 1 wt % solution is given by

$$\Delta G = RT \ln 0.23 \frac{63.54}{65.38 \times 100} = -17,800 \text{ cal.}$$

#### 2.14 INTERACTION PARAMETERS IN MULTICOMPONENT SOLUTIONS

In a multicomponent solution, the thermodynamic properties of a given solute are influenced by the presence of other dissolved elements. For example, the presence of 2 wt % carbon in liquid iron increases the activity coefficient of the silicon present in it by a factor of two. In the recent past, many attempts have been made to derive models of solutions to predict the effect of other components in solution on the activity coefficient of a given solute. Wagner (1952) introduced the concept of the interaction parameter for predicting the activities in multicomponent solutions. Based on this concept, he has given a method for calculating the activity coefficient of a solute in a multicomponent solution in the metal M, if the activities in simple binary and ternary solutions are known.

Consider a binary solution of a solute x dissolved in a metal M to form a dilute solution. Let the activity coefficient of x in this solution be  $\gamma_x^*$  on the Raoultian scale. It should be noted that  $\gamma_x^*$  is a measure of the interaction between the atoms in solution. If another solute y is added to this solution, the activity coefficient of x is changed to  $\gamma_x$ , and this change is brought about by changes in interatomic interaction created by the addition of y. According to Wagner, in a multicomponent solution containing the solutes x, y, z, ... (dissolved in the metal M to form a dilute solution) whose atom fractions are  $X_x, X_y, X_z, \dots$ , respectively, the activity coefficient of the component x, i.e.,  $\gamma_x$  is given by

$$\ln \gamma_x = \ln \gamma_x^* + X_x \left( \frac{\partial \ln \gamma_x}{\partial X_x} \right)_{M \rightarrow 1} + X_y \left( \frac{\partial \ln \gamma_x}{\partial X_y} \right)_{M \rightarrow 1} + X_z \left( \frac{\partial \ln \gamma_x}{\partial X_z} \right)_{M \rightarrow 1} + \dots, \quad (2.105)$$

where  $\gamma_x^*$  is the activity coefficient of x in the binary x dissolved in the metal M and  $X_M$  is the atom fraction of the solvent metal M.

In eq. (2.105),  $(\partial \ln \gamma_x / \partial X_x)_{M \rightarrow 1}$  is defined as the self-interaction parameter  $e_x^*$  and represents the variation of  $\gamma_x$  with  $X_x$  in the binary solution of x dissolved in M. Similarly,  $(\partial \ln \gamma_x / \partial X_y)_{M \rightarrow 1}$  is defined as the ternary interaction parameter of y on x,  $e_x^y$  and represents the variation of  $\gamma_x$  with  $X_y$  in the ternary solution of x and y dissolved in M. Also,  $(\partial \ln \gamma_x / \partial X_z)_{M \rightarrow 1}$  is the ternary interaction parameter of z on x,  $e_x^z$  and represents the variation of  $\gamma_x$  with  $X_z$  in the ternary solution of x and z dissolved in M.

Thus,  $\gamma_x$  in the foregoing multicomponent solution is given by

$$\ln \gamma_x = \ln \gamma_x^* + X_x e_x^* + X_y e_x^y + X_z e_x^z + \dots \quad (2.106)$$

#### INTERACTION PARAMETER IN TERMS OF HENRIAN ACTIVITY COEFFICIENT

In industrial applications, the common practice is to use the Henrian activity coefficient  $f_x$  (of a solute x) and also to express its concentration on a wt % basis.

By expressing the concentration in wt % and by replacing the natural logarithm by the common logarithm, the equation we obtain for the activity coefficient  $f_x$  in the multicomponent

solution is

$$\begin{aligned} \log f_x &= \log f_x^* + \% x \left( \frac{\partial \log f_x}{\partial \% x} \right)_{M \rightarrow 100} + \% y \left( \frac{\partial \log f_x}{\partial \% y} \right)_{M \rightarrow 100} \\ &\quad + \% z \left( \frac{\partial \log f_x}{\partial \% z} \right)_{M \rightarrow 100} + \dots \end{aligned} \quad (2.107)$$

Now,

$$(\partial \log f_x / \partial \% x)_{M \rightarrow 100}$$

is defined as the self-interaction parameter  $e_x^*$ ,

$$(\partial \log f_x / \partial \% y)_{M \rightarrow 100}$$

as the ternary interaction parameter  $e_x^y$  of y on x, and

$$(\partial \log f_x / \partial \% z)_{M \rightarrow 100}$$

as the ternary interaction parameter  $e_x^z$  of z on x.  $f_x^*$  is the activity coefficient of x in the binary solution of x dissolved in M. Therefore,

$$\log f_x = \log f_x^* + \% x e_x^* + \% y e_x^y + \% z e_x^z + \dots \quad (2.108)$$

Strictly speaking, eqs. (2.105)–(2.108) are valid only for dilute solutions but can also be applied to moderately dilute solutions without introducing any serious error. The interaction parameters can be determined from the experimental data on binary and ternary dilute alloys. Let us consider a simple example.

**Example** Estimate the activity coefficient of sulphur in a metallic bath containing 0.05 wt % sulphur, 1.2 wt % silicon, 4 wt % carbon, and 1.8 wt % manganese, given that  $e_S^S = -0.028$ ,  $e_S^{Si} = 0.065$ ,  $e_S^C = 0.24$ , and  $e_S^{Mn} = -0.02$ .

[Hint]

$$\log f_S = \% S \cdot e_S^S + \% Si \cdot e_S^{Si} + \% C \cdot e_S^C + \% Mn \cdot e_S^{Mn} = 1.0006.$$

Note that it is assumed that all concentrations are over Henry's law range.]

The reader is referred to standard reference books for the values of interaction parameters applicable to various ferrous and nonferrous solutions.

#### 2.15 KINETIC PRINCIPLES: REACTION RATE

Thermodynamic principles help us determine the direction in which a given reaction will proceed, but they cannot give any useful information on the rate at which a reaction will take place. Many common base metals and their alloys are thermodynamically unstable in air even at the room temperature, since their final equilibrium state is the oxide. The use of these metals depends on the extremely slow kinetics that governs their oxidation. In metal extraction, it is important to know the kinetics of a reaction precisely, because a slow reaction can make a process unsuitable even if the thermodynamic factors are highly favourable. Kinetics also helps us understand the factors that govern the rates of constituent reactions, thus making it possible to increase the efficiency of the entire process.

**RATE OF CHEMICAL REACTION**

Consider the reaction



The rate of the forward reaction can be expressed in terms of the amount of A (or B) transformed in unit time. If  $C$  is the concentration of one of the substances, the reaction rate is given by  $dC/dt$ .

The reaction rates vary from the extremely fast to the extremely slow, depending on the factors which govern them. It has been found experimentally that the reaction rate is a function of concentration and temperature.

**ORDER OF REACTIONS**

Consider the general reaction



where  $a, b, c, \dots$  are the number of molecules of A, B, C, ..., respectively, that react to form the products. The rate of this reaction, expressed as  $(-dC_A/dt)$ , is found to depend on the product of the concentration terms, i.e.,

$$-\frac{dC_A}{dt} = k \cdot C_A^a \cdot C_B^b \cdot C_C^c \dots \quad (2.109)$$

where  $k$  is a constant known as the velocity constant or rate constant,  $C_A, C_B, C_C, \dots$  are the concentrations at time  $t$ . The order of the reaction is defined as the sum of the exponents of the concentration terms ( $a + b + c \dots$ ) in the rate equation, i.e., eq. (2.109).

**FIRST-ORDER REACTION**

A typical first-order reaction may be written as

$$\begin{aligned} A &= B + C, \\ -\frac{dC_A}{dt} &= kC_A. \end{aligned} \quad (2.110)$$

In eq. (2.110), the reaction rate is proportional to a single concentration term, therefore, it is a first-order reaction.

**SECOND-ORDER REACTION**

Second-order reactions can be represented by the reaction

$$\begin{aligned} A + B &= C + D, \\ -\frac{dC_A}{dt} &= -\frac{dC_B}{dt} = kC_A \cdot C_B. \end{aligned} \quad (2.111)$$

In the rate equation (2.111), the sum of the exponents of the concentration terms is two. Reactions of a higher order can be written in a similar manner.

**REACTIONS CLOSE TO EQUILIBRIUM**

For a reaction that is far from equilibrium, i.e., when the free energy difference between the

reactants and the products is large and negative, the rate of reaction depends on the concentration of the reactants. In such a situation, the backward reaction is unimportant [as in the rate equations (2.110) and (2.111)]. For a reaction close to equilibrium, the overall rate of reaction depends on the rates of both forward and backward reactions.

Suppose the reaction



is close to equilibrium. We then have

$$V_f = k_f C_A, \quad (2.112)$$

$$V_b = k_b C_B, \quad (2.113)$$

where  $V_f$  and  $V_b$  are the velocities and  $k_f$  and  $k_b$  the rate constants of the forward and backward reactions, respectively. At equilibrium,

$$V_f = V_b.$$

Therefore,

$$k_f \cdot C_A^* = k_b \cdot C_B^*$$

where  $C_A^*$  and  $C_B^*$  are the equilibrium concentrations of A and B, respectively. Hence, the equilibrium constant  $K$  is given by

$$K = \frac{C_B^*}{C_A^*} = \frac{k_f}{k_b}. \quad (2.114)$$

Therefore, for the overall rate at which A is consumed, we obtain the expression

$$\begin{aligned} -\frac{dC_A}{dt} &= V_f - V_b \\ &= k_f \cdot C_A - k_b \cdot C_B \\ &= k_f(C_A - \frac{C_B}{K}). \end{aligned} \quad (2.115)$$

**EFFECT OF CONCENTRATION ON REACTION RATE**

Consider the reaction



As already noted [see eqs. (2.112) and (2.113)],

$$V_f = k_f[A][B], \quad V_b = k_b[C][D],$$

where  $[A]$ ,  $[B]$ ,  $[C]$ , and  $[D]$  denote the concentrations of A, B, C, and D, respectively. When the reaction attains stable equilibrium,  $V_f = V_b$ , i.e.,

$$\frac{[C][D]}{[A][B]} = \frac{k_f}{k_b} = K. \quad (2.117)$$

**EFFECT OF TEMPERATURE ON REACTION RATE**

The temperature coefficient of the equilibrium constant  $K$  is given by the Vant Hoff equation, which can be derived from eq. (2.29) as

(2.118)

$$\frac{d}{dT} \ln K = \frac{\Delta H}{RT^2}$$

Since  $K = k_f/k_b$ ,

$$\frac{d}{dT} \ln k_f - \frac{d}{dT} \ln k_b = \frac{\Delta H}{RT^2}$$

S. Arrhenius suggested, in 1889, that equations similar to eq. (2.118) can be written for the rate constants  $k_f$  and  $k_b$ , i.e.,

$$\frac{d}{dT} \ln k_f = \frac{E_a}{RT^2} + I, \quad \frac{d}{dT} \ln k_b = \frac{E'_a}{RT^2} + I,$$

where the energy terms  $E_a$  and  $E'_a$  are related to  $\Delta H$  by the equation  $(E'_a - E_a) = \Delta H$ , and  $I$  is a constant.

Assuming  $I$  to be zero and  $E_a$  to be independent of temperature, on integrating the foregoing two equations, we get

$$\ln k_f = -\frac{E_a}{RT} + \text{constant}, \quad (2.120)$$

$$\ln k_b = -\frac{E'_a}{RT} + \text{constant} \quad (2.121)$$

or, in general, the velocity constant or rate constant  $k$  is given by

$$k = A \exp\left(-\frac{E_a}{RT}\right), \quad (2.122)$$

where  $A$  is the constant of integration, called the frequency factor. Equation (2.122) is the well-known Arrhenius equation for the rate constant. The quantity  $E_a$  is called the activation energy of the reaction. Arrhenius found a plot of  $\ln k$  versus  $1/T$  to be a straight line for numerous reactions. This means that the assumption  $I = 0$  is generally valid.

The Arrhenius equation [eq. (2.122)] requires that each molecule acquire an activation energy  $E_a$  before it can react with another molecule. In eq. (2.122),  $\exp(-E_a/RT)$  represents the fraction of molecules which acquire the necessary activation energy.

The two main theories that theoretically interpret the term activation energy are the collision theory and the theory of absolute reaction rates.

**COLLISION THEORY**

The constant  $A$  in the Arrhenius equation includes a probability factor. For a reaction to occur, two molecules, say, A and B must collide. But every collision does not result in the formation of a product. The probability of a collision resulting in a reaction depends on several factors, such as size and orientation. A reaction occurs only if the colliding molecules possess an energy in excess of a specified critical amount. If the temperature is increased, there is no appreciable change in

the total number of collisions, but the proportion of effective collisions considerably increases. The collision theory, though successful in the case of simple reactions, was found not to be so successful for complex molecules, and is not considered here in detail.

**2.16 THEORY OF ABSOLUTE REACTION RATES**

The theory of absolute reaction rates, proposed by H. Eyring in 1935 assumes that when two reactants come together with sufficient energy to react, they form an activated complex which instantaneously breaks up to give the reaction products. An activated complex is assumed to be formed from the reactants as an intermediate step in all chemical reactions, i.e.,

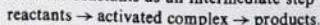


Figure 2.8 depicts the change in potential energy along a so-called reaction coordinate leading from the reactants to the products.

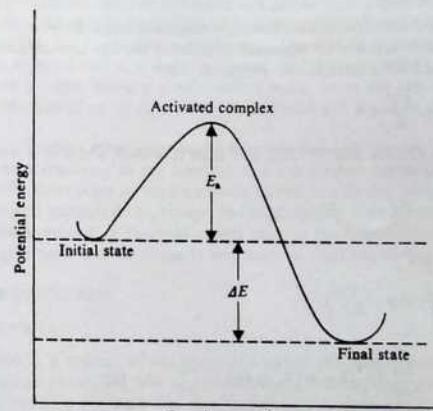


Fig. 2.8 Activation Energy.

The activation energy  $E_a$  is the additional energy which the reactant molecules must acquire to form the activated complex. The reactants acquire the activation energy from the kinetic and vibrational energies of colliding molecules. It is further assumed that the activated complex at any instant is in thermodynamic equilibrium with the reactants, even though each complex has an exceedingly short life. Based on this assumption, the rate of a chemical reaction is the number of activated complexes decomposing per second into the products. The theory also assumes that the activated complex decomposes into the products at a universal rate independent of the nature of the reaction or complex. This rate is given by  $KT/h$ , where  $K$  is Boltzmann's constant,  $T$  the absolute temperature, and  $h$  Planck's constant.

Consider reaction (2.116). In Fig. 2.8, if the free energy is plotted instead of the potential energy, the activation energy  $E_a$  is replaced by  $\Delta G^*$ , i.e., the free energy of activation and  $\Delta E$  is

replaced by  $\Delta G$ , the free energy change of the reaction. We get  $\Delta G^*$  as

$$(2.123)$$

$$\Delta G^* = -RT \ln K^* = \Delta H^* - T\Delta S^*$$

where  $K^*$  is the equilibrium constant for reaction (2.116) (in which an activated complex is formed by reactants A and B) and,  $\Delta H^*$  and  $\Delta S^*$  are the enthalpy and entropy of activation, respectively.

Considering reaction (2.116) once again,

$$K^* = \frac{a^*}{a_A \cdot a_B}$$

where  $a^*$  is the activity of the complex, we obtain

$$(2.124) \quad K^* = \frac{C^*}{C_A \cdot C_B} \cdot \frac{\gamma^*}{\gamma_A \cdot \gamma_B}$$

where  $C$  and  $\gamma$  are the concentration and activity coefficients, respectively.

The absolute reaction rate can be expressed in terms of the equilibrium concentration of the activated complexes and their rates of decomposition, i.e.,

$$(2.125) \quad \text{reaction rate} = \frac{KT}{h} \cdot C^*$$

Combining equations (2.124) and (2.125), and since  $K = R/N$ , where  $N$  is Avogadro's number, we have

$$(2.126) \quad \text{reaction rate} = \frac{RT}{Nh} \frac{K^* \gamma_A \gamma_B}{\gamma^*} C_A \cdot C_B$$

From eq. (2.123), we get

$$K^* = \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)$$

Therefore,

$$(2.127) \quad \text{reaction rate} = \frac{RT}{Nh} \frac{\gamma_A \gamma_B}{\gamma^*} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) C_A \cdot C_B = k_T C_A \cdot C_B$$

where  $k_T$  is the specific reaction rate constant, and is given by

$$(2.128) \quad k_T = \frac{RT}{Nh} \frac{\gamma_A \gamma_B}{\gamma^*} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)$$

Equation (2.128) can be reduced to

$$(2.129) \quad k_T = K_0 T \exp\left(-\frac{\Delta H^*}{RT}\right)$$

where  $K_0$  stands for the first three terms of eq. (2.128) and  $\Delta H$  stands for activation energy  $E_a$  of a linear temperature term. In eq. (2.129), the term that is the most dependent on temperature is the exponential term, so that, over a small temperature range, eq. (2.129) reduces to the Arrhenius equation.

### SIGNIFICANCE OF ACTIVATION ENERGY

A reaction for which the driving force is large, i.e.,  $\Delta G$  is very large and negative, can still occur at a slow rate if it has a large activation energy.

The strongly temperature-dependent exponential term in eq. (2.129) indicates also that the reaction rate becomes much faster as the temperature increases. For example, a simple bimolecular reaction which takes place at room temperature with an activation energy of 30 kcal per mole would proceed about  $10^{18}$  times faster at 2000°C.

### 2.17 HOMOGENEOUS AND HETEROGENEOUS REACTIONS

In the study of kinetics, it is useful to classify chemical reactions as either homogeneous or heterogeneous. Homogeneous reactions are those which take place within a single phase, i.e., gaseous, liquid, or solid, for example, between molecules in a gas or in a liquid solution. Heterogeneous reactions are those which involve more than one phase and are characterized by the presence of an interface, e.g., between a gas and a solid, as in the case of sulphide roasting; between two immiscible fluids, as in the case of a slag-metal reaction; between a solid and a liquid, as in the case of leaching process; between a solid and a solid, as in the case of the carbothermic or metallothermic reduction of an oxide; and between a liquid and a gas, as in the case of distillation process.

Heterogeneous reactions take place at the interface between phases. Therefore, the reacting species have to be transported to the interface and the product species away from it. In solids, such a mass transfer takes place through a process known as diffusion, which involves the movement of atoms along a concentration gradient. In fluids, the flow can be either laminar or turbulent. In the former, each element of the fluid moves only in the direction of the flow. In the latter, local eddies are generated, and the elements may move at right angles to the direction of the flow.

### 2.18 LAWS OF DIFFUSION

#### FICK'S FIRST LAW

Basically, diffusion is a process which tends to equalize the concentrations of the constituent species within a single phase. The driving potential is the concentration gradient within the phase. The appropriate equation for mass flux due to diffusion is given by Fick's first law which was proposed by Adolf Fick in 1855 and is stated as

$$(2.130) \quad J = -D \frac{\partial C}{\partial X}$$

where  $J$  is the amount of material that diffuses per unit time in a direction perpendicular to a reference plane having a unit cross-sectional area,  $C$  the concentration of the constituent species,  $X$  the position coordinate measured perpendicular to the reference plane, and  $D$  the coefficient of diffusion. The negative sign in eq. (2.130) indicates that the material is transported from a high to a low concentration region and that  $X$  is measured in the direction of diffusion. If  $C$  is measured in moles/cc, then  $J$  is in moles/sec/cm<sup>2</sup>, and  $D$  has the dimensions cm<sup>2</sup>/sec<sup>-1</sup>.  $J$  may also be expressed as the molar flux ( $dn/dt$  or  $n$ ) per unit cross-sectional area in the form

$$(2.131) \quad J = \frac{dn}{dt} \frac{1}{A}$$

where  $n$  is the number of moles,  $A$  the area of the reference plane, and  $t$  the time. Combining eqs. (2.130) and (2.131), we get

$$\frac{1}{A} \frac{dn}{dt} = -D \frac{\partial C}{\partial X} \quad (2.132)$$

Under the steady-state condition (i.e., when  $J$  is constant),  $[(1/A)(dn/dt)]$  is equal to a constant value  $[-D(dC/dX)]$ .

#### FICK'S SECOND LAW

Fick's second law, i.e., a general equation for diffusion, results if we consider the variation of concentration within a reference volume.

Consider an elemental slab of thickness  $dX$  and area  $A$  perpendicular to the direction of flux. The change in the amount of material in the volume  $A dX$  with time may be calculated as the difference between the inflow and outflow of material. This difference is expressed as

$$A[J - (J + \frac{\partial J}{\partial X} dX)] = -A \frac{\partial J}{\partial X} dX. \quad (2.133)$$

The rate of change of concentration in the elemental volume is obtained by dividing this difference by  $A dX$ , i.e.,

$$\frac{\partial C}{\partial t} = \frac{\partial J}{\partial X}. \quad (2.134)$$

Differentiating eq. (2.130) (Fick's first law) with respect to  $X$  ( $D$  being constant) and combining it with eq. (2.134), we get

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2}. \quad (2.135)$$

which is Fick's second law.

Strictly speaking, the driving force for diffusion is the difference in the chemical potentials of the same element at two different points in the direction of flow and not the difference in concentrations. However, concentration terms are generally used in calculations.

#### 2.19 MASS TRANSFER BETWEEN A FLUID AND A SOLID

Let us consider a fluid flowing past a solid surface as shown in Fig. 2.9a. We assume that the velocity of the fluid relative to the solid is zero at the solid-liquid interface because the layer of fluid in contact with the solid cannot slip past the solid. (The rigidity of the solid reduces the fluid velocity to zero at the interface.) In the bulk of the fluid at a distance from the interface, the fluid velocity has a finite value  $V_B$ , resulting in a velocity gradient in the fluid layer as shown in Fig. 2.9a. Near the interface, since the fluid velocities are small, the flow is laminar, even if the bulk flow is turbulent. The laminar layer is separated from the bulk flow, if turbulent, by a buffer layer. In the velocity boundary layer  $\delta_V$  (shown in Fig. 2.9a), the velocity gradually decreases from the bulk velocity to zero at the interface.

#### EFFECTIVE CONCENTRATION BOUNDARY LAYER THICKNESS

Let us consider a substance being transferred from a solid to a flowing liquid, as in the leaching

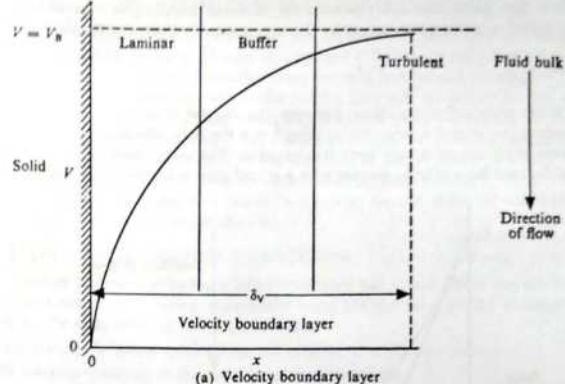


Fig. 2.9 Variation of Velocity and Concentration in Boundary Layer (cont.).

of ores and concentrates. The concentration of a substance that is being transferred from a solid to a liquid varies across the boundary layer from  $C_S$  at the interface to  $C_B$  in the bulk. This layer is termed the concentration boundary layer ( $\delta_C$ ), and is shown in Fig. 2.9b. As it is difficult to determine the thickness of this boundary layer, we assume the existence of an effective boundary layer close to the interface, across which the mass transport is controlled only by molecular diffusion. (Such an assumption is valid because in this layer the flow is laminar and turbulent flow conditions do not exist.) Therefore, the flux  $J$  of the dissolving species in the  $X$ -direction, which is perpendicular to the direction of the flow, is given by

$$J = -D \left( \frac{dC}{dX} \right)_{x=0}. \quad (2.136)$$

From Fig. 2.9b, we have

$$\frac{C_S - C_B}{\delta} = - \left( \frac{dC}{dX} \right)_{x=0}. \quad (2.137)$$

Therefore,

$$J = D \frac{C_S - C_B}{\delta}. \quad (2.138)$$

From Fig. 2.9b, it is evident that  $\delta$  is obtained by constructing the tangent to the curve at  $X = 0$ . The term  $\delta$  is known as the effective concentration boundary layer thickness.

The concept of the effective boundary layer across which the mass transport is controlled by molecular diffusion is valid even when the flow in the bulk fluid is turbulent, as is evident from the profile of the velocity boundary layer (see Fig. 2.9a). The boundary layer thickness depends on flow conditions, i.e., it is smaller for a high flow velocity and a low viscosity. The greater the stirring in the fluid, the thinner the effective boundary layer.

Turbulent flow conditions are characteristic of most metallurgical operations. Therefore, apart from diffusion, mixing also occurs by the movement of eddies, and the corresponding flux is

$$(2.139)$$

$$J = D_E \frac{dc}{dx}$$

where  $D_E$  is the eddy diffusivity. Now, consider the transfer of a particular species across the phase boundary in a stirred system. The stirring keeps the bulk concentrations uniform, so that concentration gradients exist only near the interface. The curve showing concentrations as a function of distance for a solid in contact with a stirred fluid is similar to that shown in Fig. 2.9b,

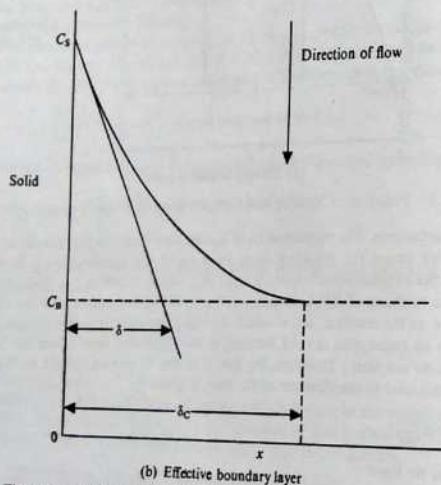


Fig. 2.9 Variation of Velocity and Concentration in Boundary Layer.

This is a time-averaged curve because of the fluctuating eddies in the liquid. The flux of the dissolving species moving from the interface to the bulk phase is given by

$$J = K_M(C_s - C_B), \quad (2.140)$$

where  $K_M$  is the mass transfer coefficient, whose units are  $\text{cm sec}^{-1}$  if  $J$  is expressed in moles  $\text{sec}^{-1} \text{cm}^{-2}$ . Comparing eqs. (2.138) and (2.140), we obtain

$$K_M = \frac{D}{\delta}. \quad (2.141)$$

It should be noted that  $K_M$  depends on factors such as the geometry of the system, the viscosity and the density of the liquid, the diffusivity of the species, and the stirring conditions.

#### MASS TRANSFER ACROSS TWO IMMISCIBLE FLUIDS IN CONTACT

In the case of two immiscible fluids in contact, the treatment is more complex because both surfaces are no longer rigid. However, if there is a marked difference in the viscosities of the two liquids, we may assume that the liquid with the lower viscosity will behave almost as if in contact with a solid phase. Also, the concentration profile in this case will be similar to that shown in Fig. 2.9b. However, in a general situation, where two fluids are being stirred, the boundary layer theory can be extended to encompass mass transfer across both the fluids. The assumption that a boundary layer exists close to both sides of the interface is characteristic of liquid slag-metal systems which feature in numerous metal extraction and refining processes. In the case of a species being transferred from the bulk metal to the slag, we can think of one mass transfer coefficient for the metal and another for the slag.

#### VARIOUS STEPS IN HETEROGENEOUS REACTIONS

Consider the case of a solute species being transferred from one liquid phase (metal) to another (slag), both being subjected to stirring, the transfer being effected through the chemical reaction at the interface. The steps involved in the process are:

- (1) transporting the solute species from the bulk metal to the interface,
- (2) the reaction occurring at the interface of the phases, and
- (3) transporting the product species from the interface to the bulk slag.

These steps operate one after the other, and one of them is slower than the rest. Therefore, the slowest step determines the rate of the overall process. If the transport in the metal is rate-controlling, the concentration profile is as shown in Fig. 2.10a, and if the transport in the slag is rate-controlling, the concentration profile is as shown in Fig. 2.10b. The chemical reaction at the

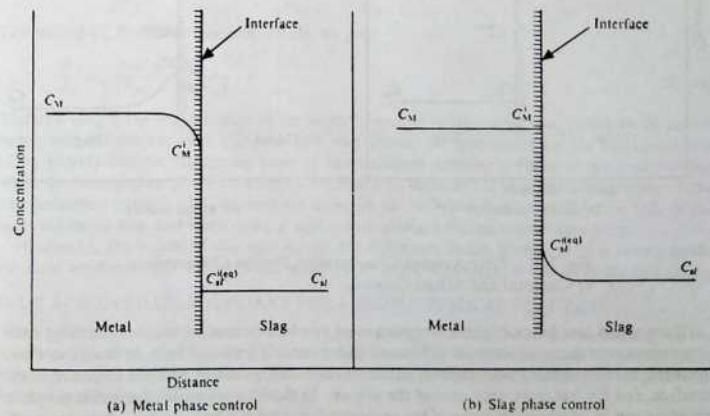


Fig. 2.10 Time Average Concentration Profiles Characteristic of Transport Control.

interface, where the slag and the metal are in equilibrium, is comparatively fast. The concentration of the species in the slag phase is given by the equilibrium value  $C_{sl}^l$ . When the transport step is slow in the metal phase and fast in the slag phase, the concentration of the species in the bulk slag is equal to that at the interface, but in the metal phase there is a concentration gradient near the interface corresponding to the boundary layer already referred to in Fig. 2.9b. This is shown in Fig. 2.10a. Figure 2.10b represents the case where transport step in the slag is slow and, hence, rate-controlling. When the reaction at the interface is rate-controlling, the slag and the metal are not in equilibrium with the species transported to the interface. The concentration of the solute in the slag  $C_{sl}$  is lower than the equilibrium value  $C_{sl}^{(eq)}$  at the interface. Since the transport steps are fast, there is no concentration gradient either in the metal or in the slag. The corresponding concentration profile existing under these conditions is shown in Fig. 2.11a. Apart from the situations existing in Figs. 2.10a, 2.10b, and 2.11a a fourth possibility exists, namely, mixed control, corresponding to a situation where both the transport steps and the chemical reaction determine the overall rate of reaction. In such an instance, the metal and the slag are out of equilibrium, and concentration gradients exist in the slag and the metal phases, as depicted in Fig. 2.11b.

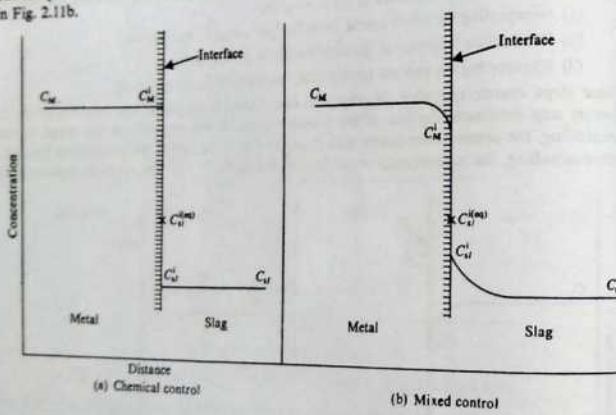


Fig. 2.11 Time Average Concentration Profiles Characteristic of Chemical and Mixed Control.

The reaction rate for each of the foregoing steps can be expressed in terms of a driving force (concentration or chemical potential difference) and a suitable resistance term. In situations where the chemical reaction takes place rapidly, equilibrium conditions can be assumed to prevail at the interface, and the transport steps control the process. In these situations, the flux across the phase boundary can be expressed in terms of the concentration gradients and the mass transfer coefficients. Richardson (1974) has derived the following relationships which permit us to assess the

relative importance of the resistances in the metal and the slag, and the way in which the transport is influenced by the partition coefficient of the species distributed between the metal and the slag.

Consider a liquid metal being refined by the action of a liquid slag lying above it. The impurity species present in the metal move from the metal to the slag (Concentration gradients are shown in Figs. 2.10a and 2.10b.). Figures 2.10a and 2.10b depict the two possible control mechanisms when the chemical reaction takes place rapidly and equilibrium conditions prevail at the interface. (It is assumed that there is no build-up of the impurity species at the interface.) The concentrations of such species in the metal and in the slag are denoted by  $C_M$  and  $C_{sl}$ , respectively, and those at the interface by  $C_M^l$  and  $C_{sl}^l$ . The flux  $\dot{n}$  across the interface is given by

$$\dot{n} = A_S K_M (C_M^l - C_M), \quad (2.142)$$

$$\dot{n} = A_S K_{sl} (C_{sl}^l - C_{sl}), \quad (2.143)$$

where  $A_S$  is the interface area, and  $K_M$  and  $K_{sl}$  the mass transfer coefficients in the metal and the slag, respectively.

If  $m$  is the partition coefficient for the equilibrium distribution of the impurity species between the metal and the slag, then we have

$$m = \frac{C_M^l}{C_{sl}^l},$$

$$\dot{n} = A_S K_M (m C_{sl}^l - C_M),$$

$$\dot{n} = A_S \frac{K_{sl}}{m} (m C_{sl}^l - m C_{sl}).$$

Eliminating  $C_M^l$  from these three equations, we get

$$\frac{\dot{n}}{A_S} = \frac{m C_{sl}^l - C_M}{(1/K_M) + (m/K_{sl})}. \quad (2.144)$$

The term  $m C_{sl}^l$  is the concentration of the impurity species in the metal that would be in equilibrium with the concentration  $C_{sl}^l$  in the bulk slag. Hence, the numerator on the right-hand side of eq. (2.144) denotes the driving force of the transport process in terms of the concentration while the denominator denotes the overall resistance to transport. The relative magnitude of the two resistance terms in the denominator depends on  $m$ . When  $m/K_{sl} \ll 1/K_M$ , then  $1/K_M$  is the main resistance term and when  $m/K_{sl} \gg m/K_M$ , then  $m/K_{sl}$  is the main resistance term.

Generally, the values of  $K_M$  and  $K_{sl}$  do not differ very much. Therefore, if  $m$  is very small, the main resistance term will be in the metal phase and if  $m$  is large, it will be in the slag phase.

#### FLUX ACROSS PHASE BOUNDARY FOR A SLOW CHEMICAL REACTION

When a chemical reaction is very slow, it can be assumed that equilibrium is not attained at the interface. Therefore,  $C_M^l/C_M \neq m$ . An equation similar to (2.144) has been derived (Richardson, 1974) for such a case by assuming that the reaction at the interface is of the first order in both forward and backward directions:

$$\frac{\dot{n}}{A_S} = C_{sl}^l k_1 - C_M^l k_2, \quad (2.145)$$

where  $k_1$  and  $k_2$  are the two chemical rate constants.  
If equilibrium can exist between the metal phase and the slag phase, the chemical rates in both directions would be equal. In such a situation, we have

$$k_1 C_M = k_2 C_M^{\prime}, \quad (2.147)$$

$$\frac{k_1}{k_2} = \frac{C_M^{\prime}}{C_M} = m.$$

Therefore,

$$\frac{n}{A_S} = m k_2 C_M^{\prime} - C_M k_2, \quad (2.148)$$

$$\frac{n}{A_S k_2} = m C_M^{\prime} - C_M.$$

Combining eqs. (2.142), (2.143), and (2.147), we get

$$\frac{n}{A_S} = \frac{m C_M^{\prime} - C_M}{\left(\frac{1}{k_M} + \frac{1}{k_2} + \frac{m}{k_M}\right)}. \quad (2.149)$$

On the right-hand side of eq. (2.149), the numerator represents the overall driving force and the denominator the resistance terms. It can be seen that the overall resistance term now contains the chemical rate constant.

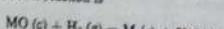
Referring back, we see that Fig. 2.11a gives the concentration profile for a chemically controlled transfer process. The interfacial concentration  $C_M^{(eq)}$  is the concentration which is or would be in equilibrium with  $C_M^{\prime}$ . In this case, the value of the chemical resistance would be much higher than that of the transport resistance terms both in the slag and the metal. Mixed control results when all the three resistance terms are of comparable magnitude. The concentration profile for such a case is shown in Fig. 2.11b.

## 2.20 GAS-SOLID REACTIONS

Besides those already mentioned, another class of heterogeneous reactions important in metallurgy are those occurring between flowing gases and reacting solids. For example, roasting of sulphide ores in air; reduction of metal oxides with reducing gases, hydrochlorination or chlorination of ores, and oxidation of metals in air. In such reactions, a solid reaction product is generally obtained which forms a layer between the unreacted solid and the reacting gas. Therefore, some material has to be transported, by diffusion, through this layer of the reaction product.

### CONSECUTIVE STEPS IN GAS-SOLID REACTIONS

When a pellet of a metal oxide MO is reduced by hydrogen, the reaction product is a layer of reduced metal. For the sake of simplicity, this type of gas-solid reaction is considered in detail. The reduction reaction is



Although more realistic models than the present one have been recently proposed to deal with gas-solid reactions, we give here a simplified treatment based on topochemical reaction behaviour. This treatment is applicable to dense pellets (see Hills, 1967). In a topochemical model, the

reaction front proceeds linearly towards the centre and the shrinking core of the unreacted material retains the initial shape of the pellet. The model is shown in Fig. 2.12.

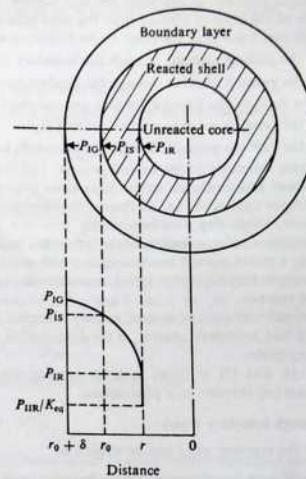


Fig. 2.12 Topochemical Reaction Model.

In this model, irrespective of the actual reaction mechanism, the equation

$$\dot{n} = 4\pi r^2 \rho \frac{dr}{dt} \quad (2.151)$$

is valid. Here,  $\dot{n}$  is the rate of the reaction (moles/sec),  $r$  the radius (cm) of the reaction front, and  $\rho$  the molar density ( $\text{gm mole cm}^{-3}$ ).

When a gas reacts with a solid, irrespective of the conceptual model of the reduction process, three basic steps are involved.

#### Step I

An external mass transfer step involving the diffusion of the reactant and product gases through the film boundary layer surrounding the spherical oxide pellet undergoing reduction.

#### Step II

The diffusion of the reactant and product gases through the porous solid product layer or the solid-state diffusion of ions through this layer.

**Step III**  
The adsorption of the gaseous reactant at the solid reactant surface, chemical reaction at the interface, and the desorption of the gaseous product from the solid reactant surface.

The aforementioned steps occur one after the other in the following sequence:

- I (a) Diffusion of the gaseous reactant through the boundary layer.
- II (a) Diffusion of the gaseous reactant through the product layer.
- III Chemical reaction between the gaseous reactant and the solid at the interface.
- II (b) Diffusion of the product gas through the product layer.
- I (b) Diffusion of the gaseous product through the boundary layer.

Each of these steps offers some resistance to the overall process. The overall effect of the steps is additive, analogous to electrical resistances in series. Since these steps take place consecutively, the bottle-neck principle becomes applicable, i.e., in theory, the slowest step of those just listed determines the rate. However, single-step rate-determining processes are extremely rare, the majority of the solid-gas reactions being simultaneously influenced by more than one step. The latter situation corresponds to a mixed control mechanism in which two or more of the resistances involved in the aforementioned steps make roughly equal contributions to the overall resistance offered to the progress of the reaction.

We generally consider two extreme cases of control, namely, chemical control, if the diffusional resistance is negligibly small and transport control, if the contribution of the chemical reaction to the overall resistance is negligible.

We now discuss Steps I, II, and III in detail in order to understand the interplay between transport phenomena and chemical reaction rate phenomena.

#### Step I (a) Mass transfer through boundary layer

The reaction rate in terms of the reactant gas I can be written as

$$\begin{aligned} \dot{n}_I &= \text{mass transfer coefficient} \times \text{surface area} \times \text{concentration gradient} \\ &= K_{M(I)} A \pi r_0^2 \left( \frac{P_{IG}}{RT} - \frac{P_{IS}}{RT} \right) \\ &= \frac{P_{IG} - P_{IS}}{RT [1/(4\pi r_0 K_{M(I)})]} \end{aligned} \quad (2.152)$$

where  $K_{M(I)}$  is the mass transfer coefficient for the transfer of the gaseous species between the gas phase and the surface of the pellet,  $r_0$  the initial radius of the pellet,  $P_{IG}$  the partial pressure of the reactant gas I in the bulk,  $P_{IS}$  the partial pressure of the reactant gas I at the surface of the pellet (both shown in Fig. 2.12),  $R$  the gas constant, and  $T$  the temperature in K.

An equation similar to eq. (2.152) may be written in terms of the product gas II and the mass transfer coefficient  $K_{M(II)}$ . Henceforth, subscripts I and II, respectively, denote reactant and product gases. In the example, given by reaction (2.150), I stands for  $H_2$  and II stands for  $H_2O$ . Eliminating  $\dot{n}_I$  between eqs. (2.151) and (2.152), and integrating the resulting equation between the limits  $r_0$  and  $r$ , and 0 and  $t$ , we obtain

$$t = \frac{(1 - r^{*2}) \rho_{IG} RT}{3(P_{IG} - P_{IS}) K_{M(II)}} \quad (2.153)$$

where  $r^*$  is the dimensionless radius of the reaction front given by  $r/r_0$ .

If  $t_c$  is the time required for the complete reduction of the pellet and if  $t$  is the time taken for the radius of the reaction front to be changed to  $r$ , then we have

$$\frac{t}{t_c} = (1 - r^{*2}). \quad (2.154)$$

#### Step II(a) (Diffusion through product layer)

As in Step I(a), the following equations can be derived assuming a quasi-steady state condition:

$$\begin{aligned} \dot{n}_I &= D_{I(\text{eff})} \frac{4\pi r_0}{r_0 - r} \left( \frac{P_{IS}}{RT} - \frac{P_{IR}}{RT} \right) \\ &= \frac{P_{IS} - P_{IR}}{RT((r_0 - r)/(4\pi r_0 D_{I(\text{eff})}))}, \end{aligned} \quad (2.155)$$

where  $D_{I(\text{eff})}$  is the effective diffusivity of the reactant gas in the product layer and  $P_{IR}$  the pressure of the reactant gas at the reaction front.

As before, eliminating  $\dot{n}_I$  between eqs. (2.151) and (2.155), and integrating the resulting equation between the limits  $r_0$  and  $r$ , and 0 and  $t$ , we get

$$t = \frac{r_0^2 \rho RT [1 - 3r^{*2} + 2r^{*3}]}{6D_{I(\text{eff})}[P_{IS} - P_{IR}]} \quad (2.156)$$

If  $t_c$  is the time taken for complete reduction, then

$$\frac{t}{t_c} = 1 - 3r^{*2} + 2r^{*3}. \quad (2.157)$$

Step II(a) involves the diffusion of the gaseous species through a porous solid. Most experimental observations show that the oxide pellet retains its original shape during the reaction and that the product layer formed has a higher porosity than the original compacted pellet. While the diffusivity of a gas in a multicomponent system can be theoretically derived, empirical methods are needed to determine diffusivity in a porous solid. The relation between the effective diffusivity in a porous solid, which is lower than the bulk diffusivity, is given by

$$D_{(\text{eff})} = D \frac{\epsilon}{\tau}, \quad (2.158)$$

where  $\epsilon$  is the porosity factor and  $\tau$  the tortuosity factor.

#### Step III (Chemical reaction at interface)

It is generally assumed that the gaseous reactants get adsorbed at the solid reactant surface and that the adsorbed molecules take part in a chemical reaction to form the product solid and a gas. The gas gets desorbed from the surface before it is transported out through the product layer. Since the reaction rate depends on the concentration of the reactants adsorbed at the surface, in computations, we use the first-order kinetics. Therefore, rate reaction is written as

$$\dot{n}_I = 4\pi r^2 k_f \frac{P_{IG}}{RT} \quad (2.159)$$

where  $k_f$  ( $\text{cm sec}^{-1}$ ) is the chemical rate constant of the forward rate reaction. If the reaction is reversible, as in the case of  $\text{FeO}$ , and if  $k_b$  ( $\text{cm sec}^{-1}$ ) is the chemical rate constant of the backward reaction, then

$$\begin{aligned} k_f &= 4\pi r^2 k_f \frac{P_{IO}}{RT} - 4\pi r^2 k_b \frac{P_{IO}}{RT} \\ &= 4\pi r^2 \frac{k_f}{RT} (P_{IO} - \frac{P_{IO}}{K_{eq}}) \end{aligned} \quad (2.160)$$

where  $K_{eq}$  is the equilibrium constant. This is because

$$k_f(P_{IO})_{eq} = k_b(P_{IO})_{eq} \quad (2.161)$$

$$\frac{(P_{IO})_{eq}}{(P_{IO})_{eq}} = K_{eq} = \frac{k_f}{k_b} \quad (2.162)$$

It may be noted that  $k_f$  is normally called the chemical rate constant  $k_c$ . Further,

$$k_f = \frac{P_{IO} - (P_{IO}/K_{eq})}{RT[1/(4\pi r^2 k_c)]} \quad (2.163)$$

Eliminating  $k_f$  between eqs. (2.151) and (2.163) and integrating the resulting equation between the limits  $r_0$  and  $r$  and 0 and  $t$ , we obtain the equation showing the dependence of fractional reduction on time  $t$  as

$$1 - r^* = \frac{k_c}{\rho \nu_0 RT} [P_{IO} - \frac{P_{IO}}{K_{eq}}] t \quad (2.164)$$

or

$$1 - r^* = k'_c t, \quad (2.165)$$

where  $k'_c$  is a constant. If  $t_e$  is the time taken for complete reduction, then

$$\frac{t}{t_e} = 1 - r^*. \quad (2.166)$$

The driving force for the aforementioned three steps is the difference in the concentration of the gas in the bulk and at the reaction front, and may be written as follows:

(1) For mass transfer through the boundary layer, the driving force is  $[P_{IO}/(RT)] - [P_{IR}/(RT)]$ .

(2) For diffusion through the product layer, the driving force is  $[P_{IS}/(RT)] - [P_{IR}/(RT)]$ .

(3) For the chemical reaction, the driving force, taking into account the forward and backward reaction, is  $[P_{IO}/(RT)] - [P_{IR}/(RT K_{eq})]$ .

Hence, the overall driving force is  $[1/(RT)][P_{IO} - (P_{IR}/K_{eq})]$ .

The rate of reduction of the pellet can be expressed in terms of an overall concentration difference or driving force and an overall resistance corresponding to the aforementioned three steps.

$$R_f = \frac{P_{IO} - (P_{IR}/K_{eq})}{[1/(RT)][1/(4\pi r^2 K_{M(I)}) + (r_0 - r)/(4\pi r_0 D_{IR,eff}) + 1/(4\pi r^2 k_c)]} \quad (2.167)$$

In practice, the concentrations of the reactant and product gases are difficult to determine at intermediate stages. The partial pressure of the gas in the bulk  $P_{IO}$  can be estimated, whereas the concentration of the product gas  $P_{IR}$  at the interface cannot. However,  $P_{te}$ , the equilibrium pressure at the interface can be determined if we assume that equilibrium prevails at the interface. Now, it can be shown that

$$\frac{P_{IR}}{RT} - \frac{P_{IR}}{RT K_{eq}} = \frac{1}{RT}(P_{IO} - P_{te})(1 + \frac{1}{K_{eq}}). \quad (2.168)$$

Therefore,

$$R_f = \frac{P_{IO} - P_{te}}{RT \frac{1}{4\pi r^2 K_{M(I)}} + \frac{r_0 - r}{4\pi r_0 D_{IR,eff}} + \frac{1}{4\pi r^2 k_c (1 + 1/K_{eq})}}. \quad (2.169)$$

In the denominator of eq. (2.169), the first term represents the resistance in the boundary layer, the second term the resistance in the product layer, and the third term the chemical resistance.

#### IDENTIFICATION OF RATE-CONTROLLING STEPS

From the foregoing discussion, we may contend that it should be easy to identify the rate-controlling step because the pattern of reduction is different under different rate-controlling steps. For example, plots of  $t/t_e$  versus  $r^*$  should have different shapes, depending on the rate-controlling step, as shown by eqs. (2.154), (2.157), and (2.166). Although three curves with differing shapes are predicted, in actual practice, it is rather difficult to distinguish among them except when one control mechanism predominates to the exclusion of the two others. The difficulty in most cases arises due to the probability of mixed control and due to the scatter in the plot as a result of experimental errors. Moreover, isothermal behaviour of the reacting pellet is assumed in deriving the equations, which may not be true. If the reaction is highly exothermic or endothermic, the temperature of the pellet could be substantially different from that of the surroundings, and this, in turn, affects the diffusivities and reaction rates. Therefore, due allowance should be made for the temperature difference generated.

#### 2.21 ELECTROCHEMISTRY

Electrochemistry is the study of processes involved in the interconversion of *electrical energy* and *chemical energy*—generally in ionically conducting media. Such media include aqueous solutions (usually acidulated to make them better conductors of electricity), molten salts and silicates, and organic liquids. In electrochemical reactions, the current flows over finite distances which are greater than interatomic distances.

Ionic conductance may exist for both the solid and liquid states. Ohm's law, generally valid for metallic conduction, is applicable to it. Ionic conductance is ascribed to the movement of positively and negatively charged particles under the influence of a potential gradient. Since the ions have a significant mass by themselves, ionic conduction is accompanied by mass transfer. The current, which is a measure of the mobility of ions, depends on various factors, such as the size of the ions, the total ionic interactions, the temperature, and the applied voltage. During electrodeposition, charged particles move to either of the two electrodes, namely, the cathode or the anode, depending on the charge they carry. The ions are neutralized at the electrodes and then set free as atoms or molecules. Figure 2.13 shows a basic electrical circuit and gives some electrochemical terms.

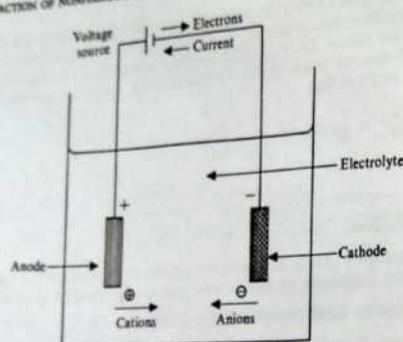
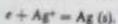


Fig. 2.13 Basic Electric Circuit.

## FARADAY'S LAWS OF ELECTROLYSIS

Faraday's first law states that, during electrolysis, the chemical action produced by a current at an electrode is proportional to the quantity of electricity passed, and his second law states that the masses of substances deposited on or dissolved at several electrodes (which are in series) by the same quantity of electricity are directly proportional to their chemical equivalent weights. (It may be noted that the quantity of charge that generates 1 gm equivalent weight of any chemical is called a *faraday*. A faraday is equal to 96,493.1 coulombs.)

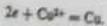
In an electrolytic cell, the reaction for the deposition of silver on the cathode is



The equivalent weight of Ag is here equal to its atomic weight 107.88. Therefore, 96,493.1 coulombs would deposit 107.88 gm of silver. The same amount of electricity would deposit 1 gm of hydrogen and 8 gm of oxygen. Faraday's laws can be stated simply as follows. One gm equivalent of any substance is produced or dissolved by the passage of 96,493.1 coulombs of electricity. We now consider two examples of the application of Faraday's laws.

**Example 1** Calculate the time required to deposit 1 gm of copper from a solution of  $CuSO_4$ , using a current of 3 amperes.

Assume that the only reaction taking place is



Since two electrons are required for depositing one  $Cu^{2+}$  ion, the gm equivalent weight of copper is  $63.54/2$  or 31.77. Thus, number of equivalent weights required to be deposited is  $1/31.77$  and the quantity of current required is  $96,493/31.77$  coulombs. Therefore,

$$\text{time required} = \frac{96,493}{31.77 \times 3} = 1012.4 \text{ sec.}$$

**Example 2** Three electrolytic cells which are connected in series contain, respectively, silver nitrate, copper sulphate, and dilute sulphuric acid at  $17^\circ C$  and 750 mm pressure. An electric current is passed through the electrodes (made of platinum) of each cell. If 3.6 gm of silver are deposited in the first cell, what is the weight of copper deposited in the second cell and what is the volume of hydrogen evolved in the third cell?

According to Faraday's second law, the amounts deposited are proportional to their equivalent weights, that is,

$$\frac{\text{wt of copper}}{\text{wt of silver}} = \frac{(\text{at wt of copper}/2)}{\text{at wt of silver}} = \frac{31.78}{108}$$

Therefore,

$$\text{wt of copper deposited} = \frac{31.78}{108} \times 3.6 = 1.06 \text{ gm.}$$

Similarly,

$$\text{wt of hydrogen evolved} = \frac{3.6 \times 1}{108} = \frac{1}{30} \text{ gm.}$$

Therefore,

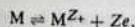
$$\text{volume of } H_2 \text{ at NTP} = \frac{22,400}{2 \times 30} = \frac{1120}{3} \text{ ml,}$$

$$\text{volume at } 17^\circ C \text{ and 750 mm} = \frac{1120}{3} \times \frac{760}{273} \times \frac{290}{750} = 401.87 \text{ ml.}$$

## ELECTRODE POTENTIAL

When a metal that conducts electricity is immersed in a fused salt or aqueous solution possessing ionic conductivity, a potential difference (potential jump) builds up at the interface between the two phases. This potential difference, called *electrode potential*, arises due to the transfer of ions or electrons on breaking their bonds with the substances in one phase and reacting to form new bonds with substances in the other phase. Such charge-transfer reactions are electrochemical in nature. The metal electrode consists of metal ions bound together by the attraction of free electrons which enable it to conduct electricity.

We can look at the foregoing discussion from another viewpoint. When the metal is in contact with the liquid phase of a melt, the cations of the metal (located at the surface of the metal electrode) are subjected to the strong action of the anions of the melt. As a result of such interaction, a few cations leave the bulk metal and migrate to the neighbouring layers of the liquid. Thus, the metal electrode becomes negatively charged. The dissolution of the metal cannot continue indefinitely because of the electrostatic interaction between the ions which have migrated from the bulk metal and because of the metallic surface which has now acquired a negative potential. The reaction is



where Z is the number of positive charges on the ion.

Various factors, such as the nature of the chemical activity of the metal itself (unity for a

pure metal) and the concentration of its ions in the liquid determine the magnitude of the electrode potential and, hence, its dynamic equilibrium state.

In an electrolytic cell, the potential difference at the interface between the metal and the liquid surface cannot be measured experimentally, only the potential difference between two electrodes (or the emf (electromotive force)) of a cell (composed of the electrode undergoing decomposition and another electrode—known as a reference electrode—whose potential is arbitrarily taken as zero) can be measured directly. Electrode potentials are expressed with respect to a reference electrode. There are, however, a large number of reference electrodes. For an aqueous solution, the standard hydrogen electrode is conventionally used as the reference electrode.

## 2.22 CELLS AND THERMODYNAMIC RELATIONS

Consider a simple cell consisting of two electrodes (see Fig. 2.14). The negative electrode (cathode)

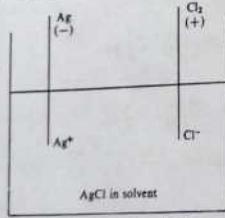


Fig. 2.14 Simple emf Cell.

is made of silver and the positive electrode (anode) of graphite bathed in chlorine under 1 atm. The electrolyte is AgCl dissolved in a solvent. The reaction at the cathode is



and the reaction at the anode is



The overall cell reaction in the solution is



In this cell, the emf measured between the two electrodes is the difference between the two electrode potentials. The magnitude of the external work performed by the cell depends on the emf generated by the cell, its value being a maximum when the cell reaction takes place reversibly. Such a condition can be attained if an external potential source is connected in opposition to, and adjusted to exactly balance, the cell emf so that no current flows in the external circuit. Under these conditions, the reversible free energy change  $\Delta G$  is related to the emf generated.

Equation (2.25) has been derived on the assumption that the only reversible work done by

the system is that of expansion. However, if the system also does some electrical work, the equation should be modified to

$$dG = v dp - S dt - w', \quad (2.170)$$

where  $w'$  is the electrical work done. Therefore, at constant temperature and pressure,  $dG = -w'$ . For a cell reaction involving stoichiometric quantities of reactants and products, the quantity of electricity required is  $ZF$ , where  $Z$  is the number of electrons required for the cell reaction to occur and  $F$  is Faraday's constant. The amount of electrical work done when  $Z$  electrons are involved in the cell reaction is  $ZFE$  joules, where  $E$  is the emf of the cell in volts. Therefore,

$$\Delta G = -ZFE. \quad (2.171)$$

When all the reactants and products that take part in a reaction in a reversible cell are in their standard states, i.e., at unit activity, the emf of the cell is the standard value  $E^\circ$ . For the cell shown in Fig. 2.14, the standard value  $E^\circ$  is measured if AgCl is pure. Such a standard value is the standard formation potential and the standard free energy of formation of AgCl is given by

$$\Delta G^\circ = -ZFE^\circ = -RT^\circ K. \quad (2.172)$$

For a reaction involving  $a$  atoms of A and  $b$  atoms of B as reactants, and  $l$  atoms of L and  $m$  atoms of M as products,

$$aA + bB = lL + mM, \quad (2.173)$$

and equations similar to (2.35) can be written as

$$\Delta G = \Delta G^\circ + RT \ln \left( \frac{a_L^l \cdot a_M^m}{a_A^a \cdot a_B^b} \right).$$

Therefore, if the reaction takes place in a cell, for the passage of  $Z$  faradays,

$$\begin{aligned} ZFE &= ZFE^\circ - RT \ln \left( \frac{a_L^l \cdot a_M^m}{a_A^a \cdot a_B^b} \right), \\ E &= E^\circ - \frac{RT}{ZF} \ln \left( \frac{a_L^l \cdot a_M^m}{a_A^a \cdot a_B^b} \right). \end{aligned} \quad (2.174)$$

By regarding  $E^\circ$  as the difference between two constants  $E_1^\circ$  and  $E_2^\circ$  corresponding, respectively, to two electrode reactions which together make up the cell reaction, and by separating the activities into two parts we may write

$$E = (E_1^\circ - \frac{RT}{ZF} Z \ln a_1^\circ) - (E_2^\circ - \frac{RT}{ZF} Z \ln a_2^\circ), \quad (2.175)$$

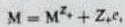
where  $a_1$  and  $a_2$  are the activity terms applicable to the two electrodes and  $v_1$  and  $v_2$  are the number of molecules or ions of the corresponding species, respectively, involved in the cell reaction. Equation (2.175) effectively splits the cell emf  $E$  into two parts,  $E_1$  and  $E_2$  which give the separate electrode potentials.

In general, the electrode potential is given by

$$E_i = E_i^\circ - \frac{RT}{ZF} Z \ln a_i^\circ \quad (2.176)$$

in terms of the standard potential ( $E^\circ$ ) and of the activities of the species  $i$  involved in the electrode reaction. The standard potential, obviously, is the potential of the electrode when all the species are at unit activity, i.e., they are in their standard states.

If the electrode consists of a metal M whose valency is  $Z_+$ , reversible with respect to  $M^{Z_+}$  ions, so that the electrode reaction is



the equation for the potential becomes

$$E_+ = E^\circ - \frac{RT}{Z_+F} \ln \frac{a_{M^{Z_+}}}{a_M}, \quad (2.177)$$

where  $a_M$  is the activity of the solid metal and  $a_{M^{Z_+}}$  is that of the cations in the solution with which the metal is in equilibrium. By convention, the solid state of the metal is taken as the standard state of unit activity; therefore, for an electrode consisting of the pure metal, replacing  $a_M$  by unity, we have

$$E_+ = E^\circ - \frac{RT}{Z_+F} \ln a_{M^{Z_+}}. \quad (2.178)$$

For an electrode consisting of a substance A which is reversible with respect to the anions  $A^{Z_-}$ , the electrode reaction is



and the equation for the electrode potential is

$$E_- = E^\circ - \frac{RT}{Z_-F} \ln \frac{a_A}{a_{A^{Z_-}}}. \quad (2.179)$$

As already mentioned, the activity  $a_A$  of the substance A in the pure state, or, if A is a gas, then the activity at 1 atm is taken as unity, so that the eq. (2.179) can be rewritten as

$$E_- = E^\circ + \frac{RT}{Z_-F} \ln a_{A^{Z_-}}. \quad (2.180)$$

The general equation for any electrode reversible with respect to a single ion of valence  $Z_\pm$  is

$$E_\pm = E^\circ \mp \frac{RT}{Z_\pm F} \ln a_i, \quad (2.181)$$

where  $a_i$  is the activity of the particular ionic species  $i$ . In eq. (2.181), the  $+$  sign in the subscripts refers to a positive ion, whereas the  $-$  sign refers to a negative ion.

### 2.23 ARBITRARY POTENTIAL ZERO: THE HYDROGEN SCALE

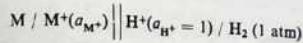
The activity of an individual ionic species cannot be determined experimentally, and is not a well-defined quantity. Since a single electrode potential involves the activity of an individual ionic species, it has no strict thermodynamic significance; however, by employing such a potential, we overcome the difficulty by defining the arbitrary zero of potential. Such a definition becomes necessary because a single electrode potential also cannot be measured experimentally. This

definition, which is now widely adopted, was first put forth by W. Nernst; subsequently modified, it reads as follows: The potential of a reversible hydrogen electrode, with hydrogen gas at 1 atm in equilibrium with a solution of hydrogen ions at unit activity, shall be taken as zero at all temperatures.

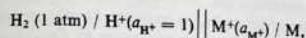
According to the foregoing definition, the standard potential of the hydrogen electrode is the arbitrary zero of potential; electrode potentials based on this zero are referred to as the hydrogen given electrode with a standard hydrogen electrode.

### SIGN OF ELECTRODE POTENTIAL

The emf of the cell



is clearly equal and opposite to that of the cell



so that the sign of the electrode potential when expressed as  $M / M^+$ , must be equal and opposite to that expressed as  $M^+ / M$ . Although it has generally been agreed that the arbitrary zero of potential is that of the standard hydrogen electrode, two opposing conventions exist with respect to the sign of the electrode potential, i.e., those electrode potentials which are accepted as positive on the hydrogen scale in the U.S.A. are considered negative in Europe. A list of standard electrode potentials is given in Table 3.2, the sign convention being American. It may be noted that the International Union of Pure and Applied Chemists has adopted the European sign convention.

The magnitude of the electrode potential is related to the ease with which a metal passes into solution; it should be numerically equal to the potential that must be applied in the opposite direction to just prevent the dissolution of the metal. The electrode potential series (see Table 3.2) gives the order of the decreasing tendency of the metals to form ions, or, in other words, the order of decreasing chemical reactivity. Noble metals such as gold, silver, and mercury (so named because they are extremely difficult to dissolve) appear at the bottom of the electrode potential series and the most reactive metals such as potassium and sodium (which are extremely difficult to obtain as free metals) appear at the top. The lower down the series a metal appears, the more noble it is. Further, if a metal A is placed in a solution containing ions of another metal B, then, if A is less noble than B, it tends to replace B in the solution and B tends to get deposited as free metal.

### EMF SERIES IN NONAQUEOUS SOLVENTS

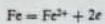
It should be noted that the hydrogen reference electrode is applicable only to aqueous solutions, i.e., solutions in which hydrogen ions are always present. Since some nonaqueous solvents, such as fused salts, do not contain hydrogen ions, the concept of other kinds of reference electrodes becomes necessary. Although the discussion of such a concept is beyond the scope of this work, it may be noted that various emf series, based on different reference electrodes, have much in common. In other words, the orders of reactivity of elements remain almost the same in all reaction media.

## APPLICATIONS OF ELECTRODE POTENTIALS

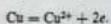
We now give examples of the application of the concept of the electrode potential.

## Plating of Copper on Iron (by Immersion of Iron Plate in Copper Sulphate Solution)

In the electrochemical series, iron is placed above copper. This implies that the tendency of iron to pass into solution as  $\text{Fe}^{2+}$  is greater than that of copper to pass into solution as  $\text{Cu}^{2+}$ . In other words, for comparable activities of the ions, the reaction



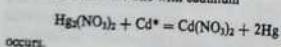
is thermodynamically more favourable than the reaction



The foregoing reactions show that some iron dissolves and precipitates copper on the iron plate. However, we should remember that the plating reaction cannot continue indefinitely. The final result depends on both thermodynamic and kinetic factors. As iron dissolves, the  $\text{Fe}^{2+}$  concentration in the solution increases and the  $\text{Cu}^{2+}$  concentration decreases. Therefore, the  $\text{Fe}/\text{Fe}^{2+}$  potential gradually decreases and the  $\text{Cu}/\text{Cu}^{2+}$  potential gradually increases. In other words, with the passage of time, it becomes more difficult to dissolve iron and easier to dissolve copper. Equilibrium is reached when the  $\text{Fe}/\text{Fe}^{2+}$  potential becomes equal to the  $\text{Cu}/\text{Cu}^{2+}$  potential. If copper forms a coherent deposit on the iron plate, preventing it from coming in contact with the solution, then the reaction may stop prematurely.

## Purification of Mercury

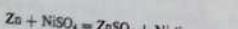
Impurities that are less noble than mercury may be removed by allowing very fine droplets of mercury to fall through a column of nitric acid containing dissolved mercurous nitrate, when reactions such as the one with cadmium



occurs.

## Purification of Zinc

Impurities more noble than zinc can be removed from zinc by dissolving it in sulphuric acid to form a zinc sulphate solution and by adding to this solution a small amount of extremely pure zinc. This pure zinc passes into solution at the expense of impurities more noble than zinc. For example,



The electrolysis of the zinc sulphate solution yields exceptionally pure zinc metal after the deposited impurities have been removed by filtration.

## Protection of Iron by Zinc

In the galvanizing of iron, a metal such as zinc or cadmium (both of which are less noble than iron) is used. In the event of a flaw in the coating of the iron, or of damage, which exposes the

\*Impurity in mercury.

underlying iron, contact with a corrosive solution such as condensed atmospheric moisture containing dissolved carbon dioxide, air, etc., results in the preferential dissolution of the coating metal.

## 2.24 KINETICS OF ELECTRODE PROCESSES

Consider a metal M in contact with its metal ions  $M^{2+}$  in solution. The tendency of the metal ions from the electrode to go into solution is opposed by the ions in solution which try to get themselves discharged on to the metal. The rates of transfer of metal ions can be expressed in terms of the absolute reaction rate theory (discussed in Section 2.16) as

$$M = M^{2+} + Ze$$

Figure 2.15a represents the energy barriers that the ions have to surmount. (This figure is similar to Fig. 2.8, except that the reaction coordinate is replaced by actual distances extending outwards from the surface of the electrode.) The free energy of the metal ion  $M^{2+}$  in solution is  $G_e$ ; when it is a part of the metal electrode,  $G_M$  is its free energy. In Fig. 2.15a, the activation energies for the forward anodic reaction and the backward cathodic reaction are shown as  $\Delta G_a^*$  and  $\Delta G_c^*$ , respectively. Since the free energy of the ion in solution is at a lower level, the free energy decreases when the ions migrate to the solution from the electrode. Therefore, under the conditions shown in Fig. 2.15a, the metal is not in equilibrium with the ions in solution. What actually happens is that an increasing number of metal ions move into the solution, the metal becomes more negatively charged because of the electrons left behind, and, consequently, the value of  $G_M$  falls. As more ions go into solution, the metal ion concentration increases, and the solution becomes more positively charged, resulting in an increase in the value of  $G_e$ . When equilibrium is attained between the ions in the metal and those in the solution,  $G_M$  becomes equal to  $G_e$ . Such a condition is shown in Fig. 2.15b. This equilibrium is dynamic; i.e., the ions move from the metal to the solution and vice versa. A definite potential difference builds up between the metal and the solution; the currents flowing in opposite directions are equal and there is no net flow of ions. The potential difference between the metal and the solution, under these conditions, is called the equilibrium electrode potential (already discussed in Section 2.22). Since no finite current is passed, the metal solution system is truly thermodynamically reversible.

According to the absolute reaction rate theory, the rate of transfer of ions from the metal to the solution  $V_1$  is given by

$$V_1 = K_1 \exp \left( -\frac{\Delta G_a^*}{RT} \right), \quad (2.182)$$

where  $K_1$  is a constant depending on the nature of the metal M and the temperature. Similarly, the rate of discharge of ions on the metal  $V_2$  is given by

$$V_2 = K_2 \exp \left( -\frac{\Delta G_c^*}{RT} \right), \quad (2.183)$$

where  $K_2$  is another constant. Since the system operates under conditions of reversible equilibrium,  $V_1 = V_2$ . Now, we assume that the metal electrode forms a part of a system where a net reaction takes place and the ions leave the metal at a rate faster than that of the ion discharge at the electrode. Under these conditions, the system loses thermodynamic reversibility and the reversible electrode potential changes its value by an amount  $\eta$ . The electrode is now said to be

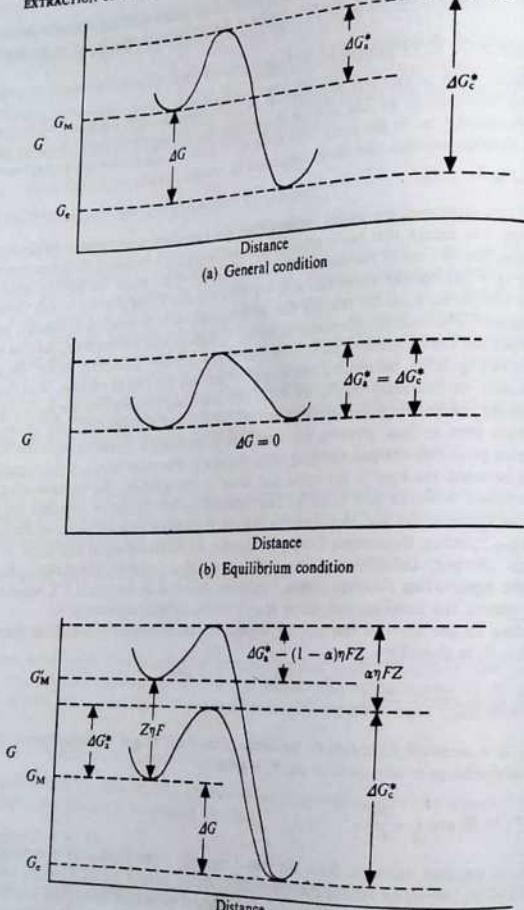


Fig. 2.15 Energy Barriers Under Different Conditions.

polarized with respect to the solution; the value of  $G_M$  is raised to  $G'_M$  for anodic polarization and lowered for cathodic polarization. Figure 2.15c shows the energetics of the anodic polarization. The effect of the *overpotential*  $\eta$  on energetics is twofold: a part of it makes the dissolution of the metal M more rapid and the remainder diminishes the rate of discharge of  $M^{2+}$  ions. This results in the value of  $\Delta G_a^*$  being reduced to  $\Delta G_a^* - (1 - \alpha)\eta FZ$  and the value of  $\Delta G_c^*$  being increased to  $\Delta G_c^* + \alpha\eta ZF$ , where  $(1 - \alpha)$  is the fraction of  $\eta$  assisting the transfer of ions from the metal to the solution, and  $F$  is Faraday's constant. Consequently, the reaction rates  $V_1$  and  $V_2$  are changed to  $V'_1$  and  $V'_2$ , respectively, that is

$$V'_1 = K_1 \exp \left[ -\frac{\Delta G_a^* - (1 - \alpha)\eta FZ}{RT} \right] \quad (2.184)$$

$$= V_1 \exp \left[ \frac{(1 - \alpha)\eta FZ}{RT} \right], \quad (2.185)$$

$$V'_2 = K_2 \exp \left[ -\frac{\Delta G_c^* + \alpha\eta ZF}{RT} \right] \quad (2.186)$$

$$= V_2 \exp \left[ -\frac{\alpha\eta ZF}{RT} \right]. \quad (2.187)$$

The rates of reaction are related to the current density  $i$ . Therefore,  $V_1$  and  $V_2$  may be replaced by  $i_0$ , the exchange current, i.e., the current flowing across a unit area of the electrode in each direction at the reversible potential when  $\eta = 0$ .  $V'_1$  and  $V'_2$  may also be replaced by the corresponding current densities  $i_1$  and  $i_2$ .

The observed anode current density  $i_a$ , corresponding to the net rate of the dissolution of M, is given by

$$i_a = i_1 - i_2 = i_0 \exp \left[ \frac{(1 - \alpha)\eta FZ}{RT} \right] - i_0 \exp \left[ -\frac{\alpha\eta ZF}{RT} \right]. \quad (2.188)$$

An equation similar to eq. (2.188) can be written for the cathode current density  $i_c$ , i.e., for the reverse process. In general, for an anodic or a cathodic process,

$$i = i_0 \exp \left[ \frac{\alpha\eta FZ}{RT} \right] - i_0 \exp \left[ -\frac{(1 - \alpha)\eta FZ}{RT} \right]. \quad (2.189)$$

#### TAFEL EQUATION

In a highly polarized electrode, i.e., when  $\eta$  is large and greater than 0.05 V, eq. (2.189) can be reduced to

$$\eta = a + b \log i, \quad (2.190)$$

where  $a = \pm [2.303 RT / (\alpha FZ)] \log i_0$ ,  $b = [2.303 RT / (\alpha FZ)]$ , and  $i$  can be either  $i_a$  or  $i_c$ . Equation (2.190) is known as the *Tafel equation*.

#### ACTIVATION POLARIZATION

The polarization of the electrodes just described is referred to as *activation polarization*. Activation polarization is dependent on the current density, and  $\eta$  is called the activation overpotential. The overpotential at an electrode is the difference between the reversible electrode potential and the polarized electrode potential.

## HYDROGEN OVERVOLTAGE

Several factors cause polarization at an electrode, for example, interference with the electrode reaction which leads to equilibrium being attained slowly. Although the discharge of hydrogen gas, at an electrode, from an aqueous solution is the result of various intermediate steps, the overall reaction may be written as

(2.191)



Any one of the intermediate reactions can contribute to the activation overpotential, which, in this case is called the *hydrogen overvoltage*. The electrode polarization during the evolution of hydrogen at the cathode is strongly dependent on the nature of the electrode surface. For example, hydrogen activation overpotential for the evolution of hydrogen at a platinum electrode is very small, such an electrode can be conveniently used as a reversible hydrogen electrode. At a mercury surface, the hydrogen overvoltage is approximately 1 volt. Normally, electrolytic deposition from an aqueous solution is restricted to those metals whose electrode potentials lie above that of hydrogen in Table 3.2.

Overvoltage plays a significant role in applied electrochemistry. For example, let us consider an aqueous solution containing zinc ions and hydrogen ions at unit activity. If an electrochemical cell is formed by dipping platinum electrodes into the solution, the reversible electrode potentials  $E_0$  at the two half cells are



So, during electrolysis, were hydrogen to be discharged from the solution at its reversible potential, it should have been liberated at the cathode at a voltage much lower than that required to liberate zinc. In reality, however, since the hydrogen overvoltage on a zinc surface is of the order of 1 V, zinc is deposited on the cathode. The hydrogen ion will be discharged only when the zinc concentration becomes so small that the emf value of the zinc cell lies above the hydrogen overvoltage value. Hydrogen overvoltage enables us to plate metals from aqueous solutions in which the values of their reversible discharge potentials are much higher than that of hydrogen (as given in Table 3.2).

## CONCENTRATION POLARIZATION

Apart from the foregoing factors, polarization also results from the concentration gradients in a solution. Ions that are discharged at an electrode must be replaced by other ions in the vicinity of the electrode. Such a replacement is brought about by ionic migration, agitation, and diffusion. If migration and agitation cannot provide ions rapidly enough to replace those discharged, the concentration at the electrode surface falls below that in the bulk solution. In such a situation, ions are transported by diffusion across the thin film surrounding the electrode and a concentration gradient is built up across this film. Therefore, we see that the electrode kinetics is controlled by the rate of diffusion. This control causes a change in the reversible electrode potential. Such a change is known as *concentration overpotential* or *concentration polarization*. It should be noted that concentration polarization arises from concentration gradients within the solution. So, concentration polarization of the type just described can be minimized by stirring the solution vigorously. An increase in the temperature also tends to decrease the concentration polarization by accelerating the diffusion of ions.

## OHMIC OVERPOTENTIAL OR RESISTANCE OVERPOTENTIAL

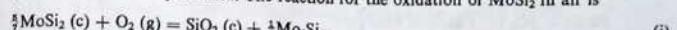
Several factors generate Ohmic overpotential, the main one being the current flowing through the cell. A part of the voltage difference due to polarization is utilized in overcoming the resistance of the cell and is equal to  $IR$ ; the electrical energy is dissipated as heat.

## PROBLEMS

1. A liquid zinc-lead system exhibits a marked positive deviation from ideality. At 1000 K, this system forms two liquids: one containing 35 atom per cent zinc and the other 90 atom per cent zinc. Draw an approximate plot of the activity of zinc versus its atom fraction at 1000 K.

In a dilute solution of zinc in lead at 1000 K, the activity coefficient  $\gamma_{Zn}$  is 6, relative to pure liquid zinc taken as the standard state. Calculate  $\Delta H_{Zn}$  at 1000 K and  $\Delta G_{Zn}^{X_0}$  at 1200 K.

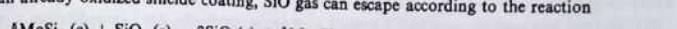
2. Molybdenum silicide ( $MoSi_2$ ) is generally used as a heating element in electric resistance furnaces. Its long life is due to protection against further oxidation provided by an impervious sheathing that consists mainly of silica. The reaction for the oxidation of  $MoSi_2$  in air is



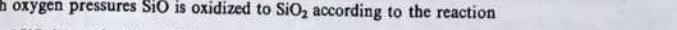
If the oxygen pressure is low, the molybdenum silicide can be removed by the formation of  $SiO$  gas, as shown by the reaction



From an already oxidized silicide coating,  $SiO$  gas can escape according to the reaction



At high oxygen pressures  $SiO$  is oxidized to  $SiO_2$  according to the reaction



Discuss the thermodynamics of the protection of the molybdenum silicide heating element and calculate the minimum oxygen pressure required for its protection at 1800 K.

[Hint: When reaction (ii) is thermodynamically more favourable than reaction (i), then  $\Delta G_{(ii)} - \Delta G_{(i)} = \Delta G_{(iii)}$  should be less than zero. This requirement for reaction (iii), together with reaction (iv), will determine the partial pressure of oxygen below which reaction (i) will cease to protect the molybdenum silicide. The required thermodynamic data may be obtained from standard tables.]

3. Discuss the two-film theory of mass transfer. A soluble species is transferred from a gaseous phase to a liquid phase. Draw the typical concentration profiles in the two phases when all the resistance is ( $r$ ) in the liquid phase, (b) in the gaseous phase, and (c) solely at the interface.

4. For a topochemical gas-solid reaction controlled entirely by diffusion of the reactant gas through a layer of the porous reaction product, the variation of the radius  $r$  of the unreacted core with time  $t$  is given by

$$\frac{t}{\tau} = 1 - \left(\frac{3r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^3,$$

where  $\tau$  is the time taken for the reaction to be completed and  $R$  the solid particle radius. Explain how this equation can be derived and discuss how it is applicable in process design.

5. In the production of pigment grade titanium dioxide in a reactor, purified titanium tetrachloride gas is made to react with oxygen at 1000°C according to the reaction
- $$\text{TiCl}_4(\text{g}) + \text{O}_2(\text{g}) = \text{TiO}_2(\text{c}) + 2\text{Cl}_2(\text{g})$$
- Assuming that  $\text{TiCl}_4$  and  $\text{O}_2$  are admitted to the reactor in stoichiometric proportions, calculate, for equilibrium conditions, the fraction of the  $\text{TiCl}_4$  initially admitted that remains unreacted and leaves the reactor along with the chlorine evolved. Use the relevant thermodynamic data given in Kubaschewski *et al.*, 1974.
6. Use the standard free energy diagrams, i.e., Figs. 2.1 and 2.3, to determine:
- The entropy of vaporization of zinc at its normal boiling point.
  - The partial oxygen pressure at 1300°C in equilibrium with a CO-CO<sub>2</sub> gas mixture having a volumetric CO/CO<sub>2</sub> ratio of 10<sup>3</sup>.
  - The enthalpy change for the reaction
- $$\text{Pb}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g}, 1 \text{ atm}) = \text{PbO}(\text{c})$$
- at 700°C.
- The minimum volumetric CO/CO<sub>2</sub> ratio in a gas mixture that reduces NiO to Ni at 1000°C.
  - The maximum efficiency of utilization of CO gas as a reductant, at 1350°C, for reducing MnO to Mn.
  - The temperature at which Fe, FeO, and O<sub>2</sub> at 10<sup>-10</sup> atm are in equilibrium.
  - The H<sub>2</sub>/H<sub>2</sub>S ratio in a gas mixture in equilibrium with ZnS and Zn vapour at 1 atm at 1100°C.
  - The maximum pressure of the Zn vapour that can be built up when iron and zinc sulphide are heated together at 1000°C.
7. Outline the thermodynamic factors that dictate the nature of the blast furnace process for making zinc and lead simultaneously from an oxide sinter. For quantitative data, the oxide free energy diagram (Fig. 2.1) may be referred to.

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### 3 Minerals, Ores, and Methods of Beneficiation

This chapter is divided into two parts. The first part deals with the modes of occurrence of various metals, their minerals and ores, and the second part gives a brief account of the physical methods employed for upgrading various kinds of ores to render them suitable for subsequent metal extraction processes.

J. MINERALS AND ORES

### 3.0 INTRODUCTION

In this part, we first discuss the general properties of metals. Next, the metals are arranged, based on certain criteria, in the order of their reactivities, to which the general modes of their occurrence are related. The distribution and abundance of the mineral resources are of considerable interest in extraction metallurgy. We have made an attempt to provide here the relevant information on the occurrence, deposition, and abundance of mineral resources, including a section on the nonferrous mineral deposit of India.

METALS

Elements are broadly divided into two groups—metals and nonmetals. The properties of elements are largely governed by factors such as size, polarizability, and the charge carried by the ions that they form. These factors are functions of the atomic structures; the latter provide a fundamental basis for the classification of elements, i.e., the periodic table of elements (given in Table 3.1). Although the periodic table shows a classification of elements based on certain universally accepted criteria, the division of elements into metals and nonmetals is rather imprecise. There are several borderline cases where the element is neither distinctly metallic nor distinctly nonmetallic. This table, however, explains the gradual transition from the metallic to the nonmetallic properties of the elements, and vice versa, as shown below.

Although it is difficult to define a metal precisely, material scientists classify as metals those elements whose electrical resistivities increase with temperature. However, in common parlance, an element may be considered a metal if it exhibits a lustre (commonly called 'metallic lustre') and possesses a good electronic conductivity and good mechanical properties such as ductility, malleability, strength, hardness, impact strength, and fatigue strength. The metallic behaviour of an element depends also on its basic nature, i.e., its tendency to react with an acid. There are, however, many exceptions to the aforesigned criteria. For example, brittle metals such as arsenic and bismuth hardly possess any ductility, whereas nonmetals such as iodine and graphite (a form of carbon) exhibit a metallic lustre. Graphite also possesses a remarkable electrical conductivity. Diamond (another form of carbon and a nonmetal) is one of the hardest substances known.

Table 3.1 Periodic Table of Elements

Further, the mechanical properties of metals change with heat treatment and with the concentration of impurities. Despite such exceptions, we can make some general predictions on the properties of metals, knowing their positions in the periodic table.

In the periodic table, the properties of the elements show that the metallic nature of the elements increases along a vertical column (known as a group) as we proceed from the top to the bottom and along a horizontal row (known as a period) as we proceed from the right to the left. The extranuclear electronic structures of elements, within each particular group, are similar to each other. However, in the periods, the elements towards the right have an increasing number of electrons in their outermost shell, which indicates that the metallic behaviour of elements increases as the atomic number in the groups increases. It follows that the elements are decidedly nonmetallic at the extreme right of the periods. For instance, iodine, although it forms a few salts such as iodine sulphate, is a nonmetal.

### 3.1 REACTIVITIES OF METALS

The electronic structure of elements serves as a basis for determining their reactivities. Such a procedure would, however, be too fundamental when dealing with metals alone. Extractive metallurgists have employed many criteria simpler than the electronic structure to estimate the reactivities of metals. These criteria are based on the properties of the metals or their compounds that are now listed:

- (1) The reversible electrode potential in aqueous solutions and fused salts.
- (2) The free energy of formation of compounds such as oxides and sulphides.
- (3) Electronegativity.

### REVERSIBLE ELECTRODE POTENTIALS

Numerous reactions in metallurgical extraction processes are electrochemical in nature and depend on the transition of a metal from an ionic state to the elemental form or vice versa. The chemical equilibria of the reactions during such a transition are determined, among other factors, by the value of the electrode potential of a system constituted by a metal and its ion under the given conditions of temperature and activities. (This has already been discussed in Section 2.21.) Since reactions in extraction processes generally take place in media such as aqueous solutions and molten salts, we shall now discuss electrode potentials in these media.

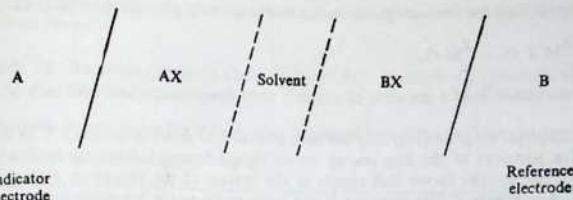
### ELECTRODE POTENTIALS IN AQUEOUS SOLUTIONS

As already discussed in Section 2.21, the electrode potential  $E$  directly indicates the tendency of a metal to form an ion, i.e., its reactivity in the aqueous medium. As is obvious, the higher the reactivity, the greater is the negative free energy change and, therefore, the greater the hydrogen scale. It should be noted that the metals placed in higher positions in the electrode potential series form ions more readily than those in lower positions.

### ELECTRODE POTENTIAL IN FUSED SALTS

The difficulty faced in finding a reference electrode for expressing electrode potentials in fused salt systems has already been discussed in Section 2.21. While the hydrogen electrode serves as a universally accepted reference for aqueous systems, no such electrode exists for fused salt systems. However, for a quantitative comparison of the electrode potential of one element with

that of another, we set up a galvanic cell of the following type (which contains metal electrodes and salts in fused salt solvents):



Electrodes made of different metals are used on the left-hand side of the cell. The right-hand side consists of a reference metal and its salt, together constituting the reference electrode. The emf's of the cell for the left-hand side-electrode are measured, for each metal, at a particular temperature. These emf's, when tabulated, give the electrode potentials of different metals used on the left-hand side of the cell with respect to the right-hand side as an arbitrary reference.

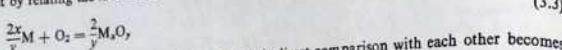
For a long time, scientists were of the view that the order of metals in an emf series was independent of the electrolytic medium. Subsequently, it was shown that, at the same temperature, this order was different in different media. For example, the order of the emf series obtained by using a pure fluoride such as NaF as the medium would differ from that obtained by changing the medium to, say, a solution of NaF (e.g., NaF-KF). Further, if the temperature varies, the values of the electrode potentials in the emf series, for the same medium, would vary and so may the sequence of metals. It is virtually impossible to theoretically compare the electrode potential series obtained by using one medium with that obtained by using another. We shall discuss this subject in detail in Chapter 4. Here, it would be sufficient to note that the electrode potentials of metals in fused salts reflect the tendency of the metals to pass into these media as ions and, therefore, indicate the reactivity of the metals. This interpretation of electrode potentials in fused salts is analogous to that of the electrode potential in aqueous systems. Although it is theoretically impossible to compare the electrode potentials of metals in an aqueous system with those in a fused salt, some common features exist. A general observation is that, in the emf series, reactive metals occupy very high positions whereas noble metals occupy very low positions.

### FREE ENERGIES OF FORMATION OF COMPOUNDS

Various workers have attempted to define the reactivities of metals on the basis of the relative stabilities of their oxides, sulphides, or some other compounds. The different series based on the relative stabilities of the different compounds are not strictly identical to each other. The minor dissimilarities could be ascribed to the inaccuracies in the data on stability and in the assumptions on which these data have been calculated. Consider the relative free energies of formation of oxides of various metals. It should be noted that the free energy data for oxides having different chemical formulas cannot be directly compared with each other. For example, in the oxidation reactions



the free energies of formation of the two oxides cannot be meaningfully compared as the left-hand sides show the consumption of unequal moles of oxygen. Ellingham (1944) has pointed out that by relating the free energies of oxide formation to a general equation of the type



(i.e., the consumption of 1 gm mole of oxygen), their direct comparison with each other becomes possible.

The Ellingham diagram (Fig. 2.1) has been discussed in detail in Section 2.7. In this diagram, the relative positions of the free energy curves should directly indicate the relative stabilities of the various oxides. The curves that appear at the bottom of the Ellingham diagram necessarily refer to comparatively stable compounds and those at the top to less stable compounds. In other words, the formation of the compounds of more reactive metals is accompanied by greater negative free energy changes.

#### ELECTRONEGATIVITY

The emf series is useful in indicating the chemical reactivity of metals in ionic media. However, this series is not so useful in indicating the tendency of metals to form solid solutions or intermetallic compounds. Sometimes, a parameter more useful than the emf series is *electronegativity*. Electronegativity is an arbitrarily defined parameter that expresses the reactivity of a metal only in terms of its individual characteristics.

We know that neither of the two most common types of bonds, namely, the covalent bond and the ionic bond, usually occurs exclusively. Most bonds in chemical compounds are partly ionic and partly covalent; the degree of their being ionic or covalent varying widely from one compound to another. It was L. Pauling who first assumed the energy of a normal covalent bond to be independent of the elements bonded. Any measurable energy change during a reaction can be related to the difference in the ionic nature of the bonds in the products and in the reactants.

Initially, attempts were made to arrange the elements in an order such that the difference between the numbers assigned to any two elements would directly give the heat evolved when a chemical bond is formed between them. Unfortunately, this could not be done. However, Pauling subsequently arrived at a numbered scale in which the square of the difference between the numbers assigned to any two elements was roughly proportional to the heat evolved during the formation of a bond between these two elements. Thus, according to this scale (known as the *electronegativity scale*), the values of all heats of formation must be positive, which is generally true. It may be noted that the unit of electronegativity is the square root of electron volts per second.

Gordy (1946) has shown that the electronegativity  $x$  may be expressed in terms of the number of valence electrons  $n'$  and the single-bond covalent radius  $r$  as given by

$$x = 0.31\left(\frac{n' + 1}{r}\right) + 0.50. \quad (3.4)$$

#### COMPARISON OF REACTIVITIES OF METALS

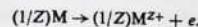
In Table 3.2, the metals are listed according to the different criteria mentioned in the foregoing discussion. It should be noted that the sequence of elements in this table is somewhat similar in all the series. The alkali and alkaline earth metals are generally placed higher up in the table

whereas the noble metals are placed lower down. The transition elements occupy positions somewhere in between.

From the foregoing discussion, we may conclude that the relative reactivities of elements are indicated in all the series.

Table 3.2 Electrode Potentials Compared with Free Energies of Formation, and Electronegativities

Electrode potentials are for the reactions expressed according to the reaction



Electrode potential in aqueous solutions at 25°C (volts)	Apparent standard potential* in LiCl-KCl eutectic at 450°C (volts)	Standard formation potential for pure chloride at 1000°C (volts)	Free energy of formation of compound at 1000 K (kcal per mole of O <sub>2</sub> or Cl <sub>2</sub> )		Electro-negativity
			Oxide	Chloride	
Cs=3.02	Li=3.41	Ba=3.412	Ca=-254.4	Ba=-166.7	Cs=0.75
Li=2.957	Mg=2.58	Li=3.352	Mg=-236.1	Li=-163.0	K=0.80
K=2.922	Th (4)=2.411	Ca=3.208	Ba=-222.2	K=-162.8	Ba=0.90
Ba=2.90	Hf (4)=1.88	K=3.155	U (4)=-218.1	Ca=-155.7	Na=0.90
Ca=2.87	Zr (4)=1.86	Cs=3.078	Al=-216.8	Na=-152.2	Li=0.95
Na=2.712	Mn (2)=1.849	Zr (2)=2.45	Li=-201.0	U (3)=-107.1	Ca=1.0
Mg=2.4	Al=1.797	Th (4)=2.208	Ti (4)=-182.9	Al=-94.14	Hg=1.0
Ti=1.75	Ti (3)=1.64	U (3)=2.162	V (3)=-156.3	Mn (2)=-84.5	Sr=1.0
Al=1.7	Zn=1.566	U (4)=1.953	Mn (2)=-149.0	V (2)=-81.4	Cd=1.1
Be=1.69	Cr (2)=1.425	Be=1.725	Na=-131.4	Ti (3)=-80.23	Mg=1.2
U (4)=1.4	Cd=1.316	Zn=1.40	V (4)=-130.6		Zn=1.21
Mn=1.12	U (4)=1.19				Be=1.45
Zn=0.758	Fe (2)=1.172				
Cr=0.6	Pb=1.101	Cr (3)=1.113	Zn=-118.0	Ti (4)=-76.5	Al=1.5
Fe (2)=0.44	Sn=1.082	Pb=1.112	Ba=-111	Zn=-70	Zr=1.6
Co=0.29	Co=0.991	Sn=1.05	K=-100	Fe (2)=-53.1	Sn=1.7
Ni=0.22	Cu (1)=0.851	Cd=1.002	Fe (3)=-89.7	Co=-46	Si=1.8
Sn=0.13	Ni=0.795	Ag=0.784	Sn=-89.2	Cu (1)=-43.9	Sb=1.8
Pb=0.12	Cr (3)=0.685	Pt(3) very small	Co=-71.4	Ag=-38.2	Ag=1.9

Table 3.2 Electrode Potentials Compared with Free Energies of Formation, and  
Electronegativities (cont.)

Electrode potential in aqueous solutions at 25°C (volts)	Apparent standard potential* in LiCl-KCl eutectic at 450°C (volts)	Standard formation potential for pure chloride at 1000°C (volts)	Free energy of formation of compound at 1000 K (kcal per mole of O <sub>2</sub> or Cl <sub>2</sub> )		Electro-negativity
			Oxide	Chloride	
H <sub>2</sub> =0.000	Sb (3)=0.67	Pt(4) very small	Sb (3)=-70.1	Ni=-37.1	V=1.9
Sb=-0.10	Bi (3)=0.67		Pb=-56.0	Pt (2)=+4	As=2.0
Bi=-0.2	Mo (3)=0.638		Bi (2)=-53	Pt (1)=+6	Mo=2.1
As=-0.3	As=0.637		Cu (1)=-47.5	Pt (3)=+13.5	Cr=2.2
Cu (2)=-0.344	Hg (2)=0.5		Cu (2)=-32.1		Cu=2.2
Cu (1)=-0.51	Fe (3)=0.397		Ag=-15.4		Mn=2.6
Hg (2)=-0.798	Rb (3)=0.231				Au=3.1
Ag=-0.799	Pt (3)=0.000				
Pd=-0.820	Au (1)=-0.311				
Hg (1)=-0.86					
Pt (4)=-0.863					
Au (3)=-1.360					

\*The apparent standard potential  $E_{app}$  is defined as

$$E_{app} = E^{\circ} - \frac{RT}{2F} \ln f,$$

where  $E^{\circ}$  is the standard decomposition potential and  $f$  the Henrian activity coefficient of salt MX in the given solvent.

### 3.2 RELATIVE REACTIVITIES AND MODES OF OCCURRENCE OF METALS IN NATURE

Some general observations on the modes of occurrence of metals in relation to their positions in the various series (given in Table 3.2) are as follows:

(I) Highly reactive metals which are characterized by factors such as high electrode potentials and high negative free energies of formation of compounds occur in nature mainly as simple compounds. Thus, the alkali and alkaline earth metals are mostly found as chlorides, carbonates, and sulphates. Simple oxides of these metals are however rare as they would react with other acidic oxides such as silica. Consequently, these metals are often found in the form of minerals such as aluminates or alumino-silicates.

(2) The metals that occupy the intermediate position in Table 3.2 are principally found as silicates. Some of these which are placed higher up in the intermediate position may form simple oxides as well, whereas those occupying a lower position may be found abundantly also as sulphides. Sulphides become quite important (from the point of view of winning) for metals placed in the lower half of the series (given in Table 3.2). Metals occupying very low positions show an increasing tendency to occur either as selenides, tellurides, arsenides, and antimonides or in the native state. All the metals that appear below lead in the first column of Table 3.2 may be found in the free state, which becomes the most common state of occurrence for silver and all the metals placed below it.

The sequence of elements in the series (given in Table 3.2) reflects a gradual transition of properties according to the change in the reactivities. Some general properties of metals in relation to their positions in the emf series are summarized in Table 3.3.

Table 3.3 Properties of Metals in Relation to Their Positions in Electrochemical Series (after Nutt, 1968)

Metal	Electrode potential range (volts)	Remarks
Li, Rb, Cs, K, B, Sr, Ca, Na, La, Mg	3.01 to 2.38	Forms chlorides, carbonates, and sulphates; is easily oxidized in air; gives very stable oxides; reacts spontaneously with water; forms ionic compounds
Th, Ce, Ti, Be, Hf, Al, Zr, V	2.1 to 1.44	Forms mainly oxides, silicates, or complex oxides; oxidizes on heating; gives stable oxides; is attacked by steam; forms mainly ionic compounds
W, Mn, U, Se, Zn, Cr, Ga, Fe, Cd, In, Tl	1.1 to 0.335	Forms simple or complex oxides or sulphides; oxidizes on strong heating; forms moderately stable oxides; oxides of less reactive metals are easily reduced; is attacked by steam
Tl, Co, Ni, Mo, Sn, Pb, Sb, As, Bi, Cu, Te, Rh, Re, Hg, Ag	0.335 to -0.799	Forms some selenides, tellurides, and arsenides in addition to sulphides and complex oxides; forms relatively unstable oxides, some of which decompose at high temperature; is not attacked by steam; in many cases shows complex bonding in compounds
Sb, As, Bi, Cu, Te, Rh, Re, Hg, Ag, Pd, Ir, Pt, Au	-0.1 to -1.7	Occurs as sulphides, tellurides, or in free state; gives less stable oxide, some unstable even at room temperature (Pb-Au); is not attacked by steam or ordinary acids; shows complex bonding in salts

**3.3 NATURE OF ATOMIC BONDING IN COMPOUNDS**  
 There are two principal ways in which atoms combine to form compounds; the ultimate aim of such a combination is to acquire the electronic configuration stability as found in the inert gases. First, *ionic bonds* between compounds are formed by the *transfer* of electrons from an atom that has more electrons than the inert gas structure to another atom that has less. Ionic compounds have two kinds of ions, namely, positive and negative. It may be noted that such bonds often easily dissociate in water, which has a high dielectric constant. Second, *covalent bonds* (between compounds or between atoms of the same element) are formed by the *sharing* of electrons between atoms whose outermost shells are incomplete, i.e., do not have the inert gas shells such that each outermost shell gets eight electrons instead of the normal seven (in a stable inert gas the outermost shell has eight electrons).

A third type of bond, known as *intermetallic bond*, is usually found in metals when the mass is held together in an electron cloud. This cloud is created by the relatively free outermost electrons. Such electrons are not linked with individual atoms but are freely distributed over the entire mass so as to envelop the positive metallic cations. Several naturally occurring sulphides are formed by metallic bonding.

#### 3.4 EXPLORATION FOR MINERAL DEPOSITS

##### DEFINITION OF MINERAL AND ORE

A mineral is a naturally occurring inorganic compound of one or more metals in association with nonmetals such as oxygen, sulphur, and the halogens. A mineral has a fixed composition and well-defined physical and chemical properties.

An ore may be defined as a naturally occurring aggregate or a combination of minerals from which one or more metals or minerals may be economically extracted.

The economy of extraction generally depends on fundamental factors such as

- (1) the percentage of valuable metal in the ore,
- (2) the form in which the metal occurs, i.e., the nature of the mineral in the ore,
- (3) the percentage of impurities in the ore (i.e., which are difficult to remove and which impart undesirable properties to the metal),
- (4) the physical condition of the ore,
- (5) the location and magnitude of the ore deposits,
- (6) the proximity to transport facilities, and
- (7) the market value of the metal.

In ancient times, some minerals must have been spotted on the earth's surface itself because of their striking physical characteristics such as vivid colours and crystalline shapes, whereas those hidden under the soil would have remained unnoticed. Therefore, scientific methods are necessary for an accurate location and a quantitative estimation of mineral deposits. The principal methods employed in mineral exploration are generally based on the magnetic, electrical, and electromagnetic properties of the ore bodies. Other geophysical methods, namely, gravitational, seismic, and radioactive methods are normally used for oil exploration.

##### MAGNETIC METHODS

Magnetic methods are based on the fact that magnetic ore deposits disturb the earth's magnetic field in their vicinity. Instruments such as magnetometers and variometers are capable of detecting buried deposits of magnetite (an iron ore) and nickel- and cobalt-bearing ores. Indirectly, they also help locating alluvial deposits of gold and platinum which often contain abundant grains of magnetite. A magnetic survey performed by these instruments yields contour maps of the ore deposits. By measuring the variations in the magnetic intensities in both the vertical and horizontal directions, the dimensions of the ore body can be estimated. Figure 3.1 shows typical anomalies in vertical and horizontal intensities over a hidden ore body. The vertical and horizontal intensity curves are easily related to the location and orientation of the ore body.

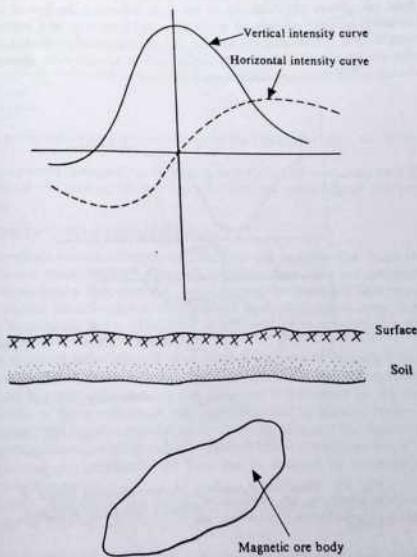


Fig. 3.1 Profiles of Horizontal and Vertical Components of Magnetic Field across Magnetic Ore Body (after Jones and Williams, 1948).

**ELECTRICAL METHODS**

Electrical methods are based on the differences between the electrical conductivities of certain ore deposits and those of the surrounding rocks. These methods are recommended particularly for certain sulphide minerals which have remarkably high conductivities—often several thousand times higher than the conductivity of the surrounding rocks. Conductivity measurements, therefore, directly indicate both the presence and the magnitude of the ore deposits.

Electrical flow lines, obtained by passing either a direct or an alternating current into the ground between a pair of earthed electrodes, crowd in towards any mass of conducting material. Conductivity measurements are supplemented by the measurement of potentials at the ground surface. From these potential data, we can draw equipotential lines on a map of the area. Equipotential lines are always perpendicular to the lines indicating the flow of current and diverge from the ore body. Modern instruments which measure conductivity and potential measurements simultaneously help in determining the location and orientation of ore bodies.

The technique of measuring electrical conductivity is schematically shown in Fig. 3.2 and a survey of electrical flow lines and equipotential lines in Fig. 3.3.

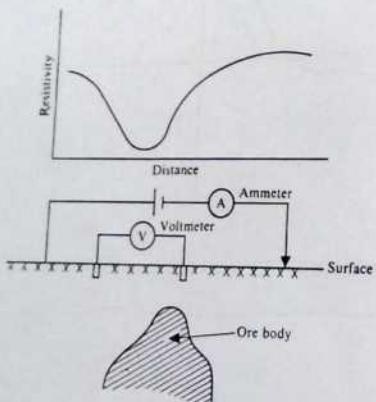


Fig. 3.2 Electrical Resistivity Method Showing Effect of Ore Body on Resistivity Curve (after Jones and Williams, 1948).

There is a rather unique electrical technique to detect and determine the volume of a sulphide ore body. Most sulphide deposits present in the upper layers of the soil undergo oxidation. The resulting electrochemical conditions induce a positive polarity in the upper layers and a negative polarity in the lower ones. Consequently, a current flows down the ore body and completes the

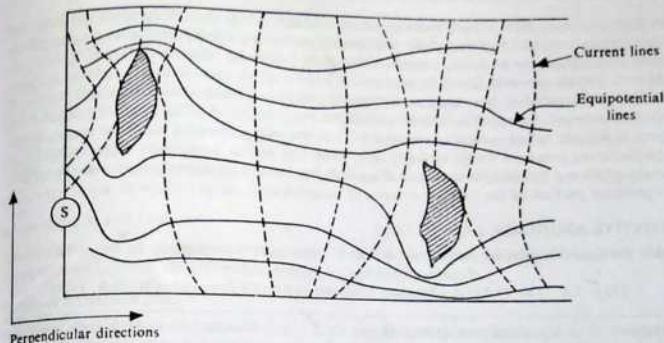


Fig. 3.3 Survey of Electrical Flow Lines and Equipotential Lines (after Jones and Williams, 1948).

circuit by moving upwards through the surrounding rock strata. By measuring both the direction and the magnitude of the current, we can establish both the location and the volume of the sulphide ore body.

**ELECTROMAGNETIC AND OTHER METHODS**

Electromagnetic methods provide comprehensive data on the position and shape of electrically conducting ore bodies hidden beneath the earth's surface. Such data are gathered by sending electromagnetic waves over a wide area, and then recording the secondary field reradiated by the conducting ore bodies. Electromagnetic methods find ready application even in mountainous regions, deserts, snow-laden areas, ice-covered lakes, and areas covered by nonconducting surface rock strata.

Besides those discussed, other methods of exploration for mineral deposits depend on various other physical properties of the ore bodies. For example, gravitational methods depend on detecting variations in gravitational forces which arise due to variations in the densities of the rocks. The variation in the gravitational fields can be detected by suitable devices, for example, a sensitive pendulum. The seismic methods depend on the density and the elasticity of the rock strata, which together determine the speed with which artificial earthquake waves travel through the rocks. The presence of a radioactive ore body can be detected by a Geiger counter which also measures the radioactivity.

Once preliminary exploration has helped in locating the ore body, further experimental work is carried out to establish the quality of the ore through actual sampling and analysis.

**3.5 SOURCES OF METALS**

The three main sources of metals and their compounds are the earth's crust, the sea, and scrap metal, the most important one being the earth's crust. The seas, which cover more than 70

per cent of the earth's surface, contain, on an average, 3.5 per cent of dissolved solids. In the future, metals could be extracted by deliberately cultivating specific marine organisms which would concentrate one or more elements within their bodies by inherent biological activity. In addition, metals are also found in deposits of nodules which cover large areas of the sea floor. Finally, scrap metal is becoming an increasingly important, and a freely available source of metal in view of the rapid industrial growth all over the world. (The metals recovered from scrap metal are called *secondary metals*.) In fact, we may envisage a situation where metal-manufacturing processes would virtually only refine and recycle increasingly huge quantities of metals which are periodically used and discarded. For instance, in current steel-making processes, a significant portion of the 'charge' consists of scrap metal.

#### RELATIVE ABUNDANCE OF METALS

Table 3.4 lists the relative abundance of the 45 most prevalent elements in the earth's crust.

Table 3.4 The 45 Most Abundant Elements in Earth's Crust (after Hurlich, 1977)

Element	Abundance (ppm/wt)	Element	Abundance (ppm/wt)
Oxygen	466,000 (46.6%)	Zinc	70 (0.007%)
Silicon	277,000	Cerium	60
Aluminium	81,300	Copper	55
Iron	50,000	Yttrium	33
Calcium	36,300	Lanthanum	30
Sodium	28,300	Neodymium	28
Potassium	25,900	Cobalt	25
Magnesium	20,900	Scandium	22
Titanium	4400	Lithium	20
Hydrogen	1400	Columbium	20
Phosphorus	1050	Nitrogen	20
Manganese	950	Gallium	15
Fluorine	625	Lead	13
Barium	425	Radium	13
Strontrium	375	Boron	10
Sulphur	260	Krypton	9.8
Carbon	200	Praseodymium	8.2
Zirconium	165	Protoactinium	8.0
Vanadium	135	Thorium	7.2
Chlorine	130	Neon	7.0
Chromium	100	Samarium	6.0
Rubidium	90	Gadolinium	5.4
Nickel	75		

This table reveals some interesting facts. There is a tremendous amount of oxygen and silicon in the earth's crust, oxygen comprising almost half by weight. The first eight elements account for more than 98 per cent, of which nearly 75 per cent is composed of only two elements, namely, oxygen and silicon. The tonnage usage of several abundant elements does not conform to their abundance. For example, elements that are abundant in the earth's crust but have only limited use include titanium, rubidium, and vanadium. On the other hand, elements such as copper, zinc, and lead, which are far less abundant in the earth's crust, find numerous applications in everyday life.

Apart from a metal's natural abundance, various factors, some of which are now listed, govern the extent to which a metal can be used.

#### Accessibility to Ore Deposits

Some rich ore deposits, for example, the bauxite ores of Kashmir, are located in areas with poor transportation facilities, rendering their economic exploitation difficult.

#### Nature of Extraction Process

A process for the extraction of ores that is both simple and economical ought to be available before large-scale projects can be contemplated. Thus, although bauxite ores were discovered a long time back, the large-scale industrial production of aluminium has been made possible only after the development of the electrolytic process. Further, since at present there is no simple process for the extraction of titanium from its ores, the metal is yet to be produced on a large scale in many countries including India.

#### Properties and Demand

If a metal has useful and attractive properties—physical and chemical—then the demand for it would be high, justifying large-scale production. For example, the development of new metal products or new alloys leads to an increase in the demand for the basic raw material, i.e., the metals.

#### 3.6 SEA AS SOURCE OF METALS

Sea-water can be considered a dilute solution containing valuable minerals and chemical compounds. About 70 elements have so far been discovered in sea-water; Table 3.5 gives the values of the relative abundance of some of these elements. Since the seas form one continuous, nearly homogeneous body of water, these values are, remarkably, the same all over the globe.

It should be noted that the values of the relative abundance of the elements given in Table 3.5 differ from those given in Table 3.4 for the earth's crust as a whole (including the seas). This is primarily because solubilities in silicate solutions, which form the earth's crust, are basically different from those in sea-water. Moreover, geochemical reactions in the earth's crust and in the sea have not been identical over the millennia. It should be noted that not all the dissolved matter in sea-water has come from the land masses; some of it has emerged from cracks in the seabed.

There is a mid-ocean rift that runs approximately 64,000 km through the major ocean basins. At some of the places where the ocean floor seems to be spreading apart, the earth's mantle supplies fresh mantle rock, namely, basalt, from below. Along with this basalt, emanates a form of water called 'juvenile water' which contains many components of sea-water such as chlorine, bromine, carbon, boron, nitrogen, and various trace elements. Undersea volcanoes also release

Table 3.5 Elements Present in Solution in Sea-Water (excluding dissolved gases)  
(after Hampel, 1961)

Element	Concentration (gm/ton)	Element	Concentration (gm/ton)
Cl	18,980	Zn	0.005-0.014
Na	10,562	Cu	0.001-0.09
Mg	1272	Mn	0.001-0.01
S	884	Pb	0.004-0.005
Ca	400	Se	0.004
K	380	Sn	0.003
Br	65	Cs	0.002
C (inorganic)	28	U	0.00015-0.00016
Se	13	Mo	0.0003-0.002
B	4.6	Ga	0.0005
Si	0.02-4.0	Ni	0.0001-0.0005
C (organic)	1.2-3.0	Th	0.0005
Al	0.16-1.9	Ce	0.0004
F	1.4	Hg	0.0003
N (as nitrate)	0.001-0.7	La	0.0003
N (organic)	0.03-0.2	V	0.0003
Rb	0.2	Y	0.0003
Li	0.1	Ag	0.00015-0.0003
P (as phosphate)	0.10	Bi	0.0002
Ba	0.05	Co	0.0001
N (as nitrate)	0.0001-0.05	Sc	0.00004
N (as ammonia)	0.005-0.05	Au	0.00004-0.00008
As	0.003-0.024	Ra, Ge, Ti,	
Fe	0.002-0.02	W, Cr, Ti,	Present
P (organic)	0-0.016	Sb, Zr, Pt	

juvenile water whose compositions vary from one place to another. The elements that are most abundant in juvenile water are precisely those that cannot be accounted for if the solids dissolved in sea-water were simply those provided by the weathering of rocks on the earth's surface.

In fact, the salts transported to the seas by rivers account for only a fraction of the dissolved compounds.

Although sea-water all over the earth is nearly homogeneous, there is a localized concentration of some elements in sea organisms. For example, algae, a kind of seaweed, contain a very high concentration of iodine. Other sea organisms may contain elements such as Ba, Co, Cu, Pb, Ni, Ag, and Zn.

### 3.7 OCEAN-FLOOR NODULES

Trillions of tons of nodules are scattered across the ocean floor. These nodules whose principal constituents are manganese, nickel, iron, copper, cobalt, and siliceous ocean-floor silt are collectively termed as 'manganese nodules'. In terms of their nickel content, they can also be called 'nickel nodules' since they are a potential source of nickel.

The process that leads to the formation of nodules is rather complicated and is yet to be

Table 3.6 Reserves of Metals in Pacific Ocean Nodules  
(after Mero, 1972)

Element	Amount of element		Ratio Nodule reserves Land reserves
	Weight %	10 <sup>9</sup> tons	
Co	0.35	5.2	5000
Mn	23.86	358	4000
Ni	0.98	14.7	1500
Zr	0.06	0.93	1000
Al	2.86	43	200
Cu	0.52	7.9	150
Mo	0.05	0.77	60
Pb	0.09	1.3	50
Zn	0.46	0.7	10
Fe	13.80	207	4
Ag	0.0001	0.001	1
Mg*	1.66	25	
Ti*	0.66	9.9	
V*	0.05	0.8	
Ga	0.001	0.015	

\*Land reserves are unlimited.

clearly established. Although manganese nodule deposits are found along various depths of the ocean floor, only those lying below 300 m can be economically mined. The average size of a nodule is about 4 cm and the concentration considered economic for mining is about 150,000 tons per sq. km of the seabed.

Mero (1972) has estimated that approximately one and a half trillion tons of nodules are scattered across the floor of the Pacific Ocean alone. He has also observed that nodules form afresh at the rate of 10 million tons a year. The data collected by Mero on the resources of metals in the Pacific Ocean nodules are given in Table 3.6. From this table, it is evident that nodule reserves can provide large quantities of nickel, cobalt, copper, and manganese. The nodule reserves have an advantage over land reserves in that they are being constantly renewed whereas the latter are being constantly depleted.

### 3.8 MINERAL RESOURCES OF THE WORLD

From Table 3.7, which shows the world-wide distribution of some important metals, we see that a high proportion of them is concentrated in a few regions.

Table 3.7 World-Wide Distribution of Important Metals (after Bureau of Mines, 1976)

Manganese	South Africa has 45% of world's high-grade ore reserves (25-50% Mn content) and U.S.S.R. 38%
Cobalt	Zaire and Zambia together have almost 50% of world's high-grade ore reserves and New Caledonia and Australia together have 27%
Chromium	South Africa and Zimbabwe together have 97% of world's high-grade ore reserves and 95% of low-grade ore reserves
Aluminium	Australia and Guinea each has 25% of world's high-grade bauxite ores, Brazil 15%, and Jamaica 6% (India also possesses large deposits of aluminium ores)
Tin	China has 24% of world's reserves, Thailand 15%, Malaysia 12%, and Bolivia 10%
Nickel	New Caledonia has 44% of world's reserves, Canada 16%, Australia and Indonesia approximately 9% each, and Cuba 6%
Antimony	China has 50% of world's reserves, Bolivia 9%, U.S.S.R. 7%, and Mexico 5%
Tungsten	China has 54% of world's reserves, Canada 12%, U.S.S.R., North Korea, and South Korea approximately 9% each, and U.S.A. 6%
Iron	U.S.S.R. has 31% of world's high-grade ore reserves, Brazil 17%, Canada 12%, Australia 10%, India 6%, and U.S.A. 4%
Uranium	U.S.A. has 25% of world's reserves, Australia 22%, South Africa 20%, and Canada 19% (These figures are exclusive of U.S.S.R. and East European nations which have not made available data on their uranium resources)
Copper	U.S.A. and Chile each has 20% of world's reserves, Canada and U.S.S.R. approximately 9% each, and Peru and Zambia 7% each. However, Chile, Peru, Zambia, and Zaire account for more than 80% of world's trade of copper ores

Table 3.7 World-Wide Distribution of Important Metals (after Bureau of Mines, 1976) (cont.)

Molybdenum	U.S.A. has 50% of world's reserves, U.S.S.R. 15%, and Canada and Chile approximately 14% each
Columbium	Brazil has 75% of world's reserves, Canada approximately 8%, and U.S.S.R. 6%
Titanium	Brazil has 65% of world's reserves of rutile ( $TiO_2$ ), India 21%, Australia 5%, and U.S.A. 3% [World's reserves of ilmenite ( $FeO \cdot TiO_2$ ) ore, containing approximately 50% $TiO_2$ , are much larger than those of rutile; Canada has 20% of world's reserves of ilmenite, Norway 15%, U.S.A. 10%, and India 4%]
Vanadium	U.S.S.R. has 75% of world's reserves and South Africa 19%

It should be noted that six countries, namely, the U.S.A., the U.S.S.R., Canada, South Africa, Australia, and China possess most of the world's mineral reserves and, consequently, dominate the production of minerals (see Table 3.8).

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits (after Ryan, 1968)

Mineral	Location	Remarks
<b>ALUMINIUM</b>		
Bauxite ( $Al_2O_3 \cdot xH_2O$ )	Jamaica, U.S.S.R., Surinam, Guyana, France, Guinea, U.S.A., Hungary, Greece, and India	The degree of hydration of ores $x$ varies between one and three
Orthoclase feldspar ( $K_2O \cdot Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$ )		The monohydrate mineral is called diaspore or bohemite and the trihydrate gibbsite or hydrargillite
Muscovite (mica) ( $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$ )		The minerals are believed to have been formed as a result of prolonged weathering of aluminium-bearing rocks
Kaolinite ( $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ )		Common impurities are ferric oxide, silica, and titanium
Leucite ( $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ )		Minerals other than hydrated oxides are rarely used in extraction of aluminium
Cyanite ( $Al_2O_3 \cdot SiO_2$ )		
Sillimanite ( $Al_2O_3 \cdot SiO_2$ )		
Corundum ( $Al_2O_3$ )		
Cryolite ( $Na_3AlF_6$ )		
Aluminite ( $Al_2O_3 \cdot SO_3 \cdot 9H_2O$ )		

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits  
(after Ryan, 1968) (cont.)

Mineral	Location	Remarks
<b>ANTIMONY</b>		
Stibnite (Sb <sub>2</sub> S <sub>3</sub> )	South China, South Africa, Bolivia, U.S.S.R., Mexico	Sulphide minerals are most common; these are often associated with sulphide minerals of elements such as lead, arsenic, copper, zinc, and mercury (antimony is often recovered as a byproduct during extraction of lead or copper)
Cervantite (Sb <sub>2</sub> O <sub>3</sub> Sb <sub>2</sub> O <sub>3</sub> )	Turkey, and Czechoslovakia	Common impurities are silica and lime
Valentinite (Sb <sub>2</sub> O <sub>3</sub> )		
Kermesite (2Sb <sub>2</sub> S <sub>3</sub> Sb <sub>2</sub> O <sub>3</sub> )		
Jamesonite (2Pb <sub>5</sub> Sb <sub>2</sub> S <sub>3</sub> )		
Bournonite (2PbS-Cu <sub>2</sub> S Sb <sub>2</sub> S <sub>3</sub> )		
<b>BARIUM</b>		
Barite (heavy spar) (BaSO <sub>4</sub> )	Germany, Yugoslavia, Czechoslovakia, Greece, Sardinia, France, Spain, England, U.S.S.R., North Africa, North America, and South America	Common ores are carbonate and sulphate
Bromlite [(Ba, Ca)CO <sub>3</sub> ]		Celestite (SrSO <sub>4</sub> ) and anglesite (PbSO <sub>4</sub> ) also contain significant quantities of barium compounds
Witherite (BaCO <sub>3</sub> )		
<b>BERYLLOIUM</b>		
Beryl (3BeO-Al <sub>2</sub> O <sub>3</sub> -6SiO <sub>2</sub> )	South Zimbabwe, U.S.A., and India	Of the nearly 30 minerals known, beryl is the only important mineral commercially exploited
<b>BISMUTH</b>		
Bismite (bismuth ochre) (Bi <sub>2</sub> O <sub>3</sub> )	Peru, U.S.A., Mexico, Japan, South Korea, and Canada	Both oxide and sulphide minerals are common
Bismuthinite (bismuth glance) (Bi <sub>2</sub> S <sub>3</sub> )		Minerals are often associated with compounds of lead, cobalt, arsenic, niobium, and tantalum
Bismutite (Bi <sub>2</sub> O <sub>3</sub> -CO <sub>2</sub> -H <sub>2</sub> O)		

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits  
(after Ryan, 1968) (cont.)

Mineral	Location	Remarks
<b>BORON</b>		
Colemanite (2CaO-3B <sub>2</sub> O <sub>3</sub> -5H <sub>2</sub> O)	U.S.A., Italy, and South America	Most minerals are complex oxides
Tincal (Na <sub>2</sub> O-2B <sub>2</sub> O <sub>3</sub> -10H <sub>2</sub> O)		
Kernite (Na <sub>2</sub> O-2B <sub>2</sub> O <sub>3</sub> -4H <sub>2</sub> O)		
Ulexite (Na <sub>2</sub> O-2CaO-5B <sub>2</sub> O <sub>3</sub> -16H <sub>2</sub> O)		
<b>CADMIUM</b>		
Not many well-defined minerals		
<b>CHROMIUM</b>		
Chromite (FeO-Cr <sub>2</sub> O <sub>3</sub> )	Turkey, Pakistan, South Africa, U.S.S.R., Zimbabwe, Philippines, Cuba, Yugoslavia, and India	Regions with ore deposits of zinc, copper, and lead. Major cadmium (by-product) producers are U.S.A., U.S.S.R., Canada, Mexico, Japan, Australia, Zaire, and Belgium
<b>COPPER</b>		
Sulphides		Chromite is the only mineral used in extraction of chromium although other minerals of chromium are known. Common impurities are magnesia, alumina, and silica
Bornite (FeS <sub>2</sub> 2Cu <sub>2</sub> S-CuS)	North America and South America, Zambia, Canada, U.S.S.R., Chile, Zaire, Australia, Japan, China, and Philippines	The most important mineral is chalcocite. Apart from sulphide, oxide, hydroxide, and carbonate minerals, other minerals of copper such as silicates are known to exist.
Chalcocite (Cu <sub>2</sub> S)		
Chalcopyrite (CuFeS <sub>2</sub> )		
Covellite (CuS)		
Enargite (3Cu <sub>2</sub> S As <sub>2</sub> S <sub>3</sub> )		Most sulphide minerals of copper are associated with sulphides of lead and zinc

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits (after Ryan, 1968) (cont.)

Mineral	Location	Remarks
<i>Oxides, Hydroxides, and Carbonates</i>		
Antlerite [Cu <sub>2</sub> SO <sub>4</sub> (OH) <sub>4</sub> ]		
Atacamite [Cu <sub>2</sub> (OH) <sub>6</sub> Cl]		
Aurrite [2CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub> ]		
Brocianite [CuSO <sub>4</sub> ·3Cu(OH) <sub>2</sub> ]		
Cuprite (Cu <sub>2</sub> O)		
Malachite [CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub> ]		
Tenorite (CuO)		
Chrysocolla (CuSiO <sub>3</sub> ·2H <sub>2</sub> O)		
<i>GOLD</i>		
Sylvanite [(Au, Ag)Te <sub>2</sub> ]	U.S.S.R., Australia, South Africa, Ghana, Zaire, Zimbabwe, Canada, and U.S.A.	The only known minerals are tellurides such as lysvanite and calaverite
Calaverite (AuTe <sub>2</sub> )		The most important sources of gold are the local concentrations in lodes and quartz veins of some rock formations, alluvial deposits of certain stream beds, and deposits often worked primarily for extraction of other metals such as uranium, silver, lead, copper, and nickel
<i>LEAD</i>		
Galena (PbS)	U.S.S.R., Australia, Canada, Peru, Yugoslavia, Morocco, South Africa, Sweden, Spain, and Japan	A large number of sulphide, carbonate, sulphate, and oxychloride minerals are known. Galena is, however, by far the most important mineral; commonly associated impurities in galena are ZnS, FeS, and Ag

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits (after Ryan, 1968) (cont.)

Mineral	Location	Remarks
Bonlangierite (Pb <sub>2</sub> Sb <sub>4</sub> S <sub>11</sub> )		
Pyromorphite [Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl]		
Mimetite [Pb <sub>5</sub> (AsO <sub>4</sub> ) <sub>3</sub> Cl]		
Vanadinite [Pb <sub>5</sub> (VO <sub>4</sub> ) <sub>3</sub> Cl]		
<i>LITHIUM</i>		
Spodumene [LiAl(SiO <sub>3</sub> ) <sub>2</sub> ]	Zimbabwe, South Africa, Canada, Argentina, Brazil, Surinam, and Australia	Known minerals are silicates, phosphates, fluorides, and chlorides
Lepidolite [a complex silicate (lithium mica) containing 3-5% Li <sub>2</sub> O]		Silicates provide main commercial source
Amblygonite (LiAlFPO <sub>4</sub> or Li <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·8SiO <sub>2</sub> )		
Eucryptite [Li(AlSi) <sub>2</sub> O <sub>4</sub> ]		
<i>MAGNESIUM</i>		
Dolomite (MgCO <sub>3</sub> ·CaCO <sub>3</sub> )	All over earth	Dolomite may be considered the most important mineral source of magnesium
Magnesite (MgCO <sub>3</sub> )		Sea-water, which contains 0.13% magnesium, is also an equally important source
Carnallite (MgCl <sub>2</sub> ·KCl·6H <sub>2</sub> O)		
Brucite [Mg(OH) <sub>2</sub> ]		
Olivine [(Mg, Fe) <sub>2</sub> SiO <sub>4</sub> ]		
<i>MANGANESE</i>		
Pyrolusite (MnO <sub>2</sub> )	U.S.S.R., Brazil, India, Ghana, and South Africa	Manganese minerals are often found associated with iron ores—a useful combination for the direct production of ferromanganese
Psilomelane (MnO <sub>2</sub> ·H <sub>2</sub> O·K <sub>2</sub> BaO <sub>2</sub> )	To a lesser extent in Chile, Argentina, Mexico, Morocco, Zaire, and Japan	
Manganite [Mn <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O or MnO(OH)]		

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits  
(after Ryan, 1968) (cont.)

Mineral	Location	Remarks
Braunite $(\text{Mn}_2\text{O}_7 \cdot \text{MnSiO}_3)$		
Diallageite $(\text{MnCO}_3)$		
Rhodonite $(\text{MnSiO}_3)$		
MOLYBDENUM		
Molybdenite $(\text{MoS}_2)$	U.S.S.R., U.S.A., Canada, Chile, Norway, Japan, Philippines, and Yugoslavia	Molybdenum is produced mostly from molybdenite
Powellite $[\text{Ca}(\text{Mo}, \text{W})\text{O}_4]$		
Wulfenite $(\text{PbMoO}_4)$		
NICKEL		
Garnierite $[(\text{Ni}, \text{Mg})\text{SiO}_3 \cdot x\text{H}_2\text{O}]$	Canada	Some complex sulphide ores such as $(\text{Fe}, \text{Ni})_9\text{S}_4$ are also known
Nicolite $(\text{NiAs})$	To a lesser extent in U.S.S.R. and New Caledonia	Sulphide and oxide ores, which normally have a low nickel content, need to be specially concentrated before nickel can be extracted
Pentlandite $(\text{Fe}, \text{Ni})_9\text{S}_4$		
NIOBIUM (COLUMBIUM) AND TANTALUM		
Columbite $[(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6]$	Zaire, Brazil, Nigeria, Malagasy, Norway, Sweden, and U.S.S.R.	Niobium and tantalum always occur together as complex oxides
Euxenite (see under rare earths)		
Pyrochlore $[(\text{Na}, \text{Ca})_2(\text{Nb}, \text{Ti})(\text{OF})_7]$		Columbite—the most important mineral—is usually found associated with minerals of calcium, iron, manganese, and rare earths; tin, titanium, and zirconium may also be present The niobium-tantalum ratio can vary between extreme limits

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits  
(after Ryan, 1968) (cont.)

Mineral	Location	Remarks
PLATINUM METALS		
Not many well-defined minerals	South Africa, Canada, U.S.A., U.S.S.R., and South America	Rare sulphide minerals have different compositions such as $\text{PtAs}_2$ , $\text{Pt}(\text{AsS})_2$ , $(\text{Pt}, \text{Pd}, \text{Ni})\text{S}$ , $\text{PdSb}$ , and $\text{RuS}_2$ Local concentrations of platinum are found in certain rocks and minerals; platinum metals are often associated with ores of copper and nickel and are obtained as byproducts during extraction of copper and nickel
RARE EARTHS		
Monazite $[(\text{Ce}, \text{La}, \text{Y}, \text{Th})\text{PO}_4]$	India, Brazil, U.S.A., Australia, Malaysia, North Korea, South Korea, Sweden, and Norway	Only the important rare-earth minerals are listed under 'Mineral' although rare-earth elements are found in other mineral species too Most rare-earth minerals are found in beach sands
Bastnasite $[(\text{La}, \text{Ce})\text{FCO}_3]$		
Xenotime $(\text{YPO}_4)$		
Gadolinite $[\text{Ce}_2\text{FeY}_2\text{Si}_2\text{O}_{16}]$		
Euxenite $[(\text{Y})(\text{Nb}, \text{Ta})\text{TiO}_6 \cdot x\text{H}_2\text{O}]$		
SELENIUM		
Clausthalite $(\text{PbSe})$	Sweden, Germany, Mexico, Bolivia, Argentina, U.S.A., Canada, and Australia	Note that the minerals are combinations of selenium only with metals; compounds of selenium with nonmetals are virtually unknown
Aquilarite $[\text{Ag}_2\text{S} \text{ and } \text{Ag}_2(\text{S}, \text{Se})]$		
Naumannite $[(\text{Ag}, \text{Pb})\text{Se}]$		
Berzelianite $(\text{Cu}_2\text{Se})$		
Eucairite $(\text{Cu}_2\text{Se}, \text{Ag}_2\text{Se})$		
Crookesite $[(\text{Cu}, \text{Ti}, \text{Ag})_2\text{Se}]$		
Tiemannite $(\text{HgSe})$		

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits (after Ryan, 1968) (cont.)

Mineral	Location	Remarks
SILVER, Argentite (Ag <sub>2</sub> S)	Mexico, Bolivia, U.S.A., and Canada	Most of world's silver minerals are found in base metal ores, of which lead ores are the most important
Pyrrhotite (Fe <sub>1-x</sub> S <sub>x</sub> )		
Proustite (Ag <sub>2</sub> AsS <sub>3</sub> )		
Nessite (Ag <sub>2</sub> Te)		
Cerargyrite (AgCl)		
Iodrite (AgI)		
THORIUM <i>Oxide</i>		
Thorianite [(Th, U)O <sub>2</sub> ]	India, Brazil, Australia, Sri Lanka, Indonesia, Malaysia, South Africa	Although a very large number of thorium-bearing minerals are known, monazite is by far the most important one
Niobates, Tantalates, and Titanates	U.S.A., U.S.S.R., North Korea, South Korea, Italy, and Egypt	
Brannerite [(U, Ca, Fe, Y, Th) <sub>3</sub> Ti <sub>2</sub> O <sub>16</sub> ]		
Eschynite [(Ce, Ca, Fe <sub>2</sub> , Th) <sub>2</sub> Ti <sub>2</sub> O <sub>16</sub> ]		
Euxenite (see under rare earths)		
Phosphates and Silicates		
Xenotime (YPO <sub>4</sub> )		
Allanite [(Ca, Ce, Th) <sub>2</sub> (Al, Fe, Mg) <sub>2</sub> Si <sub>2</sub> O <sub>12</sub> (OH)]		
Cheralite [(Ce, Ca, Pr, Nd, Th, Ca, U)(PO <sub>4</sub> , SiO <sub>4</sub> )]		
Thorite (ThSiO <sub>4</sub> )		
Pilbarite (PbO·UO <sub>2</sub> ·ThO <sub>2</sub> ·2SiO <sub>2</sub> ·4H <sub>2</sub> O)		
Monazite [(Ce, La, Y, Tb)PO <sub>4</sub> ]		

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits (after Ryan, 1968) (cont.)

Mineral	Location	Remarks
TIN		
Cassiterite (SnO <sub>2</sub> )	Malaysia, Indonesia, and Bolivia	Cassiterite is the only important mineral, the others having little economic value
Stannite (Cu <sub>2</sub> S·FeS·SnS <sub>2</sub> )	To a lesser extent in China, U.S.S.R., Nigeria, Thailand, and Zaire	
Franckeit (5PbS·2SnS <sub>2</sub> ·Sb <sub>2</sub> S <sub>3</sub> )		
TITANIUM		
Ilmenite [FeTiO <sub>3</sub> ] (with Mg sometimes replacing Fe)	Canada, U.S.A., Australia, Brazil, India, Malaysia, Norway, U.S.S.R., Sweden, Finland, Portugal, China, and Africa	Ilmenite is the most important mineral Certain rock strata contain rutile in a very dilute form
Rutile (TiO <sub>2</sub> )		
Senaitite [(Fe·Mn·Pb)O·Ti·TiO <sub>2</sub> ]		
TUNGSTEN		
Wolframite [(Fe, Mn)WO <sub>4</sub> )	China, U.S.A., North Korea, South Korea, Bolivia, Portugal, Burma, Australia, Thailand, Spain, Argentina, Brazil, U.S.S.R., Peru, Zaire, Zimbabwe, and Malaysia	The minerals are mostly oxides containing hexavalent tungsten Wolframite is the most important mineral
Ferberite (FeWO <sub>4</sub> )		
Hubernite (MnWO <sub>4</sub> )		
Scheelite (CaWO <sub>4</sub> )		
Cuproscheelite [(Ca, Cu)WO <sub>4</sub> )		
Stolzite (PbWO <sub>4</sub> )		
URANIUM		
Pitchblende (U <sub>3</sub> O <sub>8</sub> )	U.S.A., Canada, France, Zaire, Australia, Norway, and Turkey	Apart from its minerals, uranium is also obtained as a byproduct from other sources such as monazite sands
Uraninite (UO <sub>2</sub> , UO <sub>3</sub> )		
Carnotite (K <sub>2</sub> O·2UO <sub>3</sub> ·V <sub>2</sub> O <sub>5</sub> ·xH <sub>2</sub> O)		

100 EXTRATION OF NONFERROUS METALS  
Table 3.8 Important Minerals and Locations of Their Major Ore Deposits  
(after Ryan, 1968) (cont.)

Mineral	Location	Remarks
Autunite (CaO-2UO <sub>3</sub> -P <sub>2</sub> O <sub>7</sub> -xH <sub>2</sub> O)		
Uranophane (CaO-2UO <sub>3</sub> -2SiO <sub>2</sub> -7H <sub>2</sub> O)		
Davideite [(Fe, Ce, U)(Ti, Fe, V, Cr) <sub>2</sub> (O-OH) <sub>7</sub> ]		
Tyuyamunite (CaO-2UO <sub>3</sub> -V <sub>2</sub> O <sub>5</sub> -xH <sub>2</sub> O)		
Brannerite [(U, Ca, Fe, Y, Th) <sub>2</sub> Ti <sub>2</sub> O <sub>10</sub> ]		
Schroedingerite (3CaO-Na <sub>2</sub> O-UO <sub>3</sub> -3CO <sub>2</sub> -SO <sub>3</sub> -10H <sub>2</sub> O)		
<b>VANADIUM</b>		
Patronite (V <sub>2</sub> S <sub>5</sub> , xS)	Mexico, U.S.A., Spain, Argentina, Turkey, South West Africa, and Zimbabwe	Roscoelite is a type of mica containing vanadium
Salvanite (3Ca <sub>2</sub> S-V <sub>2</sub> S <sub>3</sub> )		Vanadium-iron alloys can be obtained from vanadiferous ores
Roscoelite (2K <sub>2</sub> O-2Al <sub>2</sub> O <sub>3</sub> (Mg-Fe)O-3V <sub>2</sub> O <sub>5</sub> -10SiO <sub>2</sub> -4H <sub>2</sub> O)		
<b>ZINC</b>		
Sphalerite (ZnS)	Australia, Burma, Yugoslavia, Spain, and Italy	Sphalerite is the most important mineral; it may contain varying amounts of FeS, and is normally associated with sulphides of lead and copper
Zincite (ZnO)	To a lesser extent in Canada, U.S.A., Mexico, and U.S.S.R.	
Franklinite [ZnO(Fe, Mn) <sub>2</sub> O <sub>3</sub> ]		
Smithsonite (ZnCO <sub>3</sub> )		
Willemite (Zn <sub>2</sub> SiO <sub>4</sub> )		
Calamine (Zn <sub>2</sub> (OH) <sub>2</sub> SiO <sub>3</sub> )		
Hemimorphite (Zn <sub>4</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>2</sub> ·H <sub>2</sub> O)		

Table 3.8 Important Minerals and Locations of Their Major Ore Deposits  
(after Ryan, 1968) (cont.)

Mineral	Location	Remarks
<b>ZIRCONIUM AND HAFNIUM</b>		
Zircon (ZrSiO <sub>4</sub> )	U.S.A., Australia, Brazil, and India	Hafnium is always associated with zirconium to the extent of 2-2.5%
Raddelyeite (ZrO <sub>2</sub> )		Zircon is found in beach sands

### 3.9 NONFERROUS MINERAL WEALTH OF INDIA

The mineral resources\* of India are broadly classified into three categories as follows.

#### Adequate to Abundant

Minerals containing aluminium, beryllium, chromium, iron, manganese, magnesium, titanium, zirconium, thorium, and the rare earths.

#### Inadequate

Minerals containing copper, gold, carbon (graphite), lead, vanadium, zinc, nickel, cadmium, uranium, and tin.

#### Poor to So Far Not Known

Minerals containing antimony, bismuth, boron, cobalt, mercury, molybdenum, niobium and tantalum, phosphorus, selenium, sulphur, strontium, tellurium, silver, and tungsten.

The minerals in the first category, if properly exploited, can not only meet the domestic demand but can also yield a surplus for export. Although the minerals in the second category are insufficient to meet the growing domestic demand, they should be fully exploited. The resources in the third category are, at present, inadequate for commercial exploitation.

From the foregoing three categories, we see that although India is deficient in some of the common metals such as copper, zinc, lead, tin, cobalt, and nickel, its reserves of iron, manganese, magnesium, aluminium, and titanium are extensive. Further, India has abundant reserves of strategically important metals, namely, thorium, zirconium, and beryllium. We now discuss the mineral resources of individual elements.

### ALUMINUM

Bauxite is widely distributed in India, as is apparent from Table 3.9. The discovery of rich bauxite deposits has drastically changed the outlook for India's alumina industry. In the early nineteen sixties, the Geological Survey of India claimed that India had a potential reserve of about 250 million tons of bauxite which had an Al<sub>2</sub>O<sub>3</sub> content of more than 50 per cent. This figure has

\*The term 'resource' indicates the totality of a particular mineral occurrence in a region irrespective of the grade, the tonnage, or the economics of exploitation, whereas the term 'reserve' takes into account the grade and the degree of certainty with which the tonnage has been estimated for any particular cut-off grade.

Table 3.9 India's Potential Bauxite Reserves (after Das Gupta, 1979)

State/Union territory	Reserves (million tons)
Jammu and Kashmir	3.0
Bihar	45.0
Madhya Pradesh and Uttar Pradesh	105.0
Orissa and Andhra Pradesh	1614.0
Maharashtra, Karnataka, and Goa	146.0
Tamil Nadu	14.0
Kerala	13.0
Gujarat	100.0
Total	2040.0

now been conclusively established. It should be noted that the potential reserves are much more extensive. According to reliable sources, the East Coast of India has one of the world's largest deposits of bauxite. Since this deposit is rich in gibbsite and has a low content of silica and titania, it is ideal for the Bayer process (although it has a high content of iron oxides) for the extraction of alumina.

Currently, India has an installed capacity of 320,000 tons for aluminium products, which is adequate to meet the present demand. However, full capacity could not be achieved mainly due to power shortages. India's total production of aluminium in 1979 was estimated to be 208,000 tons against the consumption of 220,000 tons.

Das Gupta (1979) has predicted that after 1990, the whole of Europe, including the U.S.S.R., will have to rely largely on Africa and India for obtaining bauxite and alumina.

#### ANTIMONY

Commercially exploitable deposits of antimony have not been so far located in India, although small deposits of antimony ores have been found in Lahaul and Spiti (Himachal Pradesh). At present, the entire annual requirement, i.e., 500–700 tons, is being met by importing the metal, its ores, and concentrates.

#### BERYLLIUM

Beryl, the chief ore of beryllium, occurs in pegmatites which are associated with granites and is found in Rajasthan, Tamil Nadu, Jammu and Kashmir, and Bihar. At one time, almost the entire beryl output of India was being exported but the Atomic Energy Establishment (AEE) (a Government of India undertaking) now handles its production and sale. Although beryllium is not produced on a commercial basis in India, substantial groundwork has been done at the Bhabha Atomic Research Centre (BARC), Bombay, in beryllium production technology.

#### CHROMIUM

The principal chromite deposits of India are located in Singhbhum district (Bihar), Karnataka, Krishna and Sawantwadi (Maharashtra), and Keonjhar district (Orissa). India produces chromite on a very large scale—approximately 350,698 tons per annum in 1977, of which Orissa accounted for almost 97 per cent. The chromite reserves of India, although estimated to be limited to about 17 million tons, should be able to meet the domestic requirement for a long period, and a production of 10,000 tons per annum can be sustained for years.

#### NICKEL AND COBALT

Until recently, exploitable deposits of cobalt- and nickel-bearing minerals were considered non-existent in India. Of late, however, several low-grade nickeliferous deposits have been discovered, which are serpentinous, lateritic, or sulphidic in nature. The copper ore belt passing through Singhbhum (Bihar) contains also a nickel ore body which may provide 1000 tons of nickel annually. In fact, India's nickel reserves are about 100 million tons, of which 6.5 million tons, averaging 0.85 per cent nickel, are located at Sukinada (Orissa). Apart from the ores, copper tailings and the anode sludge from copper plants could turn out to be an important source of nickel. Nickel has also been found associated, in very minute quantities, with the gold-quartz reefs at Kolar (Karnataka) and the uranium ores at Jaduguda (Bihar). In spite of the aforementioned sources, the only domestic supply of nickel, at present, comes from the copper smelters at Khetri (Rajasthan), where nickel sulphate is recovered as a byproduct, the amount recovered in 1977–78 being 150 tons.

It may be noted that traces of cobalt have been found along with the copper ores of Khetri and the manganese ores of Kalahandi (Orissa).

At present, neither nickel nor cobalt is produced in India on a commercial scale, and the domestic requirements are met by imports. A method has yet to be found for the economic reduction of the Sukinada laterite ore with about 1 per cent nickel content.

#### CADMIUM

Cadmium is recovered as a byproduct from the zinc smelters at Debari (Rajasthan), Visakhapatnam (Andhra Pradesh), and Alwaye (Kerala). Indigenous sources meet most of the domestic cadmium requirements.

#### COPPER

India has about 370 million tons of copper reserves, and the average copper content varies from 1 per cent to 2.5 per cent. About 90 per cent of these reserves are spread over Bihar, Rajasthan, and Madhya Pradesh, the most important deposits being located in the Singhbhum copper belt in Bihar. By world standards, the copper reserves of India are small. However, the Geological Survey of India is constantly exploring for new reserves. The Mineral Exploration Corporation has recently established the existence of 58 million tons of copper reserves at Malanjkhand (Madhya Pradesh). A project to mine two million tons of ore a year, from which copper concentrates can be produced, has been cleared by the Planning Commission of India.

At present, Hindustan Copper Limited (HCL) is the sole producer of copper in India and is able to meet about 42 per cent of the country's requirements, i.e., about 23,000 tons in 1977–78. The future production is expected to go up to 40,000 tons.

**GOLD**

India's gold reserves are estimated to be 3.15 million tons (1977); a majority of them located in Karnataka. The gold content of these reserves ranges from 5.65 gm/ton to 19.98 gm/ton of ore. Minor deposits of vein gold have also been found in the Hutt gold field (Karnataka). The entire production of gold in India is by the Government of India's Bharat Gold Mines Limited (BGML) and the Karnataka state-owned Hutt Gold Mines Company.

Gold tailing dumps, which have accumulated over the years, contain scheelite, BGML proposes to recover this scheelite (from which ferrotungsten can be obtained) from the dumps.

In 1977, the gold production in India was 2854 kg compared with 3132 kg in 1976. This decrease can be attributed to the shrinking reserves, because of which, the gold production is unlikely to go up in the future, unless, of course, new reserves are found.

**SILVER**

India has no reserves of silver ores. However, small quantities of silver are recovered as a by-product during the indigenous refining of gold, copper, and lead; the major part coming from the lead smelters at Tundoo (Bihar) and the gold mines in Karnataka.

**LEAD AND ZINC**

India has about 140 million tons of lead-zinc ores, of which nearly 118 million tons are located

Table 3.10 Estimated Reserves of Lead-Zinc Ores (after Kapur, 1978)

Classification	Location of deposit	Total ore (million tons)	Production capacity (tons/day)
Operating mines	Mochia (Rajasthan)	28.61	2000
	Balaria (Rajasthan)	19.81	2000
	Rajapura-Dariba (Rajasthan)	33.78	3000
	Agnigundala (Andhra Pradesh)	9.84	300
	Rangpo (Assam)	0.12	100
Approved projects	Zawar (Rajasthan)	15.22	1500
	Ambamata (Gujarat)	6.19	1200
	Sargipalli (Orissa)	1.89	500
	Borai (Rajasthan)	11.20	1500
Advanced exploration projects	Deri (Rajasthan)	0.85	200
	Mamandur (Tamil Nadu)	1.00	200
Projects under exploration	Bhilwara (Rajasthan)	7.47	1000
	Gorubathan (West Bengal)	2.00	500
	Basantgarli (Rajasthan)	1.62	300

in two areas of Rajasthan, namely, the Zawar mines and the Rajapura-Dariba lead-zinc belt. Table 3.10 gives the estimated reserves of lead-zinc ores.

Since the indigenous reserves of lead and zinc are inadequate, India continues to rely on imports of lead and zinc and their concentrates to meet the domestic requirements.

The lead-zinc ores from the Zawar mines are beneficiated at the site to produce both zinc and lead concentrates. These concentrates are then processed; the lead concentrate at Tundoo by the Hindustan Zinc Limited's (HZL) smelter and the zinc concentrate by another HZL smelter at Debari. In 1977, HZL produced 46,500 tons of zinc concentrate, which could meet about 36 per cent of India's total demand for 1977-78. In 1978, the smelters at Tundoo and Visakhapatnam together produced 10,060 tons of lead.

The average *in situ* grade is 3.5 per cent zinc and 1.5 per cent lead, which can provide four million tons of zinc and one million tons of lead, respectively. It is thus evident that the zinc ores will last for less than 30 years and the lead ores for less than 20 years.

**MANGANESE**

India is the third largest producer of manganese in the world; the U.S.S.R. being the largest and South Africa the second largest. The ore deposits presently being worked in India are located in Singhbhum, Panchmahals (Gujarat), Balaghat (Madhya Pradesh), Bhandara and Nagpur (Maharashtra), Visakhapatnam (Andhra Pradesh), Sandur and Shimoga (Karnataka), Bonai, Keonjhar, and Koraput (Orissa), and Banswara (Rajasthan). The total manganese reserves, according to the Indian Bureau of Mines (1977), are estimated to be 108 million tons. In 1977, the total production of manganese ores in India was 1,774,000 tons; Orissa, Madhya Pradesh, Karnataka, and Maharashtra accounting for 90 per cent of the production.

The manganese ores found in India are generally mixtures of psilomelane  $[Mn, Ba, Mn_3O_4(OH)_2]$ , braunite  $(MnSi_2O_5)$ , pyrolusite  $(MnO_2)$ , and hollandite  $(Mn, Ba, Mn_3O_4)$ . These ores can be classified into four groups, namely, simple ores, ferruginous ores, garnetiferous ores, and complex ores.

**Simple Ores**

These ores contain small quantities of gangue materials that are amenable to concentration by simple methods involving only ore treatment, i.e., gravity methods, magnetic separation, or flotation.

**Ferruginous Ores**

These ores contain mainly iron minerals which can be removed by magnetizing reduction roasting followed by magnetic separation.

**Garnetiferous Ores**

These ores contain garnets and quartz as the chief gangue minerals and can be upgraded either by an electrostatic separation method or by flotation.

**Complex Ores**

These ores contain different types of gangue minerals in intimate association with manganese minerals, and complicated treatment is required for their extraction.

Manganese ores can not only sustain large-scale ferromanganese production indefinitely but can also be exported to earn valuable foreign exchange.

**MAGNESIUM**

India has extensive deposits of magnesium in the form of magnesite ( $MgCO_3$ ), chiefly found in the Chalk Hills of Salem district (Tamil Nadu). The estimated reserves of magnesite here have been put at 82.5 million tons up to a depth of 30 m and 330 million tons up to a depth of 150 m. The deposit is of a high grade, the average magnesia content being 46 per cent or above. On the whole, India's *in situ* magnesite reserves are estimated to be 524 million tons, of which the existence of 33 million tons has been conclusively established. Apart from Salem district, the other important magnesium deposits are located in southern Karnataka and Uttar Pradesh. Smaller deposits are found in Idar (Maharashtra), Kurnool (Andhra Pradesh), Tiruchirapalli (Tamil Nadu), Coorg (Karnataka), Dungarpur (Rajasthan), and Singhbhum. It should be noted that in some of these deposits, magnesium is present as dolomite ( $CaCO_3 \cdot MgCO_3$ ).

Widespread reserves of dolomite and magnesium limestones are found in Tamil Nadu, Andhra Pradesh, Bihar, Madhya Pradesh, Rajasthan, and Orissa. These reserves have not yet been accurately assessed, but should be adequate to fulfil India's increasing requirements of magnesium. Another source of magnesium that could be exploited in the near future is the Indian Ocean, which contains, on an average, 0.6 per cent  $MgCl_2$ .

**MOLYBDENUM**

There are no commercially viable reserves of molybdenum in India, but its ores are found as primary molybdenite ( $MoS_2$ ) and as a base metal sulphide containing small quantities of molybdenum. Exploration surveys in Andhra Pradesh and Tamil Nadu have shown that primary molybdenite occurs in the quartz veins that traverse porphyritic granites and, at places, in the granite itself. Molybdenum in a base metal sulphide that is in association with copper ores is found at Rakha and Bhatin in the Singhbhum district. Experiments have shown the concentration of molybdenum in the Rakha ore sample to be approximately 0.011 per cent and that in the Bhatin ore sample to be 0.1 per cent. Preliminary beneficiation of the molybdenum ore has indicated the recovery during concentration to be 95 per cent.

**TIN**

Tin is not extracted on a commercial scale in India although tin deposits have been detected in Rauchi and Hazaribagh districts of Bihar. The entire present requirement of almost 10,000 tons per year is being met by imports.

**TITANIUM**

Abundant quantities of ilmenite ( $FeO \cdot TiO_2$ ) are found in the beach sands along a 160-km stretch of the Kerala coast. In fact, a particular 23-km coastal strip contains 35 million tons of ilmenite and three million tons of rutile ( $TiO_2$ ). The ilmenite from Kerala contains a high percentage (55 per cent) of titanium. Smaller deposits of ilmenite occur near Tuticorin (Tamil Nadu), Waltair (Andhra Pradesh), and Ganjam district (Orissa). The total reserves of ilmenite in the form of beach sands are estimated to be 133 million tons. Apart from the beach sand deposits, small quantities of massive and crystalline ilmenite are found in Bhagalpur district (Bihar) and Kisengarh and Jodhpur (Rajasthan). Almost the entire volume of the metal concentrates so far produced has been exported.

The beach sands of Kerala contain a mixture of mineral sands whose specific gravities vary from 2.3 (silica) to 4.9 (monazite). Table 3.11 gives the mineralogical compositions of the beach

Table 3.11 Analysis of Beach Sands (%) (after Chatterjee, 1959)

Mineral	Manavalakurichi (Tamil Nadu) (DAE analysis)	Nindakara (Kerala)
Ilmenite	8-52	80
Zircon	0.87-10.31	4-6
Sillimanite	0.90-6.27	3-5
Rutile	0.39-39	4-5
Garnet	0.05-5.9	<0.5
Silica	5-7	4-5
Monazite	0.5-1	0.5-1
Others	<0.1	

sand samples from two regions. (Tables 8.10 and 8.11 give an analysis of Indian rutiles and ilmenites, respectively.)

**TUNGSTEN**

Since the domestic production of tungsten is insufficient, India imports the metal to meet its requirements. The presence of tungsten minerals has been detected in certain parts of the country, namely, Chandrapathan in Bankura district (West Bengal), Agargaon in Nagpur district (Maharashtra), and Degana (Rajasthan); the present production of tungsten comes from the first two sources. As already mentioned, there is a proposal to obtain ferrotungsten from the scheelite (a mineral of tungsten) that is found in the gold tailings from Kolar and Hutt. Data on tungsten reserves are given in Table 3.12. The volume of tungsten concentrate produced in 1977 was 43,046 kg, of which Rajasthan accounted for 90 per cent and West Bengal for 10 per cent.

Table 3.12 Reserves of Tungsten Minerals

Mineralization area	Estimated reserves (tons)	Grade (%)
Degana (Rajasthan)	53,330	0.54
Agargaon (Maharashtra)	1,340,000	0.215
Bankura district (West Bengal)	30,000	0.05
Kolar (Karnataka)	4,500,000	0.03-0.18

**VANADIUM**

India depends entirely on imports to meet its vanadium requirements although vanadium-bearing

titaniferous magnetite ( $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ ) has been located near Dubilabera in Singhbhum district and in the adjacent Mayurbhanj district (Orissa). Further, a small deposit near Nausahi in Keonjhar district (Orissa) is also known to contain vanadiferrous iron ores. The vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) content of the Nausahi ores varies from 0.5 per cent to 2 per cent. Some  $\text{V}_2\text{O}_5$  is also recovered from the vanadium sludge obtained during alumina processing. The total volume of vanadiferrous magnetite ores in India is estimated to be approximately 26 million tons.

#### RARE-EARTH MINERALS

Heavy rare-earth mineral sand deposits are found along the coasts of Kerala, Tamil Nadu, and Orissa. In fact, India possesses the world's richest and the most extensive resources of thorium in the form of monazite deposits along the Kerala coast. The proven reserves of monazite are put at one million tons. (Table 8.5 compares the composition of the Indian monazite with the compositions of monazite available from a few other countries.)

Abundant quantities of zircon ( $\text{ZrSiO}_4$ ) are generally found associated with beach sands along with rutile, ilmenite, and monazite.

At present, three mineral sands separation plants are in operation in India, one at Manavala-kurichi and the other two at Chavara (Kerala). Of the three plants, one is run by Kerala Minerals and Metals Limited (KMML) and the other two by Indian Rare Earths Limited (IREL) (under the DAE). The data on the production of heavy minerals during 1976-77 are given in Table 3.13.

Table 3.13 Production of Heavy Minerals (1976-77)

Mineral	Production (tons)
Ilmenite	163,016
Monazite	2799
Zircon	8579
Rutile	7064
Sillimanite	1837
Leucoxene	265

The monazite produced by the three plants is processed by IREL's rare-earth plant at Udyogamandal (Kerala) to produce a wide range of rare-earth chemicals and thorium compounds. Further, IREL has, in the development stage, a third mineral sands separation plant and a synthetic rutile plant, both at Chitrapur (Orissa) and KMML also plans to set up a 22,000-ton titanium dioxide (per annum) pigment plant near Chavara.

#### II METHODS OF BENEFICIATION

Before discussing the methods of beneficiation, it should be emphasized that ore-dressing techniques constitute a very important step in extraction processes. Therefore, it is essential that a

process metallurgist be familiar with the fundamentals of ore dressing. Further, developments and innovations in ore-dressing techniques have had a tremendous impact on industrial metal extraction processes.

#### 3.10 INTRODUCTION

In the first part of this chapter, we have discussed the natural occurrence of ores and minerals. Thus, it would be appropriate, at this stage, to describe some of the physical methods of beneficiation. All metal extraction techniques are developed keeping in mind a particular type of raw material or a particular combination of raw materials. Whether or not a particular raw material is suitable for a given extraction technique depends on both the physical nature of the ore and its chemical composition. Therefore, it is apparent that most ores and minerals require some treatment before they can be processed either to increase their chemical purity or to better utilize their physical properties so as to facilitate the extraction of the metal.

According to Gaudin (1951) mineral dressing is the processing of raw materials to yield marketable products and waste by means that do not destroy the physical and chemical identity of the minerals. Ore dressing is mineral dressing applied to ores. Taggart (1951) defines ore dressing as the sum total of treatments to which ores are subjected in order to separate and discard their worthless fractions by essentially physical means.

We have already emphasized that mineral deposits are considered useful only when they can be economically exploited. Most mineral deposits can be rendered useful by employing proper ore-dressing techniques which help to remove substantial portions of the gangue and thus upgrade the raw material. These techniques are becoming increasingly important as all the rich deposits are being rapidly depleted, leaving behind only lean deposits.

Traditionally, ore dressing had been confined to physical operations, but technology has widened considerably in recent years to also include certain chemical beneficiation techniques. In these techniques, not only is the physical appearance or the chemical composition of the mixture of minerals altered but limited changes in the chemical nature of the minerals may also be brought about. For example, in magnetizing roasting, the  $\text{FeO}$  impurity can be oxidized to  $\text{Fe}_2\text{O}_3$  which is magnetically separated in a subsequent operation. Metallurgical wastes such as off-grade ores and slags are, at present, being beneficiated by employing chemical reactions such as chlorination. Accordingly, ore dressing may be defined as the physical or chemical treatment or a combination of the two which aims at altering the physical and chemical nature of the minerals so that the final combination of the minerals can be economically treated for metal extraction. The treatment here is limited to physical methods of beneficiation.

An ore beneficiation technique may entail various unit operations, some of which are listed in Table 3.14. We shall discuss the important unit operations in Section 3.11.

Table 3.14 Unit Operations in Mineral Dressing (after Biswas, 1972)

Process	Description	Properties of mineral exploited
Comminution Crushing, grinding	Subdivision of mineral lumps and particles into smaller sizes	Brittleness

Table 3.14 Unit Operations in Mineral Dressing (after Biswas, 1972) (cont.)

Process	Description	Properties of mineral exploited
<b>Sizing</b>		
Sorting or hand-picking, screening	Separation according to size	Size difference among particles
Hydraulic classification	Settling in fluid	Relative difference in size and density among mineral particles
<b>Concentration</b>		
Gravity concentration		
Heavy media separation	Settling in liquid	Relative difference in density among particles
Jigging	Settling in liquid	Relative difference in density among particles
Tabling	Frictional movement along wet vibrating solid surface	Density, size, shape, and coefficient of friction
Magnetic separation	Separation due to magnetic field in dry or wet condition	Magnetic permeability and magnetic susceptibility of particles
Electrostatic separation	Charging and charge loss of particles and their deflections in electrostatic field	Conductivity and charge-retention characteristics
Flotation	Attachment of gas bubbles to mineral in aqueous pulp containing surfactants and frothers Subsequent preferential froth flotation for some minerals	Surface properties Affinity for specific surface-active reagents
<b>Dewatering</b>		
Sedimentation thickening	Settling of particles	Nonspecific
Coagulation	Neutralization of charge or repulsive forces	Adsorption properties of minerals may lead to beneficiation
Filtration	Solid-liquid separation	Nonspecific
Drying	Removal of moisture from moist solid	Nonspecific
<b>Agglomeration</b>		
Pelletizing, nodulizing, sintering	Obtaining bigger lumps from small particles through adhesion or incipient fusion of particles	Solid-solid reaction at interfaces of particles

**3.11 COMMINUTION (SIZE REDUCTION)**

Comminution basically serves two purposes, i.e., it detaches dissimilar mineral particles from each other so as to 'liberate' the valuable components and it produces small-sized mineral particles which are more suitable than large-sized ores for subsequent beneficiation operations.

**LIBERATION**

The particles of an ore may consist either of a single material or of two or more minerals. The former are termed *free particles* and the latter *locked particles*. According to Gaudin (1951), the degree of liberation of a certain mineral or phase is defined as the percentage of the mineral or phase occurring as free particles in relation to the total of that mineral occurring in free and locked forms. Conversely, the degree of locking of a mineral is the percentage occurring as locked particles in relation to the total occurring in the free and locked forms.

Generally, *grain* and *grain size* are used with reference to crushed or ground rock and *particle* and *particle size* with reference to uncrushed rock and *particle* and *particle size*.

There are two ways in which a large lump of rock may break. First, it may break along the grain boundaries between adjacent dissimilar minerals if the bonds along these boundaries are weak. In such a case, the mineral is liberated by detachment. Secondly, if the bonds are not very weak or are at least comparable with the cohesive energy of the individual minerals, then the bond between adjacent dissimilar minerals may not rupture. Nevertheless, the mineral would still be liberated by size reduction and locking would be restricted to a small portion of the original lump. Thus, we see that comminution increases the liberation of a mineral both by size reduction and by detachment.

**Liberation by Size Reduction**

The process of liberation by size reduction is illustrated in Fig. 3.4. This figure shows that if there

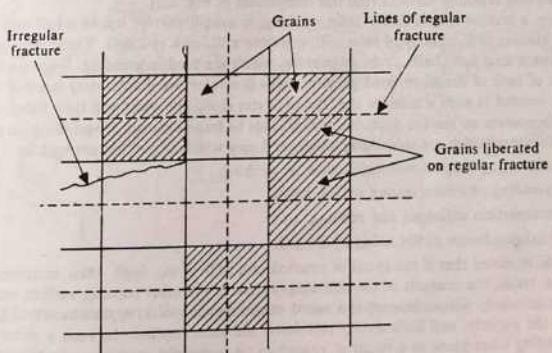


Fig. 3.4 Liberation of Locked Particles.

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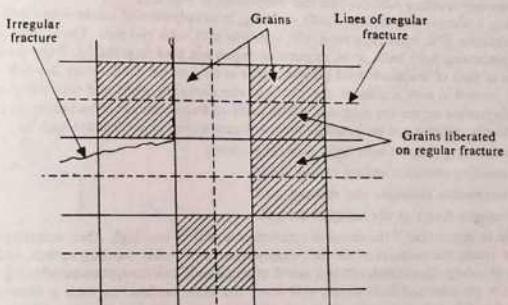


Fig. 3.4 Liberation of Locked Particles.

is a fracture across grains along regular planes, some locked particles are automatically freed. Gaudin (1951) has used a simple analytical procedure to show that when a mixture of two phases is crushed, the less abundant phase is not freed at all unless the particles are finer in composition than the original grain size. The particles must be much finer than the grain size if the less abundant phase is to be freed to any appreciable extent. An important point to be noted here is that the more abundant phase is always freer than the less abundant phase.

#### CRUSHING AND GRINDING

Ores are often available in nature as big lumps that are not suitable for most extraction processes. The majority of concentration processes requires small-sized particles. Medium-sized lumpy particles may be preferable in a blast furnace in which the raw material must be able to bear the weight of the burden and must also provide a passage for the reaction gases. On the other hand, in hydrometallurgical processes, leaching often requires fine raw material, which can be obtained by crushing or grinding.

The commination to about 6 mm (maximum) is generally referred to as *crushing* while *grinding* is the commination of an ore (that has already been reduced in size by crushing) to less than 6 mm. Although the fracture mechanism in both crushing and grinding is the same, in crushing most of the work is *preferentially* done on the 'major' fragments, whereas grinding is generally less selective.

Machines such as jaw crushers, gyratory crushers, and rolls carry out the crushing of an ore as it is mined. In most of these machines, the ore is crushed in a wedge-shaped space between two hard crushing surfaces—one fixed and the other moving. The smaller fragments of the crushed ore particles are collected as they fall through an opening provided in the machine. Further, interparticle interaction also brings about a considerable amount of crushing. Some crushing surface arrangements are shown in Fig. 3.5; it may be noted that some crushers such as slingers have two moving crushing surfaces (the last component of Fig. 3.5).

Grinding, a process that is slower than crushing, is usually carried out in a ball mill or in an equipment similar to it, namely, a tube mill, a pebble mill, or a rod mill. These mills are closed chambers containing hard balls, rods, or pebbles, which are used in grinding. Since the operating mechanism of each of the aforementioned grinding mills is similar, we discuss only the ball mill. The ball mill is rotated in such a manner that the balls rise along the walls and then either roll down or throw themselves on the ore particles, which leads to fragmentation by grinding. In this rotating mill, the ore particles are subjected to various forces which cause fracture such as

- (1) cataracting (impact with balls, rods, or pebbles),
- (2) cascading (attrition among rolling balls),
- (3) interparticle collisions and rubbing, and
- (4) frictional forces at the lining of the mill.

It should be noted that if the speed of rotation of a mill is too high, then centrifuging takes place. As a result, the contents of the mill simply stick to the inner rotating surface, and there is hardly any grinding. Conversely, if the speed of rotation is too slow, then cataracting does not occur, and the particles and balls simply roll down the inner surface. In such a situation, only limited grinding takes place as a result of cascading. A successful grinding operation aims at a judicious compromise among the various operating forces, as indicated in Fig. 3.6.

From the foregoing discussion, we observe that size reduction methods constitute an essential step in any extraction process.

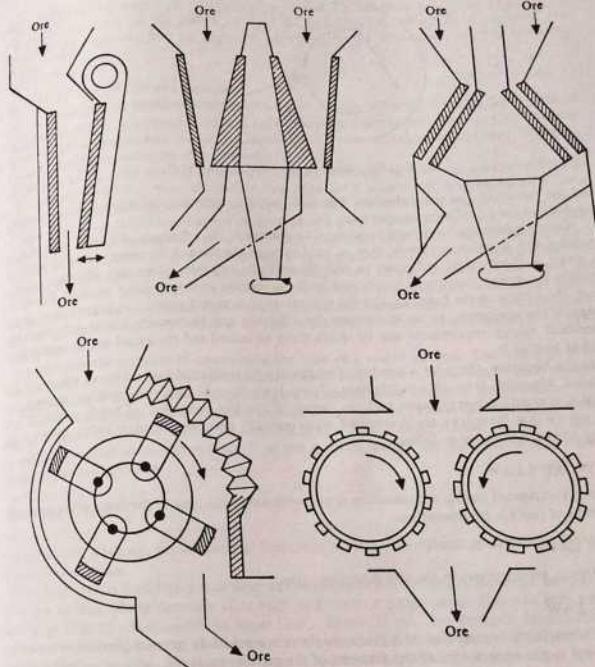


Fig. 3.5 Arrangement of Crushing Surfaces (arrows indicate direction of movement).

#### 3.12 EFFICIENCY IN COMMINUTION

The energy requirement for the comminution of brittle solids in the processing of mineral ores varies from about 5 kWh/ton to 25 kWh/ton (Orr, 1966), depending on the machine, material,

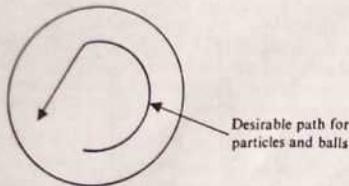


Fig. 3.6 Ideal Speed for Grinding Mills.

and the extent of the size reduction. The fact that it is necessary to ensure minimum energy expenditure need hardly be emphasized.

Many experiments have been conducted to determine the efficiency of power utilization in crushing and grinding processes, that is, to determine the ratio of the energy actually expended to effect a specific size reduction to that theoretically required. From this efficiency, we can estimate the energy lost due to factors such as the movement of the working parts of the equipment, the friction in the bearings, and the dissipation as heat and sound. An improvement in the design of the equipment so as to increase the efficiency can be brought about only when the theoretical energy requirement can be satisfactorily estimated and the actual energy requirement checked against it.

In the literature, there are a number of empirical and semi-empirical relations which are the so-called 'classical' laws of comminution. These laws describe the relationships between the cumulative grinding energy input and the degree of the size reduction of brittle solids. It has been shown that these laws are interrelated when critically examined (Kapur, 1971). Some of the widely accepted laws are as follows.

#### RITTINGER'S LAW

The energy expended during comminution is proportional to the area of the new surface produced as a result of particle fragmentation.

#### KICK'S LAW

The energy is proportional to the size reduction ratio.

#### BOND'S LAW

The total work input represented by a given weight of a crushed or ground product is inversely proportional to the square root of the diameter of the product particles.

The foregoing laws, which are used to estimate the energy requirement for comminution, have their limitations. For example, the concept of the size and surface of an ore particle which can be experimentally measured is highly arbitrary. A large part of the ore may be present as fines whose surface parameter or size parameter would be difficult to determine. Even if it could be determined by a suitable technique, the surface areas of cracks present in big particles would remain unaccounted for. Further, the energy associated with a surface depends on the medium in which the surface is kept.

From the foregoing discussion, it is evident that we should not place too much emphasis on the theoretical estimate of the energy required for comminution. Based on experience, the efficiency of the operation can be improved by modifying the dimensions and the operating conditions.

#### 1.1.3 SIZE OF A PARTICLE

In an ore beneficiation method, when mineral particles are subjected to force fields such as gravitational, magnetic, and electrical impact, their behaviour depends not only on their intrinsic properties such as density and magnetic permeability but also on their mass and size. Therefore, it becomes essential to define the size parameter.

Strictly speaking, 'size' is a rather ambiguous term. It usually signifies the narrowest regular aperture through which a mineral particle can pass. Such a criterion may be suitable for a regularly shaped polyhedron, especially a sphere, where the diameter is obviously the size. However, this criterion is rather meaningless in the case of a long, rod-shaped particle. For instance, diameter alone cannot distinguish between two rods of unequal length but identical diameter. A similar confusion exists in the case of irregularly shaped particles too. Further, when particles are sized into fractions using sieves, every fraction has bigger and smaller particles with upper and lower limits. Strictly speaking, even the narrowest fraction of the powder obtained by sieving contains grains having various dimensions, that is, it is not 'monodisperse'. The average size of grains in a fraction can be calculated by one of the several well-known formulas given in the standard texts.

Consider first the problem of determining the 'size' of a single particle. The common procedures for doing so are as follows. Microscopic or macroscopic observations can be made to obtain the dimensions of a single particle, depending on its size in three mutually perpendicular directions. These dimensions, taken together, determine the size. To express the size of a particle in terms of a single dimension, we use the diameter  $d_s$  of a sphere whose volume is equal to that of the particle. In this case, the volume  $V$  of the particle having the dimensions  $a, b, c$  can be obtained from the equation

$$V(a, b, c) = \frac{\pi d_s^3}{6} \quad (3.5)$$

This procedure, however, is not practical because it is often very difficult to determine the volume of individual particles.

The most widely used sizing technique in the laboratory is *sieving*. A standard sieve is made of square meshes whose aperture sizes vary in geometric progression. Aperture sizes used in a sieve range from 37  $\mu\text{m}$  upwards (no upper limit). Below 37  $\mu\text{m}$ , the accurate fabrication of an aperture becomes difficult. In the longest series, standardized mesh sizes extend from 3 to 400. The mesh number specifies the number of square apertures per linear inch (25.4 mm). A standard sizing scale, called the Tyler series, is given in Table 3.15. In this series, which has a constant geometric progression ratio of  $\sqrt{2}$  (or 1.414), the 200 mesh is the standard one, having an aperture of 74  $\mu\text{m}$ . The mesh immediately above the 200 mesh has an aperture of  $74/\sqrt{2}$ , i.e., 52  $\mu\text{m}$ , and that immediately below an aperture of  $74/\sqrt{2}$ , i.e., 104  $\mu\text{m}$ . Apart from the system we have mentioned, there are several other systems of grading aperture sizes.

The term 'mesh' is normally reserved for small aperture sizes. For bigger particles, screens may be made with any size of opening and down to about 2 in (50.8 mm), at size intervals of

$\frac{1}{2}$  in (12.7 mm). Between 2 in and 1/16 in (1.59 mm), the size interval diminishes to 1/32 in (0.794 mm). At 1/16 in, the aperture size overlaps the mesh size.

Table 3.15 Standard Sizing Scale (Tyler series)

Mesh	3	4	6	8	10	14	20	28
Size (mm)	6.68	4.70	3.33	2.36	1.65	1.17	0.83	0.59
Mesh	35	48	65	100	150	200	270	400
Size (mm)	0.417	0.295	0.208					
Size ( $\mu\text{m}$ )			208	147	104	74	52	37

We now consider the problem of assigning a 'size' to a group of particles. If the ratio of the largest and the smallest diameters that correspond to the width of the apertures of the 'coarser' ('bigger') and 'finer' screens, i.e.,  $d_b/d_f \leq 1.5$ , the average or mean diameter of the particles can be calculated as the arithmetic mean, the geometric mean, or the harmonic mean. It can also be calculated by the Andreesen method. The corresponding expressions are (Budnikov and Ginstling, 1968).

$$d_{\text{mean}} \text{ (arithmetic mean)} = \frac{d_b + d_f}{2}, \quad (3.6)$$

$$d_{\text{mean}} \text{ (geometric mean)} = \sqrt{(d_b d_f)}, \quad (3.7)$$

$$d_{\text{mean}} \text{ (harmonic mean)} = \frac{2}{\frac{1}{d_b} + \frac{1}{d_f}}, \quad (3.8)$$

$$d_{\text{mean}} \text{ (Andreesen mean)} = \sqrt{\frac{2d_b^2 d_f^2}{d_b + d_f}}. \quad (3.9)$$

When  $d_b/d_f \geq 1.5$ , apart from the methods mentioned, there are several other methods of calculating the mean diameter of particles. Some of these methods are based on the extreme diameter values, i.e.,  $d_b$  and  $d_f$ , while some others take into account the actual size distribution too.

It can be shown that the values of the average diameter of the particles in a fraction, calculated from different formulas, can vary a great deal. In view of this variation, it is obvious that an arbitrary choice of formula would be meaningless.

The average diameter of the particles in an ensemble may also be expressed as

$$d_{\text{mean}} = \sqrt{\frac{n_i d_i^2}{n_i}} \quad \text{or} \quad d_{\text{mean}} = \sqrt{\frac{n_i d_i^2}{n_i}}. \quad (3.10)$$

where  $n_i$  is the number of particles of size  $d_i$  and  $d_i$  the diameter of species  $i$ . These formulas, in effect, take into account either the total surface area of the particles or their total volume. Consequently, if these parameters as well as the total number of particles are known, a realistic value of the average diameter can be obtained. In terms of the specific surface area of the particles, that is, the

ratio of their surfaces to their volume (or to their weight), we may write

$$d_{\text{mean}} = \sqrt{\frac{\sum n_i d_i^3}{\sum n_i d_i^2}}. \quad (3.11)$$

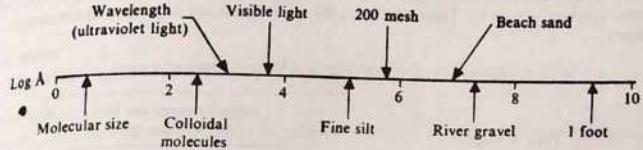
In terms of the total weight  $w$ , eq. (3.11) can be rewritten as

$$d_{\text{mean}} = \sqrt{\frac{\sum w}{\sum (w/d_i)}}. \quad (3.12)$$

Equation (3.12) can be used if the size distribution is known.

#### TYPICAL SIZE RANGES FOR VARIOUS MATERIALS

Typical size ranges for materials such as colloidal molecules and fine silt are roughly indicated on a logarithmic scale, in angstrom units ( $1 \text{ \AA} = 10^{-4} \mu\text{m} = 10^{-7} \text{ mm} = 10^{-8} \text{ cm}$ ), as



#### 3.14 SIZING

Most unit processes are designed to treat ores over certain size ranges. For example, the feed for a blast furnace must be lumpy, whereas that for fluidized bed roasting must be rather fine, but not very fine. Thus, the raw material must be chosen by a proper selection process.

A crude method of selecting the coarser particles from an ore body is *sorting* or *hand-picking*. This method yields particles (approximate diameter range 40–500 mm) which are not only ideal for certain unit processes but may also contain a high concentration of the mineral. For hand-picking to be efficient, the continuous movement of ore particles on the conveyor belt must be ensured so that they can be properly classified according to their size.

Another method of selection by sizing, which is more scientific than sorting, is *screening*, where the basis of separation is the particle size, as indicated by standardized apertures. In principle, each individual particle is tested to ascertain whether or not it can pass through an aperture of a particular size and shape. In this way, the particles can be separated into two groups, namely, oversized and undersized. A size distribution can be obtained by using a series of apertures as available in a *screen*, which is a perforated surface.

The standardization of apertures has already been discussed in Section 3.13. Here, we describe the physical characteristics of a screen. A laboratory testing screen consists of a circular brass shell whose diameter is about 200 mm and height about 50 mm. Another screening device, now widely used, is an automatic shaking device which has a provision for arranging a stack of screens with a pan at the bottom and a lid at the top.

The chief type of industrial screen, known as a 'grizzly', consists of parallel rods set at an angle to the horizontal plane and is used in conjunction with a coarse crushing unit. A 'trommel'—another screening device—consists of rotating cylindrical, prismatic, conical or pyramidal shells

made of punched plates which are 1-1.2 m in diameter and 1.5-3 m in length. The material that is to be screened is made to flow through the screen. Industrial screens are designed so as to render them cheap and rugged and to provide them with a high capacity.

#### CAPACITY OF SCREEN

The capacity of a screen primarily depends on the following factors:

- (1) The area of the screening surface.
- (2) The size of the openings on the screening surface.
- (3) Characteristics of the ore such as specific gravity, moisture content, temperature, and the proportion of fines.
- (4) The type of screening mechanism used.

Since the capacity of a screen (or screening capacity) depends directly on both the area of the screening surface and the screen aperture, it is customarily expressed as tons per sq. ft or tons/m<sup>2</sup> screen aperture per 24 hr. Table 3.16 gives the approximate capacity range of certain types of screens.

Table 3.16 Capacity Range of Various Types of Screens

Type of screen	Capacity range per 24 hr per mm aperture	
	tons/sq. ft	tons/m <sup>2</sup>
Grizzly	1-5	0.1-0.5
Trommel	0.3-2	0.03-0.2
Shaking screen	2-8	0.2-0.8
Vibrating screen	5-20	0.5-2.0

#### 3.15 CLASSIFICATION AND CONCENTRATION

Classification is a process by which particles of different sizes and specific gravities are sorted out into uniform groups. Classification differs from sizing in two ways. First, it is normally applicable to a very low range of particle size, i.e., 65-200 mesh, as in the separation of the coarse sand from the fine sands and the slimes present in an ore pulp. Second, it separates particles on the basis of their densities. Thus, if the particle sizes are comparable, then, the settling velocities of heavier and lighter particles would be different, leading to a possibility of separation and concentration.

In general, classification depends on the settling rates of the individual particles in a fluid medium (usually water). Further, the difference in the settling rates between particles of different sizes and/or different specific gravities is the controlling factor in classification.

There are two distinct kinds of settling, namely, *free settling* and *hindered settling*. Free settling takes place when the individual particles settle freely, i.e., unhindered by other particles, through a medium of still water or against a rising current of water. Hindered settling occurs when particles of different sizes, gravities, and shapes, in a crowded mass, are sorted in a rising

current of water, the velocity of which is less than the settling rate of the particles, but sufficiently high to keep them in a turbulent or fluid condition (Dorr and Bosqui, 1945).

The theory of classification processes has been thoroughly investigated and conclusively established. The settling of a particle in water depends on several factors, some of which are now listed, along with certain generalizations.

##### Specific gravity

A particle that has a higher specific gravity than another particle settles faster when other parameters such as size are comparable.

##### Shape

A rounded particle settles faster than a long narrow grain or a flat grain.

##### Size

A large particle settles faster than a small one.

##### Air bubbles

A particle that does not retain adhering air bubbles settles faster than one that does.

##### Magnetism

Particles that have a mutual magnetic attraction settle faster than those that do not have such an attraction.

##### Density of liquid

The settling rate of a particle is higher in a lighter than in a heavier liquid.

##### Viscosity

The settling rate of a particle is higher in a less viscous medium than in a more viscous one.

The relative importance of the foregoing factors varies widely, depending on the hydrodynamic conditions. It should, however, be obvious that two particles can be effectively separated from each other on the basis of their settling velocities.

##### DRAG FORCE

The exact relation between the settling velocity of a particle in a liquid and the foregoing parameters can be theoretically determined provided a clear picture of the nature of the liquid flow around the particle is available. The viscous drag, which basically governs the settling rate, depends on the liquid flow pattern.

The resistance to the movement of a particle is a function of a factor  $N_R$  known as Reynold's number. For a spherical particle, this number, which is dimensionless, is expressed as

$$N_R = \frac{dV\rho}{\mu}, \quad (3.13)$$

where  $d$  is the diameter of the spherical particle or the effective diameter facing resistance,  $V$  the velocity of the particle,  $\rho$  the density of the liquid, and  $\mu$  the viscosity of the liquid. When Reynold's number is small ( $< 1$ ), the liquid flow past the particle is laminar and if it is high, the

flow is turbulent. In the latter situation, the resistance to the movement increases considerably. Up to  $N_R = 0.5$ , the resistance or viscous drag force  $F_D$  is expressed by Stoke's equation

$$F_D = 3\pi d \mu V. \quad (3.14)$$

For turbulent flow, several equations have been derived for calculating the viscous drag force, of which a commonly used equation is that proposed by Newton and given by

$$F_D = K \rho d^2 V^2, \quad (3.15)$$

where  $K$  is a constant.

From the foregoing discussion, it should be obvious that eqs. (3.14) and (3.15) are applicable only when the liquid does not have any bulk velocity. For a general case, complete force balance equations for calculating the drag force are available in Hinze (1959) and Ray and Biswas (1971). It should be noted that for turbulent motion in the liquid, all the theoretical equations are applicable within well-defined limits.

#### HEAVY MEDIA SEPARATION

**Heavy media separation** is a special concentration process which depends exclusively on the specific gravity of a particle. In this operation, the particle size does not come into the picture at all. Generally, the comminuted ore (after the finer sizes have been removed from it) is put into a fluid whose specific gravity lies in between the specific gravities of the two minerals that are to be separated from each other. If there are more than two minerals in an ore, then the heavy mineral is generally recovered as 'sink' and the waste as 'float'. For example, the densities of most metallic oxides lie in the range 3.5–4.5 gm/cc; silica—the main component of gangue—having a density of 2.65 gm/cc. Therefore, during heavy media separation in a liquid whose density is approximately 3.0 gm/cc, the metallic oxides sink but silica floats. In reality, it is difficult to find an inexpensive liquid with a high density that lies between the densities of the mineral and the gangue. Such a liquid can, however, be obtained by suspending fine, dense particles in water. For this purpose, heavy minerals or alloys, ground up to –100 mesh, are normally used. Typical examples are galena (effective specific gravity of medium 4.3) and ferro-silicon (effective specific gravity 2.5–3.5, depending on the composition). Suspensions normally used in heavy media separation contain 70–85 per cent of solids by weight.

#### 3.16 SIZING AND SORTING EQUIPMENT

When a classifier mainly exploits the size parameter, the operation is known as *sizing*. On the other hand, when the equipment utilizes the difference in the specific gravities of minerals, the operation is called *sorting*, and is, in effect, a preliminary concentration step. For most sorting operations, hindered settling conditions are preferred. On the other hand, sizing operations normally make use of free settling conditions in dilute suspensions because the effect of the specific gravity difference is minimized. Thus, classifiers can be broadly divided into two categories.

##### Sorting Classifier

The fluid medium here is a relatively dense aqueous suspension.

##### Sizing Classifier

The fluid medium here is a relatively dilute aqueous suspension.

Some special types of classifiers have air as the fluid medium for sizing particles over various size ranges.

Some simple classifiers are shown in Fig. 3.7. Apart from the types mentioned, there are other types of classifiers such as jigs and tables. In a jig, a thick pulp is supported on a grid and is stratified by pulsating forces of water from the bottom of the apparatus. In *jigging*, all particles are suspended and the water is allowed to drain back through the grid. This cycle is continuously repeated. Eventually, those particles that are denser and smaller than others concentrate in the lower strata.

A concentrating table or a riffle table employs principles similar to jigging in a completely different way. In this case, the operation is known as *tabling*. In tabling, an inclined flat surface is divided into narrow strips by riffles of wood so as to form parallel channels. These channels are set at right angles to the direction of the water flow. During operation, the entire table is vibrated horizontally, length-wise, in the direction of the riffles. As the ore suspension flows across the vibrating table, the light particles are carried farther than the heavy particles across the riffles in the direction of water flow and the heavy particles themselves are carried, length-wise, along the riffles to the discharge end. Thus, channels that are closer to the feed inlet than others receive the coarser particles.

In both jigging and tabling, effective classification depends on a number of factors inherent in the operation itself or in the design of the equipment. For further details, the reader is referred to any standard textbook on mineral dressing.

#### 3.17 MAGNETIC SEPARATION

It is a well-known fact that many minerals exhibit magnetic properties. Minerals that are strongly attracted by magnets are called ferromagnetic, those only weakly attracted paramagnetic, and those hardly attracted diamagnetic. Table 3.17 lists the relative attractability of some minerals.

It should be noted that *magnetic concentration* entails the separation of a valuable mineral from the gangue whereas *magnetic separation* is the separation of one mineral from another, essentially based on the difference in the values of the magnetic attractability of the minerals. In

Table 3.17 Relative Magnetic Attractability of Some Minerals  
(Bailey, 1961)

Classification	Mineral	Relative attractability
Strongly magnetic	Fe (standard)	100.0
	Magnetite ( $Fe_3O_4$ )	40.2
	Ilmenite ( $FeTiO_3$ )	24.7
Weakly magnetic	Pyrrhotite ( $Fe_{11}S_{12}$ )	6.7
	Siderite ( $FeCO_3$ )	1.8
	Hematite ( $Fe_2O_3$ )	1.3
	Pyrolusite ( $MnO_2$ )	0.7

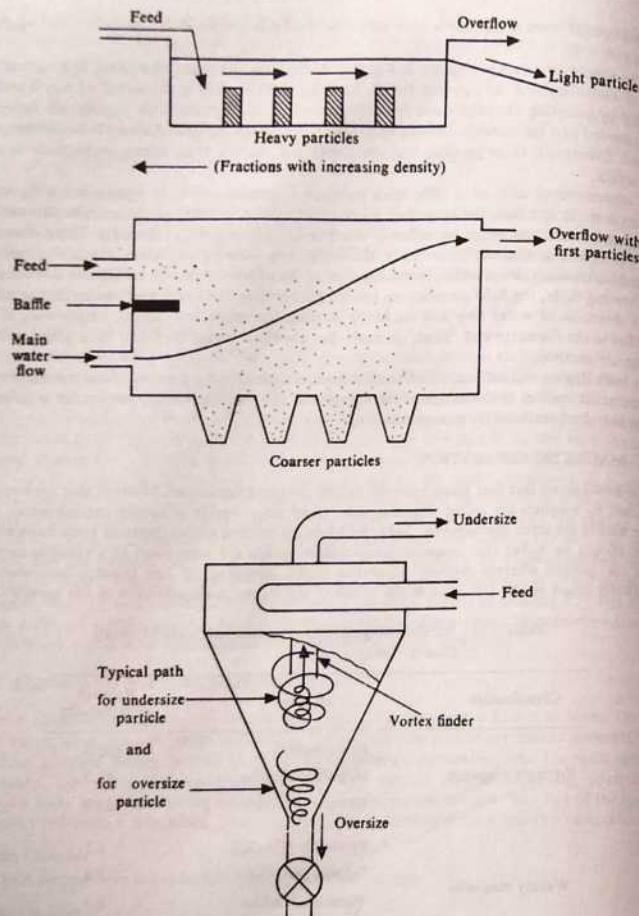


Fig. 3.7 Some Simple Classifiers (after Gilchrist, 1967).

MINERALS, ORES, AND METHODS OF BENEFICIATION  
Table 3.17 Relative Magnetic Attractability of Some Minerals (Bailey, 1961) (cont.)

Classification	Mineral	Relative attractability
Nonmagnetic	Quartz ( $\text{SiO}_2$ )	0.4
	Cerussite ( $\text{PbCO}_3$ )	0.3
	Pyrite ( $\text{FeS}_2$ )	0.2
	Sphalerite ( $\text{ZnS}$ )	0.2
	Magnesite ( $\text{MgCO}_3$ )	0.15
	Chalcocite ( $\text{Cu}_2\text{S}$ )	0.09
	Cuprite ( $\text{Cu}_2\text{O}$ )	0.08
	Galena ( $\text{PbS}$ )	0.04
	Calcite ( $\text{CaCO}_3$ )	0.03

both these operations, a continuous stream of ore is simultaneously subjected to both magnetic and gravitational fields. Figure 3.8 depicts some simple machines that are employed for magnetic concentration and separation. The principles of operation of these machines become evident from the diagram.

### 3.18 ELECTROSTATIC SEPARATION

The electrostatic separation of one mineral from another is somewhat similar to magnetic separation in that it is brought about by an external field (electrostatic) in conjunction with a gravitational field. When different types of mineral particles are given an electrostatic charge and then brought into contact with a grounded electrical conductor, the charge leaks away from a good conductor more rapidly than from a bad conductor. This process of discharging is combined with a falling of particles in air so as to separate a mineral which is a good conductor of electricity from one which is not. A typical arrangement for electrostatic separation is shown in Fig. 3.9; the diagram is self-explanatory.

### 3.19 FLOTATION

*Floation or froth flotation* is one of the most outstanding mineral beneficiation techniques. In flotation, an ore pulp is agitated and air is blown through it so as to produce froth. Some mineral particles (mostly sulphides) attach themselves to the air bubbles and are concentrated in the froth, which is skimmed from time to time. The gangue materials sink to the bottom. It is obvious that flotation entirely depends on the sensitive surface properties of the mineral particles. By making the surface properties selective, two minerals, which are both 'floatable', can be separated from each other.

A mineral particle that sticks to an air bubble is considered unwettable by water. Since the wettability of a mineral particle can be controlled by adding suitable reagents, a selective flotation

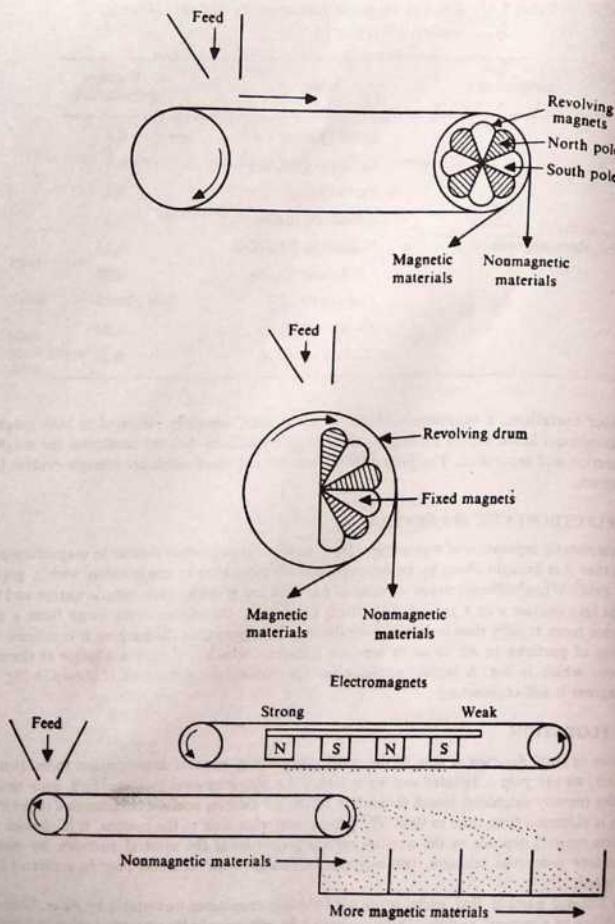


Fig. 3.8 Machines for Magnetic Concentration and Separation.

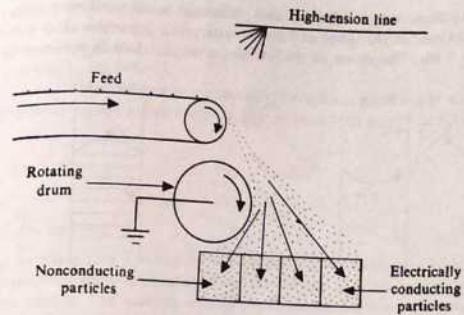


Fig. 3.9 Electrostatic Separator (after Gilchrist, 1967).

of minerals is possible. A wetted particle sinks, provided it is not lighter than the medium and a nonwetted particle floats, provided its size is sufficiently small. Some of the materials/chemicals that are used in flotation are listed in Table 3.18 along with their functions.

Table 3.18 Materials/Chemicals Used for Flotation

Material/chemical	Remark
Pulp	A suspension of fine solids (about one third) in water
Frother	A reagent added in a small quantity to produce a stable froth which brings the mineral to the surface
Collector	A reagent that modifies the surface properties of minerals by being adsorbed or chemisorbed so as to enhance the differences in the surface properties of the minerals and, consequently, to achieve selective flotation
Activator	An activator renders a mineral surface more amenable to the action of a collector; it thus has a supporting role
Depressor	A depressor has an opposite role. It opposes the action of a collector by rendering the mineral surface inactive to the action of a collector

Since flotation basically depends on the degree of wettability of a mineral surface, we now discuss it in further detail.

#### WETTABILITY

It is a well-known fact that water wets a glass surface whereas mercury does not. For example, when water is poured out of a beaker, a few drops stick on to the surface of the beaker, whereas

mercury can be poured out completely. This difference in the wetting tendencies of water and mercury manifests itself in the shape of a liquid surface in a glass tube or as a drop on a flat glass surface (see Fig. 3.10). The shape of the surface or of the drop is governed by surface tension

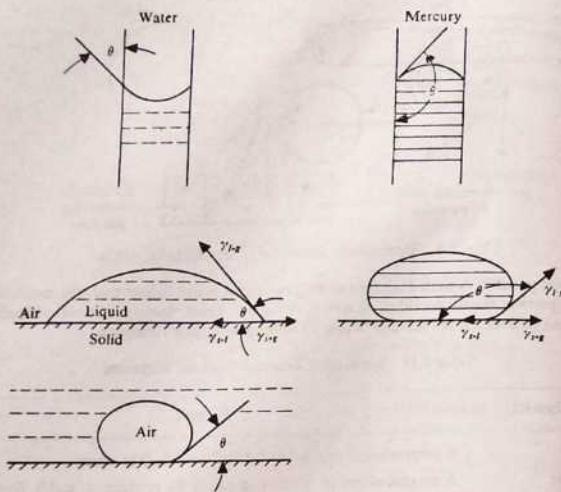


Fig. 3.10 Difference in Wettability of Glass Surface for Water and Mercury.

forces in three phases, namely, liquid, solid, and gas (air in most cases). At equilibrium, the forces acting at the points of contact of the solid, liquid, and gas phases are the three surface tension forces denoted by  $\gamma_{s-l}$ ,  $\gamma_{l-g}$ , and  $\gamma_{s-g}$ , where  $\gamma$  is the surface tension and  $s$ ,  $l$ , and  $g$  denote solid, liquid, and gas, respectively. The forces are related by the equation

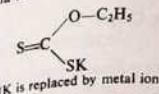
$$\gamma_{s-g} - \gamma_{s-l} = \gamma_{l-g} \cos \theta, \quad (3.16)$$

where  $\theta$  is the contact angle, as shown in Fig. 3.10.

The contact angle is the chief measure of wettability. Its value is the same both for a liquid drop on a solid surface in air and for an air bubble in the same liquid in contact with the same solid surface. In flotation, we deal with the latter situation, i.e., where an air bubble is in contact with the solid mineral particles immersed in a liquid medium. It should be obvious that if  $\theta$  is zero, the mineral is wetted by water, if  $\theta$  is finite, the air bubble is attached to the mineral surface, and if the size of the mineral particle is sufficiently small, it floats upwards along with the rising air bubble. Mineral particles, if sufficiently fine, may cover the entire surface of the air bubble. Thus, we conclude that unwettable mineral particles stick to an air bubble and tend to float towards the surface.

The values of the surface tension forces and, therefore, the magnitude of the contact angle  $\theta$  depend on factors such as temperature, mineral surface irregularities, and other extraneous reagents present in the liquid. As already stated, collectors, activators, and depressors influence these forces in one way or the other.

Xanthates, a very well-known group of collectors, have found particularly wide application in the flotation of sulphide minerals. One such xanthate is potassium ethyl xanthate whose chemical formula is



Potassium ethyl xanthate gets attached to the mineral surface when potassium is replaced by a metal ion. The resulting compound remains on the surface as a precipitate, which reduces the wettability of the surface. The stability of this precipitate depends on a number of factors, the most important one being the pH value of the solution used in flotation. The function of an activator or of a depressor is to promote or prevent, respectively, the formation of such a precipitate.

#### QUESTIONS

- What is the significance of the settling ratio  $R$  in the gravity concentration of a mineral?
- Discuss the statement: ore dressing is a necessary preliminary step in the exploitation of low-grade ores on both technological and economic grounds.
- 'Comminution is the costliest and the least efficient operation in any mineral-dressing process.' Discuss this statement paying due attention to the relationship between the input of energy and the reduction in the particle size.
- Describe the main types of reagents used in flotation. What is the significance of pH in the attachment of an anionic collector to a sulphide mineral?

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## 4 General Methods of Extraction

### 4.0 INTRODUCTION

In an extraction process, a specific amount of energy is required to reduce or release a metal ion present in a compound (solid or liquid) in association with other elements and to collect the metal in its elemental form. During metal extraction, the bulk of the metal is separated from the impurities present in the ore by using a system which invariably comprises more than one phase. The metal enters the metallic phase while the impurities enter the nonmetallic phase or phases. The driving force for the reactions involved in metal extraction depends on the differences in the chemical potentials of the chemical elements. The significance of chemical potential gradients in an extraction process has been discussed in Chapter 2. To briefly recapitulate: during a chemical reaction, an element tends to move from a high to a low chemical potential state. In each extraction process, the basic aim is to create conditions conducive to such a transfer, which facilitates the extraction of a metal or its compound.

In metal extraction, a vast majority of metallurgical reactions are made to take place at elevated temperatures because then the ore compounds become relatively unstable, facilitating the release of the metal. This is the basis of pyrometallurgy. In electrometallurgy, the dissociation or decomposition of a compound in solution (i.e., reduction of an ion) is brought about by employing electrical forces. In hydrometallurgy, the reduction process depends on the judicious manipulation of the chemical reactions taking place in an aqueous solution.

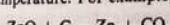
### 4.1 PYROMETALLURGY

Despite the rapid developments in hydrometallurgy and electrometallurgy over the last hundred years, pyrometallurgy still remains the principal means of metal extraction, both in the number of applications and in the tonnage of metal produced. Pyrometallurgy deals with the methods of extraction of metals from their ores and their refining, and is based on chemical and physical changes occurring at high temperatures, i.e., 500–2000°C.

A high-temperature process is often cheaper and more versatile than other competing methods such as electrometallurgy and hydrometallurgy because of the reasons now given.

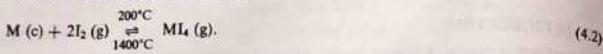
At a high temperature, the reaction rate is accelerated. A rapid reaction rate leads to the increased production of a metal (for a given size of reactor). Further, a high-temperature process permits the use of inexpensive reducing agents or raw materials that are cheaper than those required for a low-temperature process. It should be noted that the rate of most reactions is approximately doubled for every 10°C rise in temperature, and the higher the temperature, the smaller the activation energy barrier that opposes the progress of the chemical reaction.

Pyrometallurgical extraction takes advantage of the ability to shift the reaction equilibrium with temperature. For example, at 25°C, the equilibrium position of the reaction



(4.1)

is far to the left, but, at 1200°C, it shifts far to the right. In other words, carbon cannot reduce ZnO except at elevated temperatures, i.e., at a minimum of 900°C for continuous reduction at 1 atm. Another example that illustrates the effect of temperature on the reaction equilibrium is the iodide refining process for refractory metals such as titanium and zirconium. When a crude metal M is made to react with iodine at a low temperature (the reaction equilibrium being shifted to the right), metallic iodide vapour is formed. This vapour is transported to a hot zone (the reaction equilibrium being shifted to the left), where it decomposes into the pure metal and regenerates iodine according to the reaction:



The physical separation of a product metal from waste is facilitated when the products are liquefied or vaporized at high temperatures. Further, at these temperatures, the liquid metal and liquid slag that are formed separate out, facilitating metal extraction. Some of the common metals such as iron, lead, zinc, copper, aluminium, magnesium, sodium, and antimony are produced by a process where the metal is reduced to either the liquid or the gaseous state, permitting its separation from the residue. One of the reasons why refractory metals such as titanium, zirconium, molybdenum, tantalum, and niobium are very expensive is that they are reduced directly to the solid metal. This requires an expensive process either to separate the metal from the residue or to pre-purify the metal compound so that no residue remains after reduction.

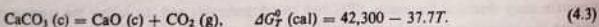
Pyrometallurgy can bring about the reduction of a compound, which cannot take place in the presence of water. This advantage stems from its ability to extract the reactive metals which cannot be reduced from an aqueous solution. Consequently, only pyrometallurgy or fused salt electrolysis can be used to extract the highly reactive metals, namely, the alkaline earth metals, zirconium, and titanium.

A high-temperature process has the inherent ability to treat large tonnages of ores in a compact space, which leads to a saving in the capital cost. Even a small electric furnace, by using a power input of a very high order, can achieve a very high production rate. This, however, is not true of an electrometallurgical process, either at the room temperature or at a high temperature, because the voltage value chosen for the process must necessarily be low, depending on the decomposition voltage of the compound to be electrolyzed. Moreover, there is always a limiting current density.

We now discuss the three main steps employed in pyrometallurgy, namely, calcination, roasting, and smelting.

#### 4.2 CALCINATION

*Calcination* is the thermal treatment of an ore that brings about its decomposition and eliminates the volatile product—usually carbon dioxide or water. The temperature required for calcination can be calculated from the free energy-temperature relationship for the reaction under consideration. For example, the reaction for the decomposition of calcium carbonate in a kiln is



When the CO<sub>2</sub> pressure is 1 atm,  $\Delta G_f^{\circ}$  becomes equal to 0 and  $T$  becomes equal to 1123 K or 850°C, so that a kiln temperature of 1000°C would be sufficient to provide a rapid temperature rise in the mineral particles and to reach the decomposition temperature. Since the reaction is

endothemic, the rate of decomposition is probably controlled by the rate of heat transfer into the particle. As a result, even higher kiln temperatures can be expected so as to increase the production rate, but at some cost in fuel. Since the solid residual product is likely to be porous in texture and permeable, the gaseous product can easily escape. Further, the pressure at the decomposition front is likely to be a little higher than the atmospheric pressure.

The decomposition temperature of a carbonate is the temperature at which the partial pressure of CO<sub>2</sub> ( $p_{CO_2}$ ) equals 1 atm. It is obvious that most carbonates actually start to decompose at temperatures lower than the decomposition temperature of calcium carbonate (e.g., MgCO<sub>3</sub> at 417°C, MnCO<sub>3</sub> at 377°C, and FeCO<sub>3</sub> at about 400°C). This fact can be used for differential calcination. For example, a magnesium ore that contains both magnesium carbonate and calcium carbonate can be beneficiated by calcining the ore around the decomposition temperature of MgCO<sub>3</sub>. Water is used to leach out the resulting MgO, and the undecomposed CaCO<sub>3</sub> is left behind.

#### 4.3 ROASTING

The *roasting* of an ore or a concentrate is a process which precedes smelting in pyrometallurgy and leaching in hydrometallurgy. In general, very few ores and concentrates in their native form are suitable for direct conversion to the metal. An oxide is more easily reduced to the metal than a sulphide, and leaching becomes easier if the metal were present as a sulphate, chloride, or oxide. Therefore, the mineral constituent of an ore must be converted into another chemical form. Such a conversion can be brought about by roasting. The main purpose of calcination is to decompose an ore, whereas roasting, by employing oxygen or some other element, aims at the chemical conversion of an ore. Traditionally, roasting was chiefly used to remove sulphur or other elements such as arsenic and tellurium in the form of a volatile oxide from an ore. Nowadays, however, roasting encompasses a wide variety of operations including reduction, sulphation, and chloridization, wherein the ore is heated to a temperature below the fusion point of its constituents. The product thus obtained becomes amenable to subsequent treatment for the extraction of the metal.

We now discuss some typical roasting operations to emphasize the importance of roasting in metal extraction processes.

#### OXIDIZING ROASTING

*Oxidizing roasting*, which is the most important roasting process, burns out the sulphur from a sulphide ore and replaces it, in whole or in part, by an oxide. The general reaction is



For example, in the case of zinc sulphide, the reaction is



Reaction (4.5), however, gives only an overall picture of roasting. In reality, a complicated series of reversible reactions occur. During roasting, metal sulphates may also be formed. A high temperature is required to break up the sulphates, especially zinc sulphate.

When a sulphide ore is roasted to a point where almost the entire sulphur content is eliminated, the residue is called *dead roast*.

A catalytic agent often speeds up the roasting process. Quartz and other gangue materials often act as catalysts during roasting.

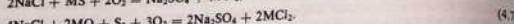
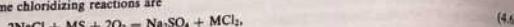
Roasting essentially depends on factors such as time (i.e., duration), temperature, the availability of oxygen or air, the physical condition of the ore, and the nature of the mechanical devices used. The durations of roasting processes vary greatly. For example, blast roasting is done in a mere flash of time, whereas hearth roasting takes hours, heap roasting months, and weather roasting years.

#### VOLATILIZING ROASTING

*Volatileizing roasting* eliminates volatile oxides such as  $As_2O_3$ ,  $Sb_2O_3$ , and  $ZnO$  from an ore. In volatileizing roasting, the inflow of oxygen should be carefully controlled, as excessive oxidation may lead to the formation of non-volatile higher oxides.

#### CHLORIDIZING ROASTING

*Chloridizing roasting* is carried out to convert certain metal compounds to chlorides under oxidizing or reducing conditions. Many metals, for example, uranium, beryllium, niobium, zirconium, and titanium, are extracted from their chlorides. Some chloridizing reactions are



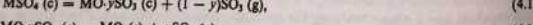
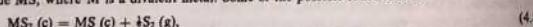
Reaction (4.6) is particularly suited to the roasting of a sulphide ore, which may be highly exothermic. For an oxide ore, reaction (4.7) is facilitated by the addition of elemental sulphur. Reaction (4.7) also represents the chlorination of a carbonate which decomposes on heating, giving an oxide. Sulphates and silicates may react with a chloride by a direct interchange of the elements and radicals without the addition of sulphur.

#### OTHER KINDS OF ROASTING

Apart from oxidizing roasting, volatileizing roasting, and chloridizing roasting, there are other kinds of roasting processes, some of which are now mentioned. *Sulphating roasting* converts certain sulphide ores to sulphates, usually prior to leaching. An example of *magnetic roasting* is the controlled reduction of hematite ( $Fe_2O_3$ ) to magnetite ( $Fe_3O_4$ ). *Reduction roasting* is the partial reduction of an oxide ore prior to actual reduction smelting. *Blast roasting* or *sinter roasting* not only modifies the physical condition of an ore (e.g., agglomeration) but also helps in its partial oxidation.

#### CHEMISTRY OF ROASTING

A large number of reactions are theoretically possible when a sulphide is roasted. Consider a sulphide  $MS$ , where  $M$  is a divalent metal. Some of the possible reactions are



[Examples of  $MO_ySO_3$  are  $PbSO_4 \cdot PbO$  ( $y = \frac{1}{2}$ ),  $PbSO_4 \cdot 2PbO$  ( $y = \frac{1}{3}$ ), . . .] At the temperatures commonly used for roasting, reactions (4.9) and (4.10) generally have large negative free energy changes and the  $SO_2/O_2$  equilibrium is far to the right. For example, in the case of  $FeS$ , the standard free energy change for reaction (4.10) is given by

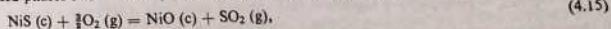
$$\Delta G^\circ(\text{cal}) = -113,000 + 9.57 \log T - 1.965(10^{-3}T^2) - 6.7T.$$

At 1100 K, the equilibrium constant  $K$  for this reaction is calculated as  $1.2 \times 10^{18}$ . Therefore, the sulphide is converted to an oxide for a relatively small value of the partial pressure of oxygen ( $p_{O_2}$ ). Similarly, at 1100 K, the equilibrium constant for reaction (4.9) is calculated as  $2.76 \times 10^{13}$ . This value shows that at a temperature as high as 1100 K,  $SO_2$  is a stable phase, even in the presence of small amounts of oxygen. On the other hand, reactions (4.11)-(4.14) are such that both the temperature and the partial pressure of  $SO_2$  ( $p_{SO_2}$ ) determine which of the phases are stable. By using the phase rule, we can show that the system is univariant for the existence of a gas and for a mixture of two solid phases such as  $MSO_4 \cdot MO$ ,  $MSO_4 \cdot MO_ySO_3$ , or  $MO \cdot MO_ySO_3$ . In other words, two solids can coexist, at any given temperature, over a range of partial pressures of  $SO_2$ . However, were the gas phase, i.e.,  $SO_2$ ,  $O_2$ , or  $SO_3$ , in equilibrium with all the three solids, namely,  $MO$ ,  $MSO_4$ , and  $MO_ySO_3$ , then the system becomes nonvariant, that is, equilibrium can be attained only at a point where both temperature and  $p_{SO_2}$  are defined.

#### 4.4 PREDOMINANCE AREA DIAGRAMS

The temperature at which roasting is carried out is an important factor in determining the nature of the product obtained. In order to get a desired product, we can determine the best operating temperature by knowing both the composition of the gas used in an industrial roaster and the equilibrium relationship in an M-S-O system. The isothermal behaviour of some M-S-O systems with respect to their relative stabilities can be represented by predominance area diagrams. These diagrams indicate, for a specified temperature, those solids which are in equilibrium with a gas having specified partial pressures of oxygen and sulphur dioxide. Thus, these diagrams serve to predict the type of solid present that would be in equilibrium with a roaster gas of a known composition. Even in the case of partial roasting, where equilibrium conditions do not prevail, these diagrams can be used to identify the type of the product formed as the reaction proceeds towards equilibrium. The high values of the equilibrium constants of reactions (4.9) and (4.10), as calculated, suggest that  $SO_2$  is always formed as soon as oxygen reacts with a sulphide, so that the concentration of  $SO_2$  must be taken into account.

The basis for drawing predominance area diagrams can be illustrated by taking Ni-S-O as an example (see Fig. 4.1a). At 1000 K, in this system, the condensed phase is made up of  $Ni$ ,  $NiO$ ,  $Ni_3S_2$ , and  $NiSO_4$ . The gas phase normally contains  $SO_2$  and  $O_2$ , but some  $SO_3$  and  $S_2$  may also be present, as indicated by reactions (4.9) and (4.11). At a specified temperature, the phase relation between any two condensed phases can be represented by a two-dimensional diagram in which the partial pressures of any two of the gaseous components are taken as the coordinates. In Fig. 4.1a,  $\log p_{SO_2}$  and  $\log p_{O_2}$  are chosen as the coordinates. Thus, the reaction between the condensed phases  $NiS$  and  $NiO$ , and the gases  $SO_2$  and  $O_2$  is represented by



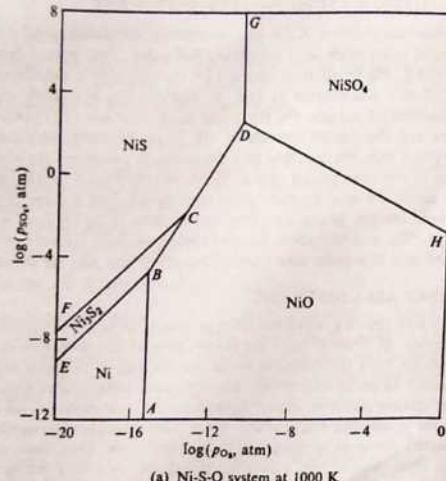
for which the equilibrium constant  $K'$  is given by

$$K' = \frac{p_{SO_2}}{p_{O_2}^{1/2}}$$

and

$$\log p_{SO_2} = \frac{1}{2} \log p_{O_2} + \log K''.$$

$K''$  can be calculated by knowing the free energy change for reaction (4.15). In Fig. 4.1a,  $CD$



(a) Ni-S-O system at 1000 K

Fig. 4.1 Predominance Area Diagrams (after Kellogg and Basu, 1960) (cont.).

corresponds to reaction (4.15) and  $BC$  represents the equilibrium of the reaction



The corresponding equilibrium constant  $K'$  is given by

$$K' = \frac{p_{SO_2}^2}{p_{O_2}^{1/2}}$$

and

$$\log p_{SO_2} = \frac{1}{2} \log p_{O_2} + \frac{1}{2} \log K'.$$

It should be noted that the slope of  $BC$  is slightly different from that of  $CD$ .  $AB$  (in Fig. 4.1a) represents the equilibrium of the reaction

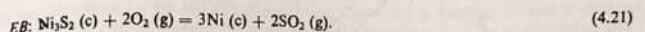
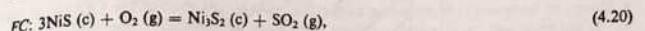
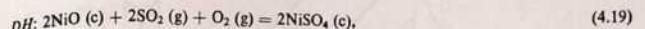


The corresponding equilibrium constant  $K'''$  is given by

$$K''' = \frac{1}{p_{O_2}^{1/2}}$$

$$\text{and } \log p_{O_2} = -2 \log K'''.$$

Obviously, the two phases Ni and NiO can coexist only at a fixed value of  $p_{O_2}$ . The equilibrium corresponding to reaction (4.17) is independent of  $p_{SO_2}$ . Other lines in Fig. 4.1a represent the equilibria for the following reactions:



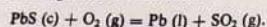
$fC$  and  $EB$  are parallel to each other, each inclined at an angle of  $45^\circ$  to both the  $x$ - and  $y$ -axis. Thus, the stable portion of each bivariate equilibrium can be demarcated if the equilibrium constants for the various reactions are known.

The areas in Fig. 4.1a correspond to the predominance area for a particular condensed phase, both  $p_{SO_2}$  and  $p_{O_2}$  can be varied, and the system has two degrees of freedom. Along the lines, the system has one degree of freedom. The system is nonvariant when three condensed phases are present, as at the points  $B$ ,  $C$ , and  $D$ .

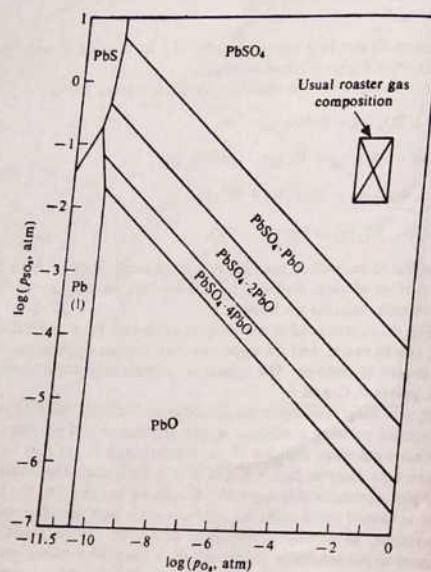
Predominance area diagrams, which are plotted from available thermodynamic data, provide data that help control roasting conditions so that the desired end products can be obtained. At 1000 K, if the roaster gas phase contains 10 per cent  $SO_2$  and 10 per cent  $O_2$ , it is evident from the predominance area diagram that  $NiSO_4$  is the thermodynamically stable phase. On the other hand, if the gas phase contains only 1 per cent  $SO_2$  and 1 per cent  $O_2$ , the final product is  $NiO$ . Nickel sulphate is formed under oxidizing conditions at a high partial pressure of  $SO_2$ . Although  $NiS$  can, in principle, be directly converted to  $NiSO_4$  at a high partial pressure of  $SO_2$ , in practice, it is more convenient to do so through the intermediate formation of  $Ni_3S_2$  and  $NiO$ .

If a given metal forms several oxides apart from the simple oxide mentioned and also sulphides, basic sulphates, and sulphates, additional equations have to be written, and the lines corresponding to them can be incorporated in Fig. 4.1a. For example, in the Pb-S-O system (see Fig. 4.1b),  $PbO$  can form several basic sulphates, namely,  $PbSO_4 \cdot 4PbO$ ,  $PbSO_4 \cdot 2PbO$ , and  $PbSO_4 \cdot PbO$  before it is converted to  $PbSO_4$ . Figure 4.1b illustrates various factors that govern roasting of lead sulphide. This figure also gives the composition of the roaster gas in a conventional roaster operating at 827°C and shows that the stable product obtained by roasting  $PbS$  should be  $PbSO_4$ . Since the  $PbS$  and  $PbO$  fields do not have a common boundary,  $PbO$  cannot be produced by roasting  $PbS$  in oxygen without some  $PbSO_4$  also being formed. This accounts for the difficulty encountered in dead roasting to  $PbO$  at 827°C. On the other hand, a sulphatizing roasting of  $PbS$  to yield  $PbSO_4$  can be carried out, but it is not desirable, as  $PbSO_4$  is insoluble in water. Figure 4.1b explains why  $PbSO_4$  is predominant in lead fumes rather than  $PbO$ . The possibility of a roast reduction reaction in which lead sulphide is converted to metallic lead by controlling  $p_{SO_2}$  and  $p_{O_2}$  is also

indicated in Fig. 4.1b. The reaction is



By studying the predominance area diagrams drawn for different temperatures, we can select the most suitable temperature for a given roasting operation. In a predominance area diagram,



(b) Pb-S-O system at 1100 K

Fig. 4.1 Predominance Area Diagrams (after Kellogg and Basu, 1960).

at a given temperature, the predominance areas for a given compound may have different locations for different metals. In the case of a mixed sulphide such as Fe-Cu sulphide, the roasting conditions can be predicted for the selective oxidation of Fe to an oxide ( $\text{Fe}_2\text{O}_3$ ) while retaining Cu as a sulphide.

Predominance area diagrams serve as a useful guide to the extraction of metals from sulphides. Moreover, by using predominance area diagrams, we can show that it would be more convenient to extract copper directly from the sulphide phase than from the oxide phase (see Chapter 7 for details). These diagrams also serve as a guide to the selective sulphation of minerals. For

example, the low stability of iron sulphates generally allows the selective sulphation of the other metals from sulphide mineral mixtures. Thus, copper ferrite can be converted to  $\text{CuSO}_4$  and  $\text{Fe}_2\text{O}_3$  by treating it with a mixture of  $\text{SO}_2$  and  $\text{O}_2$  in the range 600–800°C.

The foregoing discussion is based on the assumption that equilibrium conditions prevail. If a roasting operation is carried out under nonequilibrium conditions as is usually done in industrial processes, the nature of the solid phases formed in the roast are determined by the rates of the various reactions and by the mechanisms by which they proceed. These roasting reactions can often be catalyzed and, therefore, equilibrium is approached more easily. For example,  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  intensify the decomposition rate of  $\text{MgSO}_4$ , while  $\text{SiO}_2$  has no effect on it. The addition of  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ , or  $\text{Mn}_3\text{O}_4$  also catalyzes the formation of  $\text{CoSO}_4$  and  $\text{ZnSO}_4$  (Sheaf and Espelund, 1973).

#### 4.5 ROASTING PRACTICE

As roasting is usually a preliminary step in many extraction processes, it is necessary to choose a roasting method that would facilitate subsequent operations. There is a wide variation in the requirements and conditions for the subsequent steps. Generally, a roasting process is chosen based on two major criteria, namely, the required physical condition and the required chemical composition of the product.

##### REQUIRED PHYSICAL CONDITION OF PRODUCT

If an ore is to be smelted in a blast furnace, the product should be coarse and cellular. For a reverberatory furnace or for a retort, the product should be fine. For leaching, the product should be porous in nature and the formation of insoluble compounds should be avoided.

##### REQUIRED CHEMICAL COMPOSITION OF PRODUCT

If lead is the prime metal to be recovered from a sulphide ore, it is desirable to eliminate almost the entire sulphur content before subsequent blast furnace smelting. For copper, the entire sulphur content need not be eliminated. In fact, a sufficient quantity of sulphur should be retained so as to produce a matte, which is mainly a mixture of iron sulphides and copper sulphides of a desired grade. For zinc, as for lead, almost the entire sulphur content should be eliminated. However, the formation of zinc ferrite should be avoided when zinc is extracted by leaching because it is difficult to leach the ferrite.

There are several other factors to be considered besides those mentioned. For example, the chemical composition of an ore and of the minerals present in it may or may not favour a particular roasting process. In the manufacture of sulphuric acid from sulphurous gases that are evolved during roasting, the actual roasting process must ensure the availability of a gas rich in  $\text{SO}_2$ , for example, fluidized bed roasting. If there are precious metals or other valuable recoverable metals which may be lost at excessively high temperatures, then we must adopt a low-temperature operation.

The most desirable combination of roasting operations is one that is commercially the most satisfactory in the long run. For example, a furnace gas containing  $\text{SO}_2$  and  $\text{SO}_3$  may be allowed to escape into the atmosphere or may be utilized in the manufacture of sulphuric acid. The utilization of sulphurous gases is recommended not only because it results in economic gain but also because it prevents atmospheric pollution. In most countries, there is strict legislation against atmospheric pollution by industrial waste gases.

**INDUSTRIAL ROASTING UNITS**

The most widely accepted metallurgical roaster was first designed by MacDougall in England towards the end of the nineteenth century. It subsequently underwent many improvements but retained the basic principle of countercurrent flow of the solid ore and the oxidizing gases.

**MULTIPLE HEARTH ROASTING**

A typical MacDougall type roaster (see Fig. 4.2) consists of several (about 10) circular brick hearths superimposed on each other. The entire structure is enclosed in a cylindrical brick-lined steel shell. Revolving mechanical rabbles attached to arms move over the surface of each hearth to continuously shift the ore. The arms are attached to a rotating central shaft that passes through

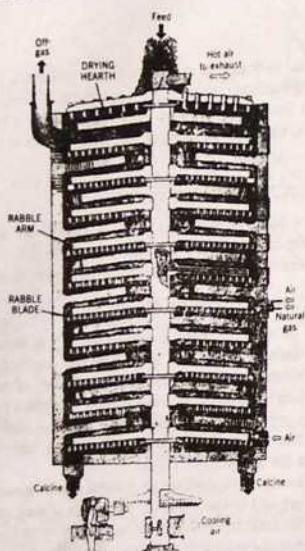


Fig. 4.2 MacDougall Type Hearth Roaster.

the centre of the roaster. The ore that is automatically discharged at the top hearth gradually moves downwards through alternate passages around the shaft and the periphery and finally emerges at the bottom. The oxidizing gases flow upwards, i.e., countercurrent to the descending charge. In a well-insulated roaster, external heating is unnecessary except when the charge is highly moist. The hearths at the top of the roaster dry and heat the charge. Ignition and oxidation of the charge occur lower down. In a MacDougall type roaster, although the roasting process can be effectively controlled, this roaster suffers from certain drawbacks, i.e., the roasting process

is slow and the sulphurous gases evolved when a sulphide is roasted are unsuitable for the production of sulphuric acid because they do not contain sufficient  $\text{SO}_2$  and  $\text{SO}_3$ .

We now discuss some recently developed roasting techniques, namely, flash roasting and fluidized bed roasting.

**FLASH ROASTING**

In *flash roasting*, preheated ore particles are made to fall through a body of hot air, resulting in the almost instantaneous oxidation or 'flashing' of the combustible constituents of the ore, mainly sulphur. Initially, a flash roaster was constructed by merely removing intermediate hearths in a MacDougall type reactor and creating a large combustible zone. At present, however, a flash roaster is specially designed to ensure a large combustion zone. One such design is shown in Fig. 4.3.

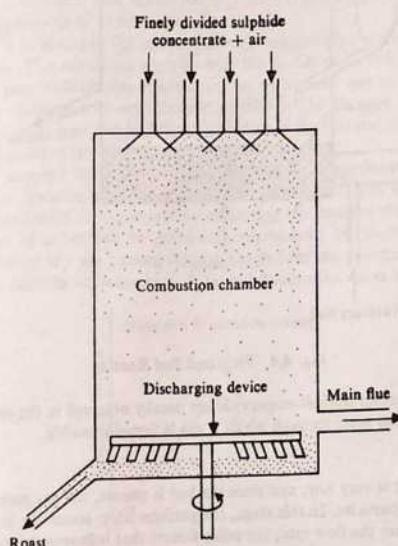


Fig. 4.3 Flash Roaster.

**FLUOSOLID ROASTING (FLUIDIZED BED ROASTING)**

In *fluosolid roasting*, the ore particles are roasted while suspended in an upward stream of gas, as shown in Fig. 4.4.

When a gas is passed upwards through a bed of solid particles—small and preferably regular in size over the range 0.005–0.05 cm in diameter—the behaviour of the bed depends on the velocity of the gas.

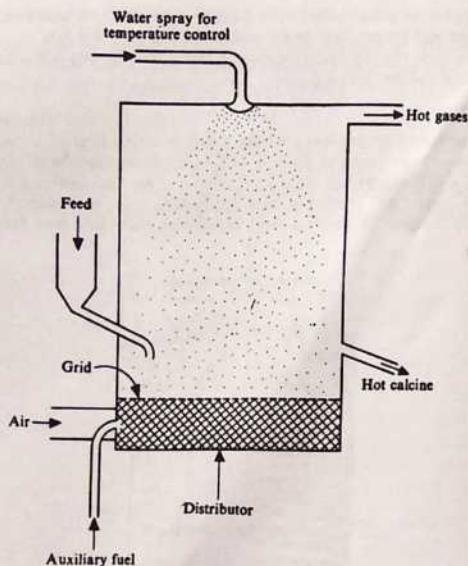


Fig. 4.4 Fluidized Bed Roaster.

We now describe certain distinct stages that are usually observed in the case of a porous bed that rests on a perforated grate through which a gas is forced upwards.

#### Stage 1

When the gas flow rate is very low, and since the bed is porous, the gas permeates the bed without disturbing the ore particles. In this stage, the pressure drop across the bed is proportional to the flow rate. Apart from the flow rate, the other factors that influence the pressure drop are the void fraction, the particle size, and the particle shape factor. (The particle shape factor is defined as the surface area of a sphere of equivalent volume divided by the actual surface area.)

#### Stage 2

As the gas velocity increases, the bed expands upwards due to the effect of the drag forces exerted by the gas stream. In this stage, the pressure drop across the bed depends on the gas velocity.

#### Stage 3

When the gas velocity is further increased, a stage is eventually reached when the pressure drop

across the bed is equal to the weight of the particles per unit area of the bed. The particles now remain individually suspended and offer less resistance to the gas flow.

#### Stage 4

An even further increase in the gas velocity leads to the continued expansion of the bed. Since such an expansion results in an increase in the interparticle distance, the pressure drop across the bed continues to decrease as the gas velocity increases.

#### Stage 5

Finally, a stage is reached when the expansion of the bed becomes independent of the gas velocity. A major portion of the outgoing gas stream appears in the form of bubbles bursting on the surface of the bed which looks like a well-stirred boiling liquid. In this condition, the bed is said to be 'fluidized'. This fluidized bed, which has an apparent density distinctly different from the density of the solid, is capable of flowing like a liquid.

It is relatively easy to maintain the bed at a uniform temperature because of the high degree of mixing of the solids. This advantage together with the facility of handling both the solid feed and the product as pseudo-fluids has resulted in the widespread use of fluidized bed reactors, especially for highly exothermic or endothermic reactions. The thermal conductivities of some fluidized beds are known to be a hundred times higher than the thermal conductivity of the best metallic conductor, namely, silver.

The gas velocity required to fluidize a given bed can be determined by visual observation wherever possible, for instance, in a low-temperature glass model. For an actual reactor, however, the state of fluidization is ascertained by measuring the pressure drop across the bed. The fluidization behaviour of a bed can be graphically represented by plotting the pressure drop against the linear velocity of a gas passing through the bed (or the volume flow rate of a gas for a reactor that has a uniform cross-section). A typical fluidization curve is shown in Fig. 4.5. In

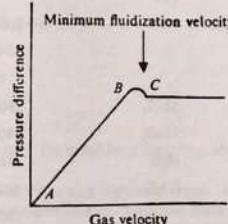


Fig. 4.5 Typical Fluidization Curve.

this figure, AB represents the pressure drop for the stationary bed, i.e., before fluidization occurs. As the pressure drop across the bed approaches the lifting points, the bed is rearranged to provide minimum resistance to the gas flow, as indicated by the segment BC. Point C corresponds to both the maximum voidage of the packed bed (or the voidage corresponding to minimum fluidization) and the minimum gas velocity required for fluidization. Beyond C, the pressure drop becomes independent of the gas velocity. The minimum fluidization velocity is one of the most important

factors that govern the design of a fluidized bed. Although this velocity can be theoretically calculated, its value obtained from an experimental observation of the pressure drop is considered more reliable.

#### Ignition Temperature and Autogenous Roasting

From the foregoing discussion, it should be obvious that fluidized bed roasting is ideal for sulphide ores because the oxidizing reactions that take place during their roasting are highly exothermic. For any exothermic reaction of this kind encountered in roasting, there is a minimum temperature above which the reaction is sustained by the heat liberated by itself. In other words, when an ore particle is initially maintained at this minimum temperature in a stream of air and the roasting initiated by an ignition device, then the reaction continues to proceed even in the absence of any external heat. Such a reaction is termed *autogenous*.

In a fluidized bed roaster, the minimum temperature (or the ignition temperature) required depends on the characteristics of the ore as well as the conditions of ignition (geometry of a reactor and fluid flow). The ignition temperatures of some sulphide minerals, as determined under standardized conditions, are listed in Table 4.1. (The values are for oxidation in air, unless otherwise specified.)

Table 4.1 Ignition Temperature of Sulphide Minerals (°C)  
(after Dwight, 1945)\*

Mineral (%)	Formula	Size of grain (mm)		
		1	1-2	2
Pyrite	FeS <sub>2</sub>	325	405	472
Pyrrhotite	Fe <sub>3</sub> S <sub>6</sub> -Fe <sub>16</sub> S <sub>17</sub>	430	525	590
	FeS	535		
Ni, 73.5; S, 26.7		700	802	886
Co, 66.37; S, 33.63		574	684	859
Co, 70.20; S, 29.80		514	751	60.9
Stibnite	Sb <sub>2</sub> S <sub>3</sub>	290	340	
Molybdenite	MoS <sub>2</sub>	240	508	
Cinnabar	HgS	338	420	
Chalcocite	Cu <sub>2</sub> S	430	679	
Bi, 83.3; S, 16.7		500	627	
Mn, 61.01; S, 33.98;				
Fe, 2.02		355	700	
Argentite	Ag <sub>2</sub> S	605	875	
Galena (in oxygen)	PbS	554	847	
Millerite	NiS	573	616	

\*See also Volsky, A. and Sergievskaya, E., Theory of Metallurgical Processes, trans. by I.V. Savin, Mir Publishers, Moscow (1971), Chapter 10.

wise mentioned.) Since the ignition temperature is the minimum temperature at which a mineral particle oxidizes fast enough to maintain or increase the temperature of the roaster, the ignition temperature values roughly indicate the temperature required for fluidized bed roasting.

A fluidized bed roaster has a high energy efficiency because it can be autogenously operated. Further, it is useful in the recovery of sulphur because the gas that it produces has a high SO<sub>2</sub> content.

#### SINTER ROASTING (BLAST ROASTING)

It should be noted that fine ores and concentrates have to be agglomerated before they can be charged into a blast furnace, otherwise heavy dust losses result. Sinter roasting is the treatment of a sulphide ore in a sintering machine where roasting and agglomeration take place simultaneously. (This is the standard practice for lead sulphide ores, in which case, the fine flotation concentrates have to be agglomerated before charging into the blast furnace.)

Sinter roasting is carried out in a Dwight-Lloyd sintering machine, as shown in Fig. 4.6. The fine concentrate is charged as a layer 15-50 cm thick on to an endlessly revolving belt of grates

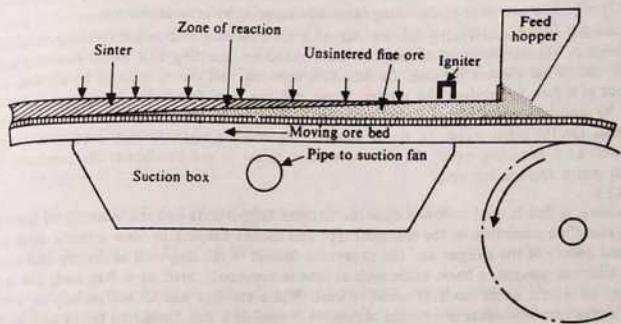


Fig. 4.6 Dwight-Lloyd Sintering Machine.

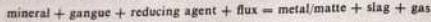
or pallets which moves over wind boxes at a regulated speed. A burner under the ignition hood is used to start the combustion of the bed surface. This combustion is then propagated through the mass of the charge by a current of air drawn through the charge into the wind box below which is connected a suction fan. Sufficiently high temperatures are developed in the material to cause partial or incipient fusion, which produces a porous cinder-like material called *sinter*. A certain amount of moisture is necessary to render the sinter porous. When the sinter reaches the end of the machine, it is discharged and cooled. The cooled sinter is sized to give a uniform product. The sinter roasting of a sulphide ore does not require the addition of any fuel to the charge, because the sulphur in the charge itself acts as fuel. In the case of an oxide ore (e.g., iron ore), however, fuel has to be added.

Although a multiple hearth roaster is conventionally used in the case of zinc ores, sinter

roasting can also be used. However, in the case of copper ores, sinter roasting finds limited application because a reverberatory furnace can handle fine ores efficiently.

#### 4.6 SMELTING

*Smelting* is a heating process for the production of a metal or matte. Generally, the process is one of reduction of the oxide of the metal with carbon/sulphur/sulphide in a suitable furnace (reverberatory furnace, blast furnace, or electric furnace). During smelting it should be remembered that since the gangue in the ore is generally less fusible than the metal, a flux must be added to form a slag that is easily fusible. The smelting process for metal extraction can be written as



Some of the general characteristics of a smelting operation are:

- (1) The materials to be smelted are usually charged in the solid state.
- (2) The products of the smelting furnace are in the liquid state; the solid material that escapes is the dust that is carried away by the furnace gases.
- (3) The heat required for smelting is usually supplied by external sources.

*Reduction smelting* is usually carried out in a blast furnace and *matte smelting* in either a reverberatory furnace or a flash smelter. Both reduction smelting and matte smelting can be carried out in an electric furnace. In reduction smelting, the ore is reduced by carbon, in the presence of a flux, to produce the molten metal and the slag. Sometimes, reduction is brought about by another metal whose oxides are much more stable than those of the metal being extracted. On the other hand, in matte smelting, a reducing agent is not used. The sulphide itself acts as a reducing agent. In this operation, metal is not produced; the products being molten matte and molten slag.

#### FLUXES

In smelting, a flux is used to lower both the liquidus temperature and the viscosity of the slag. A flux is classified according to the chemical type and chosen keeping in view criteria such as the chemical nature of the gangue and the properties desired in the slag such as density and viscosity. For a siliceous gangue, a basic oxide such as lime is commonly used as a flux and, for a basic gangue, an acidic oxide such as silica is used. When the flux has to act mainly as a 'cover', either potassium carbonate or sodium carbonate is used as a flux. Oxidizing fluxes such as  $\text{Na}_2\text{O}_2$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$ , and reducing fluxes, e.g.,  $\text{NaCN}$  are employed in the metallurgy of precious metals. A neutral flux ( $\text{CaF}_2$  or  $\text{Na}_2\text{SO}_4$ ) finds specialized application, for example, in fused electrolytic bath.

#### SLAGS

The two main functions of a slag are to collect the unreduced gangue minerals so as to form a separate layer in a metal extraction process and to provide a medium in which the impurities in a metal can collect during a refining process. (Often, the impurities get partitioned between the metal and the slag.) To effectively fulfil these functions, a slag must possess the following properties:

- (1) The difference between the specific gravities of the slag and the metal should be sufficiently high so that one can be easily separated from the other.
- (2) The slag must be fluid enough to permit its easy separation from the metal and also to

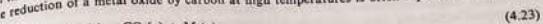
bring about a mass transfer faster (than when the slag is not fluid enough) of the reacting and product species. (If a slag is viscous, the loss of metal by entrapment in the slag is high.)

(3) The slag must have a chemical composition which ensures that the activities of the impurities and of the dissolved gangue minerals are low.

#### REDUCTION SMELTING USING CARBON

Carbon occupies a unique position as a reducing agent mainly because it is easily available and, at the same time, it is inexpensive. It has already been shown in Chapter 2 that all metal oxides can, in theory, be reduced by carbon, provided the temperature is high enough.

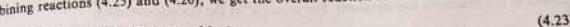
The reduction of a metal oxide by carbon at high temperatures is often represented as



As represented by reactions (4.23) and (4.24), the reaction takes place between two solids, namely,  $\text{MO}$  and  $\text{C}$ . Since this reaction (which is a reduction) is controlled by solid-state diffusion across a small area of contact, it is likely to proceed at a slow rate. On the other hand, if the reduction takes place in more than one step, i.e., if there is an intermediate reaction between a gas and a solid, it is likely to proceed faster. The reduction can be represented more accurately than in reactions (4.23) and (4.24) as



Combining reactions (4.25) and (4.26), we get the overall reaction as



Thus, it would not be correct to state that reduction takes place according to reaction (4.23). This would probably be true in the reduction of the most stable oxides, where  $p_{\text{CO}_2}$  in the resulting gas mixture would be extremely low. At a temperature lower than  $700^\circ\text{C}$ , the reduction can be represented by reaction (4.25).

The reduction of an oxide by carbon is best understood by referring to the Ellingham diagram (Fig. 2.1). Referring back to Fig. 2.1, we observe that the temperatures required for reduction by carbon in a number of cases are beyond practical limits. It is just possible to produce manganese or, at least an alloy of manganese (Fe-Mn), in a blast furnace. Metals lying above manganese in the emf series form oxides having higher negative free energies of formation and may be reduced by carbon but not in a blast furnace. For the reduction of these more stable oxides, an electric furnace is required because it can attain much higher temperatures.

During cooling (from the reacting temperature) a back reaction may occur, especially when the reduced metal is in the form of a vapour, as in the case of magnesium. Some metals, for example, zinc, can be condensed in the presence of  $\text{CO}$ , where the back reaction is limited to a great extent. However, the more reactive metals react with the  $\text{CO}$  itself when the gas mixture is cooled. For example, the back reaction in the case of magnesium has to be restrained by shock

cooling. The resulting powder, however, is pyrophoric, i.e., it ignites on contact with air. Some alkaline earth metals form carbides, for example,  $\text{CaC}_2$ .

At high temperatures, fresh problems may arise. For instance, a new stable phase, namely, the metallic carbide, may appear. This is sometimes formed when the metal reacts with the carbon itself. The formation of carbide can be suppressed if the metal were produced in the presence of another solvent metal. To illustrate: the solvent metal, in which a metal M is dissolved, reduces the chemical potential of M and pushes the reduction reaction (4.23) to the right, making reduction possible at a lower temperature. The greater the dilution, the lower is the temperature required for reduction. For the same reason, carbide formation would be discouraged if M were in the form of an alloy, for example, the production of a Be-Cu alloy (with about 4 per cent copper) by carbon reduction of  $\text{BeO}$ . The production of ferroalloys also makes use of the advantage gained by alloying. Ferrovanadium, ferrotitanium, ferrosilicon, ferroniobium, and other ferroalloys are produced by the reduction of the corresponding oxide by carbon in the presence of iron. Even alloying does not always ensure a carbide-free product. For example, ferrochromium normally contains a high proportion of carbon, the composition approaching  $\text{Cr}_3\text{C}(\text{Fe})$ . Special techniques are, therefore, necessary to produce low-carbon alloys.

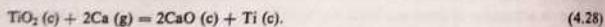
#### 4.7 METALLOHERMIC REDUCTION OF OXIDES

An oxide is reduced by a metal that forms stabler oxides. Such a metallothermic reaction, carried out in an open container or a closed container (bomb), completely avoids carbon contamination. Although the principle is similar to that of carbon reduction, metallothermic reduction is usually carried out on a small scale and is rarely referred to as smelting.

The principle of metallothermic reduction can be understood by referring again to the free energy diagram for oxides (Fig. 2.1). In theory, a metal that forms a stabler oxide (a lower line in Fig. 2.1) would replace metals from less stable oxides (an upper line in Fig. 2.1). In practice, however, the reduction would depend on factors such as the reaction rate and the physical properties of the reactants and products. For example, in the thermit reduction



the products are in a liquid state at the reaction temperature and all the constituents are relatively nonvolatile.  $\text{Al}_2\text{O}_3$  can be slagged more easily by using another oxide as a flux. A wide difference between the densities of the slag and the metal allows a clean separation. However, such a clean separation becomes difficult in the case of some other reductions, for instance, the reduction of  $\text{TiO}_2$  by calcium. The reaction is



It should be noted that titanium melts at  $1670^\circ\text{C}$ , calcium boils at  $1492^\circ\text{C}$ , and  $\text{CaO}$  melts only at  $2600^\circ\text{C}$ . A liquid product can be obtained only if these high temperatures can be attained, i.e., the application of a very high pressure becomes necessary. The final product is normally a mixture of solid titanium and  $\text{CaO}$ ; the latter can be leached out and the metal obtained in a powder form. This powder can subsequently be melted and thus consolidated. However, during remelting, sufficient precaution must be taken to avoid oxygen contamination because any residual  $\text{CaO}$  can easily oxidize the titanium metal, rendering it brittle.

It should be remembered that the free energy diagram (Fig. 2.1) is plotted for 1 atm

of oxygen. The order of reactivity of oxides can be changed by applying a vacuum. Thus, under vacuum, silicon can reduce  $\text{MgO}$  and aluminium  $\text{CaO}$ , although the reverse is expected under standard conditions. The chemical potential of magnesium is reduced by 17.5 kcal per mole at  $1000^\circ\text{C}$  by operating at about 0.001 atm, and, at the same temperature and under the same pressure the free energy change for the reduction of  $\text{MgO}$  by Si is rendered negative (see Chapter 6).

#### FORMATION OF SLAG

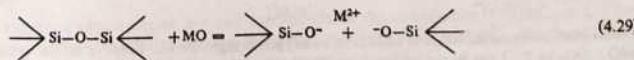
The reduction of a metal oxide by a metal necessarily results in a more stable, often highly refractory, oxide. Although carbon reduction does not produce a condensed oxide phase, it releases siliceous material or other gangue materials from the ore to form a refractory oxide phase. It is desirable to have a liquid slag so that the metal can be easily separated from the gangue. The formation of a liquid slag is facilitated by adding, to the ore, fluxing agents such as quartz and lime, which together with the gangue (the product oxide for metallothermic reduction), form a multicomponent silicate slag with a relatively low melting point.

All silicate melts are viscous. To facilitate their removal, their viscosity should be decreased either by adding a suitable basic oxide or by raising the temperature. The effect of adding a basic oxide and of raising the temperature can be understood from the structure of molten silicates. Due to the industrial importance of metallurgical slags (most of which are multicomponent silicate solutions), the structure and constitution of molten silicates have been investigated. Consequently, several theories on silicate structure have been proposed. It is now accepted that silicate melts are ionic in nature. In a silicate solution, there could be metallic ions, free oxygen ions, and complex silicate ions of varying sizes. However, there cannot be a silicon ion. A high degree of stability of the  $\text{Si}-\text{O}$  bond requires that every silicon atom always be tetrahedrally coordinated with four oxygen atoms. The viscosity of a slag essentially depends on the bulky, less mobile silicate ions, which decrease the overall fluidity.

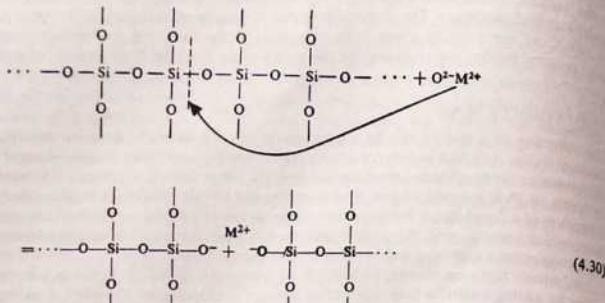
#### STRUCTURE OF SILICATE SLAGS

Consider now the variation in the silicate solution structure over a range of silicate compositions. For simplicity, consider a binary silicate system  $\text{MO-SiO}_2$ . The structure of pure crystalline silica is a three-dimensional network consisting of silicon and oxygen atoms (where each silicon atom is tetrahedrally attached to four oxygen atoms) possessing both long-range order and short-range order. Therefore, the entire bulk of the material could, in effect, be a huge molecule, i.e., a single unit. In molten silica, however, some  $\text{Si}-\text{O}-\text{Si}$  bonds rupture due to the effect of thermal energy and some depolymerization takes place. The short-range order persists, even though the long-range order is lost. In such a situation, the viscosity is very high.

When a basic metal oxide  $\text{MO}$  (e.g.,  $\text{CaO}$ ,  $\text{MgO}$ ) is added to molten silica, the three-dimensional network starts breaking. This is attributed to the reaction of the oxygen ions provided by the metal oxide with the  $\text{Si}-\text{O}$  bond in the network as shown in reactions (4.29) and (4.30):



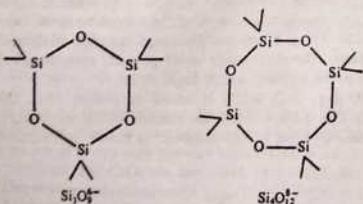
or



Here, silica (acidic oxide) accepts an oxygen ion and MO (basic oxide) donates an oxygen ion. The depolymerization reaction (4.29) essentially shows that as the quantity of the metal oxide added (i.e., the quantity of oxygen ions) increases, the silicate network is broken down into smaller and smaller units. The basic reaction is one that involves doubly bonded oxygen atoms in the network ( $O^2-$ ), the free oxygen ion donated by MO ( $O^{2-}$ ), and the single bonded or terminal oxygen atoms ( $O^-$ ) in the smaller units produced. The reaction is



According to Bockris *et al.* (1955), when a metal oxide is added to molten silica up to a concentration of 12 mole per cent, the silicate network breaks down in a random manner. This means that three-dimensional bonding would still be present throughout the melt. When more metal oxide is added, the network breaks down almost completely to give discrete globular anions of the type  $Si_2O_5^{4-}$ ,  $Si_4O_10^{4-}$ ,  $Si_6O_15^{4-}$ ,  $Si_8O_{20}^{4-}$ , and  $Si_{10}O_{25}^{4-}$ . The first two structures are now shown:



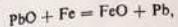
When even more metal oxide is added, more oxygen bridges break. Finally, at the composition  $MO : SiO_2 = 2 : 1$  (as in the orthosilicate  $2MO \cdot SiO_2$ ), the smallest unit  $SiO_4^{4-}$  is obtained. When

further metal oxide is added, free oxygen ions ( $O^{2-}$ ) become available in the melt.

From the foregoing discussion, it is obvious that the addition of a basic oxide lowers the viscosity of a slag because it leads to depolymerization and creates smaller flow units, which are more mobile. It should be noted that depolymerization can be brought about by raising the temperature. Thermal bond breaking is greater at higher temperatures.

#### METAL LOSSES IN SLAGS

A serious complication could arise during smelting if the reactant and product oxides themselves form compounds. This possibility exists for an oxide ore that can form a stable silicate itself. Although this situation could sometimes be advantageous in producing slags with a low melting point, it indicates that a part of the reactant raw material would be lost due to dissolution in the slag along with the gangue and fluxes. Metal recovery, consequently, would be low. For example, during the blast furnace smelting of a lead ore, a significant quantity of PbO may combine with silica to enter the slag as a silicate. This PbO loss can be minimized by adding scrap iron to the charge. Scrap iron not only reduces some of the PbO itself but also helps recover lead from the silicate slag. The reactions can be written as



The reduction of  $SnO_2$  also creates a problem similar to that of PbO because the oxide itself can form a stable silicate. Consequently, tin cannot be easily recovered, and special multistage smelting techniques must be adopted in which the tin-rich slag itself is smelted in various stages. The reduction temperature for a tin-bearing slag is around  $1250^\circ C$  as against a much lower temperature for  $SnO_2$  ( $500^\circ C$ ). Consequently, smelting operations have to be carried out at around  $1250^\circ C$ . The metal is also lost as a result of mechanical entrapment in slags.

#### CLASSIFICATION OF SLAGS

Slags used in smelting are sometimes classified according to the silicate degree defined as

$$\text{silicate degree} = \frac{\text{moles of acidic oxygen from } SiO_2}{\text{moles of basic oxygen from } CaO, MgO, FeO, \dots}$$

##### Basic Slags

According to the foregoing definition of the silicate degree, a basic slag has a silicate degree  $< 1$  and corresponds to the composition  $MO/SiO_2 > 2$ . The principal anions in a molten basic slag are  $O^{2-}$  and  $SiO_4^{4-}$ .

##### Neutral Slags

A neutral slag has a silicate degree = 1 and corresponds to the composition  $MO/SiO_2 = 2$ . The principal anion in a molten neutral slag is  $SiO_4^{4-}$ .

##### Acid Slags

An acid slag has a silicate degree  $> 1$  and corresponds to the composition  $MO/SiO_2 < 2$ . The principal anions in an acid slag are the chain silicate anions  $Si_2O_7^{4-}$ ,  $Si_3O_10^{4-}$ , the ring silicate anions  $Si_4O_10^{4-}$ , and the other globular anions.

It should be pointed out that in a melt, irrespective of the composition, there exists an equilibrium among the various types of anions. For example, some equilibria that can exist are

$$\text{O}^{2-} + \text{Si}_2\text{O}_7^{4-} \rightleftharpoons 2\text{SiO}_4^{4-}$$

$$\text{O}^{2-} + \text{Si}_3\text{O}_10^{6-} \rightleftharpoons \text{Si}_2\text{O}_7^{4-} + \text{SiO}_4^{4-}$$

Consequently, some free oxygen ions—although in very small quantities—can be present in a neutral slag and even in an acid slag.

In industrial practice, the basicity of a slag is sometimes expressed in terms of a basicity number called 'V ratio' and defined by the % ratios

$$\frac{\text{CaO}}{\text{SiO}_2} \text{ or } \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \text{ or } \frac{\text{CaO} - 4\text{P}_2\text{O}_5}{\text{SiO}_2}$$

A basic slag contains a high proportion of lime and an acid slag a high proportion of silica. The relative basicity of a slag can be expressed in terms of these ratios.

#### 4.8 SMELTING FURNACES

The blast furnace has traditionally been the most popular furnace for reduction smelting. Smelting of iron ores is the best known example of blast furnace operation. Lead is also almost exclusively produced in the blast furnace. In this case, however, the furnace is much smaller. The imperial smelting process has been developed in England for the simultaneous production of lead and zinc in the blast furnace. While lead is tapped, as is normally done, zinc is recovered by dissolving the outgoing zinc vapours in a running stream of hot molten lead. Zinc separates from lead on cooling. The blast furnace in this case must have special arrangements at the top for the collection and dissolution of the zinc vapours. There should also be a provision for the flow of a stream of molten lead which is continuously recirculated after zinc recovery.

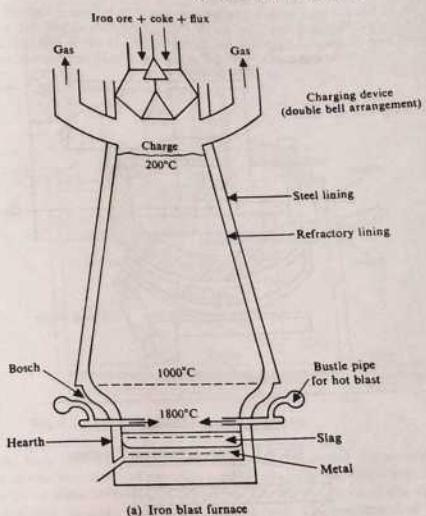
In blast furnace smelting, strongly reducing conditions can be created, but where reducing conditions are unnecessary or undesirable, a simpler furnace such as a reverberatory furnace should be used. For example, in tin smelting, tin oxide should be smelted in a reverberatory furnace so as to minimize the reduction of the more stable oxide impurities such as iron oxides.

When very high temperatures are required for reduction and fusion, electric arc smelting is employed. A temperature around 2000°C can be easily attained in an electric furnace whereas carbonaceous fuels (used in the blast furnace) usually cannot provide temperatures higher than 1600°C. Therefore, ferroalloys that require very high temperatures for reduction are smelted in the electric furnace. Figure 4.7a depicts an iron blast furnace, Fig. 4.7b a reverberatory furnace, and Fig. 4.7c a direct arc electric furnace.

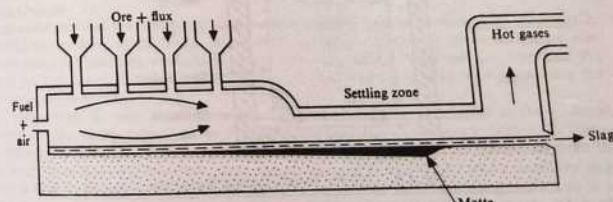
No special furnace is required for the metallothermic reduction of an oxide. The need for an external heat source is limited because, in the reduction of an oxide, the reactions are highly exothermic. Their exothermicity can be enhanced by incorporating booster reactions. A simple unit for metallothermic reduction is shown in Fig. 4.8.

#### FLASH SMELTING

In recent years, one of the most interesting developments in smelting has been the *flash smelting* of the concentrates of nickel sulphide and copper sulphide. Flash smelting is a process that combines the operations of flash roasting and smelting. The object is to burn the concentrate

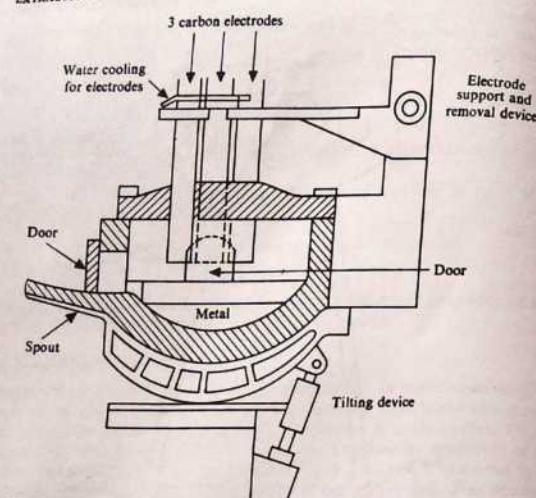


(a) Iron blast furnace



(b) Reverberatory furnace

Fig. 4.7 Types of Smelting Furnaces (cont.).



(c) Direct arc electric furnace

Fig. 4.7 Types of Smelting Furnaces.

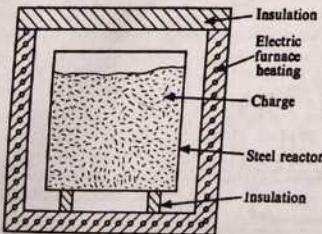


Fig. 4.8 Unit for Metallurgical Reduction.

(falling through the combustion chamber of a flash smelter) with oxygen or preheated air blown in with the concentrate. Sufficient heat is generated to form a matte and a slag which settle into the hearth.

In flash smelting, enriched preheated air or pure oxygen is usually used instead of air to increase the combustion rate and to maintain autogenous smelting. The gases coming out of the furnace are very rich in  $\text{SO}_2$  (due to the high combustion rate) and can be profitably used for sulphuric acid manufacture. A flash smelter is illustrated in Fig. 4.9.

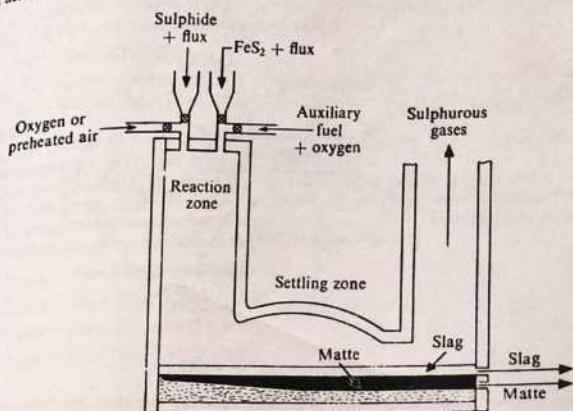


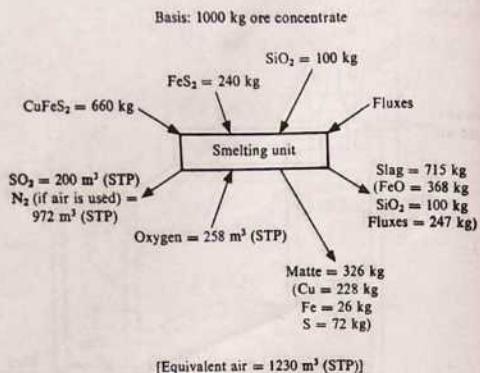
Fig. 4.9 Flash Smelter (after Gilchrist, 1967).

Flash smelting, like flash roasting, can be made autogenous, provided the exothermic heat and the sensible heat of the incoming feed materials combine to exceed the heat losses. Generally, when air is used as an oxidant, it has to be preheated. For oxygen-enriched air, the required preheating would obviously be lesser. For flash smelting with air, the extent of preheating required can be easily calculated by performing a mass and energy balance. We now give a simple example.

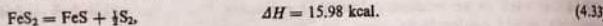
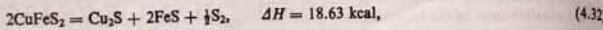
Let us assume that the concentrate used for flash smelting has the composition: chalcopyrite ( $\text{CuFeS}_2$ ) 66 per cent; pyrite ( $\text{FeS}_2$ ) 24 per cent; and gangue ( $\text{SiO}_2$ ) 10 per cent. Let us also assume that flash smelting produces a copper matte containing 70 per cent Cu, 8 per cent Fe, and 22 per cent S and a slag containing 40 per cent Fe. The matte, slag, and gases leave the furnace at, say, 1300°C.

To begin with, we must know the compositions of all the phases involved in the smelting operation. Their compositions can be easily obtained from mass balance calculations. To calculate the amount of oxygen required, we should know both the quantity of sulphur oxidized to  $\text{SO}_2$  which does not enter the matte phase and the quantity of oxidized Fe which enters the slag phase as  $\text{FeO}$ . Calculations are based on the smelting of 1000 kg of ore concentrate and it is assumed that the relevant reactions are given by (4.32)–(4.34) as described for the heat balance calculations. From reactions (4.32)–(4.34), we see that 57.4 kg of oxygen are required to oxidize

the free sulphur from 660 kg of  $\text{CuFeS}_2$  and 64 kg of oxygen are required to oxidize the free sulphur from 240 kg of  $\text{FeS}_2$ . We also note that 492 kg of  $\text{FeS}$  are formed of which 41 kg go into the matte. For oxidizing the remaining 451 kg of  $\text{FeS}$ , according to the reaction represented by (4.35), 246 kg of oxygen are required. Therefore, the total oxygen requirement is 367.4 kg or 258 m<sup>3</sup> (STP). The results of the mass balance are diagrammatically shown now:



We next proceed to make an inventory of the heat input and output on the basis of thermochemical data available from standard sources. To calculate the heat balance, we assume that  $\text{CuFeS}_2$  and  $\text{FeS}_2$  first dissociate to give  $\text{FeS}$  and  $\text{S}_2(\text{g})$ , which subsequently burn with the oxygen supplied to produce oxides of iron and sulphur. The dissociation reactions are



The free sulphur vapour, on oxidation to  $\text{SO}_2$ , generates heat according to the reaction



The total heat absorbed by  $\text{CuFeS}_2$  and  $\text{FeS}_2$  for decomposition is

$$\left( \frac{660,000}{2 \times 184} \right) 18.63 + \left( \frac{240,000}{120} \right) 15.98 = 65,500 \text{ kcal}.$$

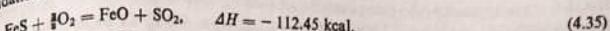
The total heat evolved due to the oxidation of sulphur is

$$\left( \frac{1000}{32} \right) \left( \frac{32}{2 \times 184} \right) 660 + \left( \frac{32}{120} \right) (240)(70.9) = 270,000 \text{ kcal}.$$

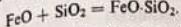
Hence, the net heat produced during sulphur oxidation is

$$(270,000 - 65,500) \text{ kcal} = 204,500 \text{ kcal}.$$

The oxidation of  $\text{FeS}$  can be written as



Matte contains 26 kg of Fe or 41 kg of  $\text{FeS}$  and the remainder is oxidized to  $\text{FeO}$ . By mass balance, the total weight of  $\text{FeS}$  is 451 kg (Fe = 286 kg) and the heat evolved on the oxidation of  $\text{FeS}$  is  $(451,000/88) 112.45 = 577,000 \text{ kcal}$ . The  $\text{FeO}$  formed in reaction (4.35) reacts with  $\text{SiO}_2$  to form a slag  $\text{FeO} \cdot \text{SiO}_2$  according to the reaction



Suppose this reaction liberates 100 kcal of heat per kg of iron, then, the heat liberated due to slag formation is 28,600 kcal. Thus, the total heat liberated is  $(204,500 + 577,000 + 28,600 =) \$10,100 \text{ kcal}$ .

It is assumed that all reactions occur at 25°C and the products of the reaction are heated to the final temperature by the heat generated by the reactions.

To estimate heat losses, we assume that the matte, slag, and gases, among them, carry away the entire heat generated in the furnace at 1300°C. In practice, the heat from the furnace that escapes into the atmosphere also must be taken into account. We now give some estimates of heat losses (based on the values available in the literature):

$$H_{1300^\circ\text{C}} - H_{25^\circ\text{C}} (\text{matte}) = 222 \text{ kcal/kg},$$

$$H_{1300^\circ\text{C}} - H_{25^\circ\text{C}} (\text{slag}) = 340 \text{ kcal/kg},$$

$$H_{1300^\circ\text{C}} - H_{25^\circ\text{C}} (\text{SO}_2) = 714 \text{ kcal/m}^3,$$

$$H_{1300^\circ\text{C}} - H_{25^\circ\text{C}} (\text{N}_2) = 445 \text{ kcal/m}^3.$$

Thus,

$$\text{heat lost through matte} = 222 \times 326 = 72,300 \text{ kcal},$$

$$\text{heat lost through slag} = 340 \times 715 = 243,100 \text{ kcal},$$

$$\text{heat lost through SO}_2 = 200 \times 714 = 142,800 \text{ kcal},$$

$$\text{heat lost through N}_2 = 972 \times 445 = 432,500 \text{ kcal}.$$

Assume that heat loss through radiation and convection is 100,000 kcal. Therefore, the total heat loss is 990,700 kcal.

The heat balance is shown as:

	Heat input (kcal)	Heat output (kcal)	
Oxidation of sulphur	204,500	Lost through matte	72,300
Oxidation of $\text{FeS}$	577,000	Lost through slag	243,100
Formation of slag	28,600	Lost through $\text{SO}_2$	142,800
		Lost through $\text{N}_2$	432,500
		Lost due to radiation and convection	100,000
Total	810,100	Total	990,700

Therefore, the heat deficit is  $(990,700 - 810,100 =) 180,600 \text{ kcal}$ .

This deficit can be made up by preheating the air used for combustion. The heat deficit per m<sup>3</sup> of air = 180,600/1230 = 146 kcal. Thus, every m<sup>3</sup> of air input must be supplied with 146 kcal of heat prior to reaction. If air is preheated to 458°C, this enthalpy is made up and the total heat input is 990,700 kcal. It should be noted that the heat carried away by gases is (575,300/990,700)100, i.e., 58 per cent of the total heat input. The gases that come out of the furnace, therefore, have sufficient heat to preheat the incoming air. This heat should be utilized by employing a suitable heat recovery unit. We may thus conclude that theoretically there is no difficulty in carrying out autogenous smelting. Starting with a rich copper concentrate, we should obtain a relatively rich matte. The grade of the matte can also be controlled by regulating the amount of air or oxygen, whichever is being injected.

#### 4.9 MATTE SMELTING

In the extraction of a metal from a sulphide ore, an important method used involves the production of a liquid matte from the ore and its subsequent conversion to the metal. In matte smelting, the sulphide ore is fused with a flux to produce a molten mixture of sulphides known as a *matte*. The gangue materials pass off into the slag, which is immiscible with the matte, i.e., it forms a separate layer. Some sulphur is lost in the furnace gases as SO<sub>2</sub> or SO<sub>3</sub>. In this sense, for a sulphide ore, matte smelting is a thermal concentrating process.

A matte is a metallic sulphide solution that contains minor amounts of oxygen and, sometimes, some metal too. A matte exhibits a high electrical conductivity comparable with that of a metal and has a density in between the density of the metal and that of the slag. Mattes, in general, are insoluble in the metal and slag phases. Thus, in some processes three distinct layers, namely, slag, matte, and metal are produced. A matte is an excellent solvent for some impurity metals, especially for valuable traces of precious metals.

Matte smelting, which is usually carried out in a reverberatory furnace, follows a roasting operation. Roasting first reduces the sulphide content of an ore in such a manner that subsequent smelting with a suitable flux produces a matte of the required grade. It should be noted that roasting brings about only the partial oxidation mainly of FeS and FeS<sub>2</sub> to FeO, which would pass off into the slag phase.

Matte smelting is adopted in the extraction of copper, nickel, and, sometimes, antimony. The common ores of these metals contain sulphide minerals including FeS. During roasting, prior to matte smelting, the sulphides of iron are oxidized more easily than those of copper and nickel. The oxidation of, say, Cu<sub>2</sub>S or Ni<sub>3</sub>S<sub>2</sub> can be avoided by controlling the oxidation of the ore so as to produce only FeO and not Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. This is necessary because the higher oxides of iron do not pass off into the slag easily and are thus difficult to remove. Copper is subsequently recovered from the matte by a process known as 'converting' in which air is blown through a side-blown converter. Initially, the residual FeS is oxidized and slagged out. Subsequently, the sulphides of copper are converted to metallic copper. For a nickel matte the procedure is somewhat more complicated. (Matte smelting of copper and nickel is discussed in detail in Chapter 7.)

#### 4.10 REDUCTION OF HALIDE BY ANOTHER ELEMENT

A number of rare and reactive metals are produced by the reduction of a halide by another metal. The basic reaction is



where M and M' are two different metals, X is a halogen (usually fluorine or chlorine), and n is the number of atoms of X. Earlier, reaction (4.36) had been the basis for the extraction of reactive metals. Presently, however, this method is almost exclusively employed only for a few metals, for example, titanium and zirconium. Kroll's process employed for the reduction of a halide using magnesium is an example of this method. The reaction is



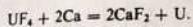
In reaction (4.37), sodium may be used instead of magnesium.

The principle of halide reduction can be understood from a chloride free energy diagram (Fig. 4.10), which is similar to that relating to oxides (Fig. 2.1). Figure 4.10 is drawn for the formation of chlorides from 1 gm mole of chlorine for each of the reactions represented. In this figure, elements such as Na, K, Li, Ca, and Mg appear at the bottom because their halides are very stable. These metals are, therefore, excellent reducing agents.

The melting, boiling, and sublimation points of the chloride are designated as M, B, and S, respectively, and those of the metals as M', B', and S', respectively. The reversible decomposition voltage E, given by  $\Delta G^\circ = -ZFE$ , is indicated on the left-hand side of the figure. The position of the line for CCl<sub>4</sub> clearly shows that carbon is not a suitable reducing agent for chlorides.

The lines for most chlorides have an upward slope, whereas the HCl line has a slight downward slope. This shows that hydrogen becomes a slightly better reducing agent at higher temperatures. Hydrogen can reduce all metallic chlorides whose lines lie above the HCl line, provided all the substances involved are in their standard states. Those metals whose chloride lines lie below the HCl line, when made to react with HCl gas, are converted to chlorides under standard conditions.

Halides usually have relatively low melting and boiling points which account for the interest of metallurgists in halide systems. If the metal produced at the reduction temperature is itself in a liquid state, then a clean liquid-liquid separation of the metal and slag is easily obtained, for example,



However, the melting points of reactive metals are generally high and these metals may be obtained in the form of a solid entrapped in a mass of slag. The situation is sometimes improved by incorporating booster reactions during bomb reduction so as to provide sufficient exothermic heat to melt the whole charge and thereby obtain a clean separation.

#### 4.11 HALIDE METALLURGY AND HALOGENATION

Halogens, particularly chlorine, are beginning to play an increasingly important role in extraction processes. Since halides are seldom found as natural ore deposits on land, they are produced from naturally occurring minerals by halogenation. The most commonly used halides are chlorides and fluorides. A chloride is preferred to a fluoride because it is less corrosive and is normally easier to handle. On the other hand, many chlorides are hygroscopic whereas fluorides are not; therefore, in some processes, for example, fused salt electrolysis, fluorides are preferred to chlorides.

Halogenation, particularly chlorination is carried out to achieve one or more of the objectives now listed:

- (1) 'Opening up' of relatively complex minerals and the recovery of the metallic values.
- (2) Beneficiation of low-grade ores to yield the metal halide, either in the vapour state or in

Temperature °C

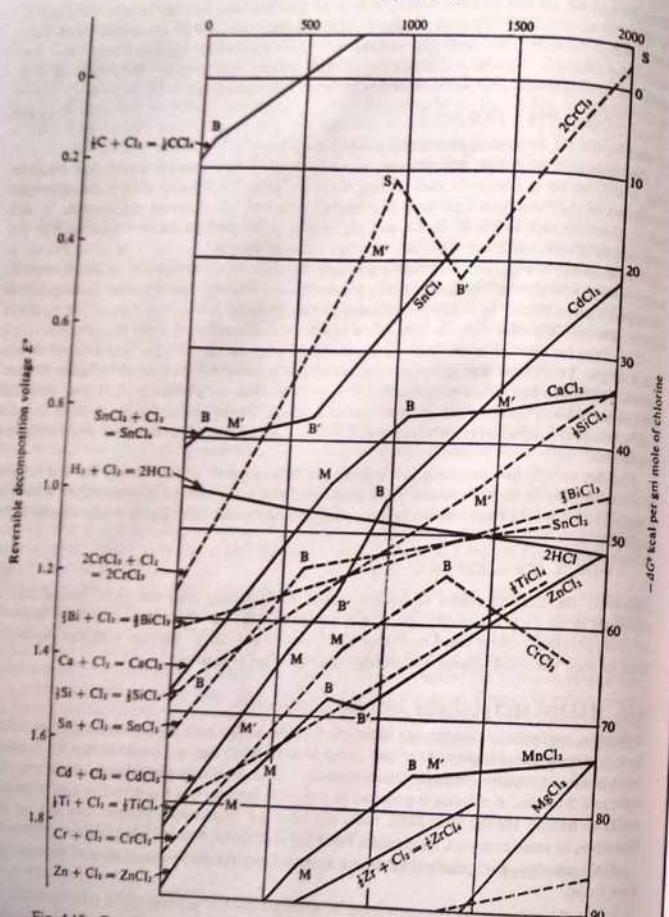


Fig. 4.10 Free Energy of Formation of Chlorides (after Kellogg, 1950) (cont.).

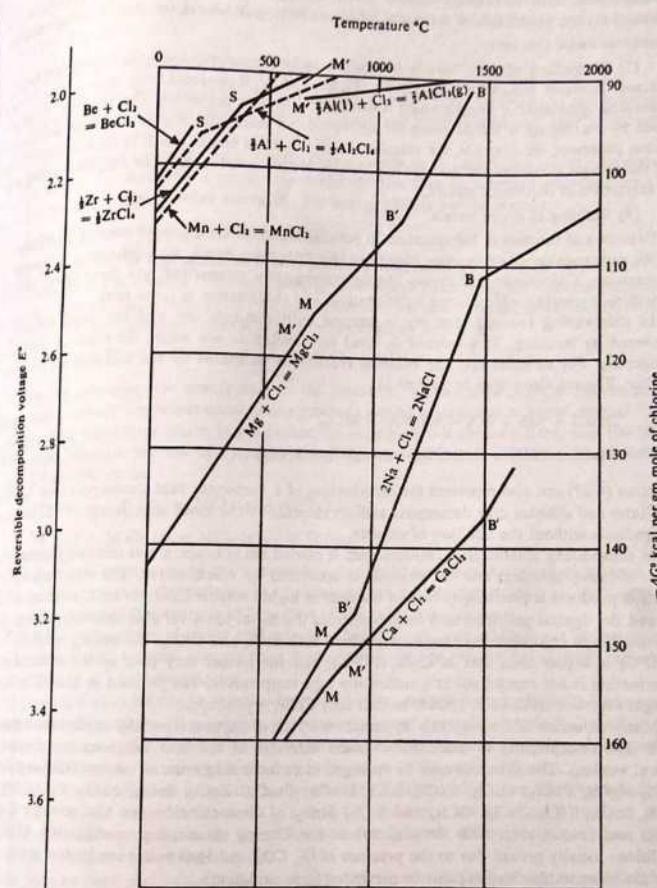


Fig. 4.10 Free Energy of Formation of Chlorides (after Kellogg, 1950).

the condensed state. A chloride can be effectively separated from the gangue materials and processed for the production of the metal. Many metallurgical wastes can also be chlorinated for subsequent metal recovery.

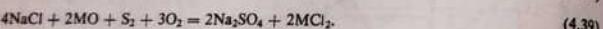
(3) Production of pure halides of reactive metals from which oxygen-free metal can be obtained. Reactive metals such as U, Th, Ti, Be, and Zr, if produced from oxides, may contain appreciable quantities of oxygen which is detrimental to their properties. The problem is largely solved by employing a halide route for extraction. (A metal can be produced from a halide by various processes, for example, the metallocerhetic reduction of a chloride, fused salt electrolysis, and the vapour transport process. These processes are discussed in detail in chapters dealing with the extraction of individual metals.)

#### (4) Refining of crude metals.

Examples of the uses of halogenation in refining reactions are discussed later in this chapter.

We now consider the foregoing objectives in a little more detail, with particular reference to chlorination. Chlorination processes can be conveniently categorized into three types, namely, chloridizing roasting, chloridizing volatilization, and chlorination in fused salts.

In chloridizing roasting, the ore is roasted with common salt and the solid chloride is recovered by leaching. This method is ideal for a sulphide ore where the roasting reaction is autogenous. For an oxide ore, the roasting reaction is facilitated by the addition of elemental sulphur. The reactions may be written as:



Reaction (4.39) can also represent the chlorination of a carbonate that decomposes on heating. Sulphates and silicates may decompose sodium chloride by the direct interchange of the elements and radicals without the addition of sulphur.

In chloridizing volatilization, chlorination is carried out at temperatures relatively higher than in chloridizing roasting, and the chloride is recovered by volatilization. The elimination of the reaction products is particularly easy in the case of highly volatile chlorides such as those of Zr, Ti, and Be. Special problems may be encountered if a metal has a variable valency. For example, chlorination of chromium ores tends to produce both  $\text{CrCl}_3$  and  $\text{CrCl}_5$ . The boiling point of  $\text{CrCl}_2$  ( $1302^\circ\text{C}$ ) is higher than that of  $\text{CrCl}_3$  ( $943^\circ\text{C}$ ), and the former may plug up the chlorinator, if chlorination is not carried out at a sufficiently high temperature. The problem is solved by using a slight excess of chlorine at  $1000^\circ\text{C}$  so that only  $\text{CrCl}_3$  is produced.

Many chlorides are susceptible to oxidation by air or oxygen, especially at elevated temperatures. The susceptibility to oxidation of some chlorides at red heat has been investigated by several workers. The chlorides may be arranged in an increasing order of susceptibility as follows:  $\text{AgCl}$ ,  $\text{HgCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{LiCl}$ ,  $\text{MnCl}_2$ ,  $\text{Cu}_2\text{Cl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{MgCl}_2$ ,  $\text{CrCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{AlCl}_3$ , and  $\text{SiCl}_4$ . Many of these chlorides are also strongly hygroscopic and readily react with the moisture in air. During chloridizing volatilization, oxidizing conditions usually prevail due to the presence of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  in the combustion gases, and only the most stable chlorides can be prevented from oxidation.

Chlorination in a fused salt bath proves useful when the metal chloride is highly hygroscopic and cannot possibly be introduced into an electrolytic cell without considerable contamination due to water. *In situ* chlorination of a dry oxide in the electrolytic cell renders the feed water-free

and avoids undesirable current losses. In some electrolytic processes, a metal chloride is produced by bubbling chlorine through a fused salt bath in which pellets of oxide or carbonate along with carbon are suspended.

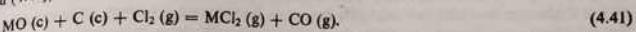
#### DIRECT AND INDIRECT CHLORINATION

There are two chief types of chlorination reactions, namely, direct chlorination and indirect or reduction chlorination. Direct chlorination is brought about by chlorine alone whereas reduction chlorination involves some reducing agents as well.

The formation of a metal chloride, usually from an oxide, in the range  $700$ – $1000^\circ\text{C}$ , depends on whether or not the metal has a greater affinity for chlorine than for oxygen under the prevailing experimental conditions. In other words, the free energy change for the reaction

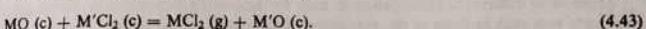
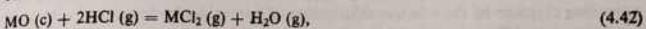


should be negative. If this condition is not fulfilled, then, reaction (4.40) must be aided (so that it can proceed in the forward direction) either by continuously removing the reaction products or by using a reducing agent such as carbon, which would lower the chemical potential of oxygen. Reaction (4.40), for the second situation, may be rewritten as



Using the available free energy data in the literature, we can show that the chlorination of all the commercially important metal oxides proceeds almost to completion under normal industrial operating conditions where, in most cases, the temperature is between  $500^\circ\text{C}$  and  $1000^\circ\text{C}$ .

We now consider the use of hydrogen chloride and other metal chlorides as chloridizing agents. The reactions are



The sign and magnitude of the free energy changes of reactions (4.42) and (4.43) and, consequently, the extent of chlorination at equilibrium, are largely determined by the differences between the standard free energies of formation of the oxide/chloride pairs.

The direct chlorination of stable oxides such as  $\text{MgO}$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  is not thermodynamically feasible unless reduced pressures are continuously used to remove the chloride vapours as they are formed at high temperatures.

In general, a sulphide can be directly chlorinated more easily than an oxide as the former reacts at very low temperatures. The vapours generated, however, generally contain  $\text{S}_2\text{Cl}_2$ , which may itself condense during the condensation of the metal chloride vapours and contaminate the product. This contamination can be avoided if the metal chloride is in the condensed state.

Where direct chlorination is not thermodynamically feasible under 1 atm, for example, in the case of very stable oxides such as  $\text{TiO}_2$  and  $\text{ZrO}_2$ , reduction chlorination is resorted to. In reduction chlorination, carbon is the most effective reducing agent, although other reducing agents such as S, CO, and  $\text{H}_2$  have been tried out.

Free silica by itself is not chlorinated at a temperature below  $1000^\circ\text{C}$  in the presence of carbon, whereas silicates such as clay and zircon, when mixed with carbon, are readily chlorinated.

Reduction chlorination can also be carried out using higher valency chloride compounds as reducing agents. For instance, compounds such as  $\text{FeCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{CuCl}_2$ ,  $\text{VCl}_4$ ,  $\text{TaCl}_5$ ,  $\text{TiCl}_4$ , and

$\text{NbCl}_3$  can be used in association with reducing agents such as  $\text{H}_2\text{S}$ ,  $\text{CO}$  and those metals which reduce these compounds to lower chlorides and release the chlorine necessary for chlorination.

A metallic sulphide can be converted to a chloride by treating it with chlorine or  $\text{HCl}$  gas in a neutral or reducing atmosphere. The presence of a reducing agent normally enhances the chlorination rate. Many sulphide ores may be amenable to selective chlorination.

#### BENEFICIATION OF LOW-GRADE ORES BY HALOGENATION

The treatment of low-grade ores by chlorination aims at either the removal of undesirable constituents in the form of volatile chlorides by selective chlorination or the recovery of the metallic values also in the form of volatile chlorides. The upgrading of minerals such as ilmenite and chromite is brought about by the selective chlorination and volatilization of the iron oxide impurity. Beneficiation by chlorination is necessary because, in these minerals, iron is present in chemical combination with the desired metals and cannot be eliminated by the conventional ore dressing methods.

During chlorination and the subsequent elimination of iron oxide, the aim is to produce only  $\text{FeCl}_3$ , which has a low boiling point ( $319^\circ\text{C}$ ). Chlorination may also produce the less volatile  $\text{FeCl}_2$  (boiling point  $1026^\circ\text{C}$ ), which tends to choke up the chlorinator. Chlorination carried out with a slight excess of chlorine markedly decreases the production of  $\text{FeCl}_2$ . For example, during the chlorination of ilmenite by  $\text{HCl}$  gas, the formation of  $\text{FeCl}_2$  may be drastically reduced, i.e., from 74 per cent to 1.5 per cent by introducing along with the  $\text{HCl}$  gas a small amount of air (2.8 per cent).

Numerous studies on the selective chlorination of ilmenite have been conducted. These refer to direct chlorination, reduction chlorination using  $\text{C}$ ,  $\text{CO}$ , and  $\text{H}_2$  as reducing agents, and the use of  $\text{CCl}_4$  and  $\text{HCl}$  also as reducing agents. Several studies have also been conducted on upgrading chromite by the selective chlorination of iron oxides in chromite.

Selective or differential chlorination is used for recovering commercially useful metals from low-grade ores such as those of tin, manganese, iron, vanadium, nickel, and tungsten. Differential chlorination is successfully employed for recovering, from monazite, rare-earth metals, thorium, and phosphorus.

Manganese has also been recovered from low-grade ores and slags through chlorination. Chlorination in this case yields chloride vapours which contain both manganese and iron. Additional processing is, therefore, necessary for the elimination of iron. This can be achieved by the selective condensation of the chloride vapours based on the wide difference in the boiling points of  $\text{MnCl}_2$  and  $\text{FeCl}_3$ , which are  $190^\circ$  and  $319^\circ\text{C}$ , respectively.

#### REFINING OF METALS BY CHLORINATION

Although Chapter 5 describes in detail various methods of refining nonferrous metals, a brief reference, at this stage, to the role of halides in a refining operation is considered appropriate.

Selective chlorination can be effectively used for refining many crude metals. For example, the Betterton process for refining lead, which uses either chlorine or  $\text{PbCl}_2$ , is based on the preferential chlorination of the main impurity zinc at about  $350$ – $400^\circ\text{C}$ . The Goldschmidt process for deleading tin, which uses fused  $\text{SnCl}_2$ , employs selective chlorination of lead in  $\text{Pb-Sn}$  alloys at around  $250$ – $260^\circ\text{C}$ .  $\text{SnCl}_2$  is reduced to tin by lead which forms a more stable chloride. Any excess  $\text{SnCl}_2$  may be subsequently recovered as volatile  $\text{SnCl}_4$  by chlorination.

Gold bullion can also be refined by chlorination. During chlorination, gold remains unaffected

while silver, lead, copper, antimony and other impurities are easily chlorinated and removed. Further, Mg can be removed from Al using  $\text{AlCl}_3$ , Zr from a Fe-Zr alloy using  $\text{FeCl}_2$ , Cu from a Cu-Ni alloy using  $\text{NiCl}_2$ , Fe from a Fe-Ni alloy using  $\text{NiCl}_2$ , Fe from a Fe-Ca alloy using  $\text{CaCl}_2$ , Pb from a Pb-Cu alloy using  $\text{CuCl}$ , and Zn from a Zn-Cu alloy also using  $\text{CuCl}$ .

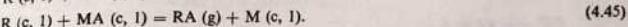
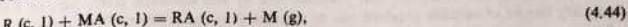
There are also numerous methods in which an intermediate halide vapour is used in metal refining. These methods, often called *vapour transport refining processes*, are discussed in Chapter 5. In Chapter 8, the metallothermic reduction of halides and the fused salt electrolysis of halide baths are discussed in detail.

#### 4.12 PYROMETALLURGICAL PROCESSES USING VACUUM

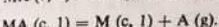
Vacuum techniques found large-scale commercial application in the metallurgical field during the First World War, i.e., when the Germans applied vacuum for degassing steel and purifying certain metals and alloys. Presently, vacuum is widely employed in an increasingly large number of operations used in the extraction and refining of metals. The newer metals such as Ti, Ge, Ta, Nb, and Zr have imparted a new impetus to vacuum processing because they possess, at elevated temperatures, a high affinity for hydrogen and nitrogen. Vacuum has also found application in various other processes such as the distillation of metals and alloys, melting and casting, various heat treatment processes, sintering of metal powders, the deposition of a metal from its vapour state, and joining of metals by brazing and welding. Here, although the emphasis is on the use of vacuum in metal extraction, a brief discussion on some other uses of vacuum is also included to bring out the similarities among the basic principles.

Reactions that are favoured by the application vacuum can be classified as follows.

##### Thermal Reduction



##### Thermal Dissociation



In reactions (4.44)–(4.46), R is a reducing agent and A is an acid radical, e.g., sulphur, oxygen.

##### Sublimation or Distillation



The equilibrium of each of the reactions (4.44)–(4.48) can be shifted by manipulating the pressure parameter. The use of vacuum helps in eliminating that reaction product which is volatile, thus driving the reaction towards completion. The pressure plays a decisive role in that it changes the free energy-temperature relationships.

The thermal decomposition of oxides under vacuum does not offer any possibilities for metal extraction. This is because most oxides require a very high degree of vacuum and high temperatures. However, relatively unstable oxides such as those of mercury and silver could be decomposed

by applying a vacuum. In both these cases, the metal would have a high vapour pressure at the temperatures required for decomposition, and, consequently, the problem of back reaction arises. Despite these difficulties, vacuum proves useful in the metalloceramic reduction of oxides.

In recent years, both the vacuum dissociation and the reduction of sulphides have been investigated. It has been experimentally shown that zinc sulphide can be directly reduced by iron

at 1000°C under a vacuum of about 1 mm mercury. This reduction offers interesting possibilities

because the roasting and reduction stages are avoided, the metal being produced in a single stage.

It is also possible that vacuum influences the metalloceramic reduction, by iron, of some other

sulphides such as PbS and HgS.

Apart from sulphides, vacuum can be used also for the dissociation and reduction of halides,

hydrides, and nitrides. However, such processes have not yet found application in industry.

When vacuum is applied, distillation and sublimation take place at lower temperatures. As a

result, vacuum has found application in titanium and zirconium metallurgy where the crude metal

sponge is separated from residual magnesium and magnesium chloride by vacuum distillation.

We now discuss some actual processes where vacuum can play a useful role.

#### REDUCTION OF OXIDE BY CARBON

In the reduction of an oxide by carbon, the volatile reaction products CO and CO<sub>2</sub> lead to an increase in the number of gaseous molecules in the metal-carbon system, and the forward reaction is favoured by lowering the pressure. For example, consider, at 1200 K, the reaction



In reaction (4.49), the positive free energy change  $\Delta G^\circ$  indicates that the forward reaction is not favourable when the reactants and products are in the standard state, i.e., at 1 atm. The necessary degree of vacuum required can be calculated by the procedure now given. We know

$$\Delta G^\circ = -RT \ln K,$$

$$68.85 \times 10^3 = -4.575 \times 1200 \log \frac{p_{\text{CO}}^5 \cdot a_{\text{Nb}}}{a_{\text{Nb}_2\text{O}_5} \cdot a_{\text{C}}^5}.$$

Here,  $a$  is the activity and  $p_{\text{CO}}$  the partial pressure of CO. Assuming the activities of Nb, Nb<sub>2</sub>O<sub>5</sub>, and C to be unity,  $p_{\text{CO}}$  is found to be approximately  $3 \times 10^{-3}$  atm or 2.28 mm Hg. Thus, the reaction is made feasible by using a vacuum better than 2.28 mm Hg.

On the other hand, during the reduction of a metal oxide by either hydrogen or carbon monoxide, the number of gaseous molecules in the system remains unchanged. For example, consider the reactions

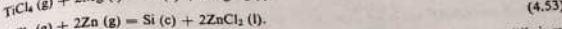
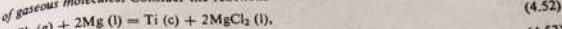


Vacuum would have no effect on the equilibria of these two reactions.

#### METALLOHERMIC REDUCTION OF OXIDES AND HALIDES

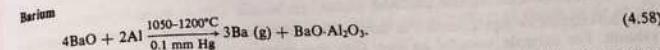
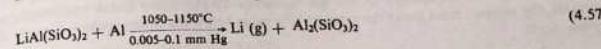
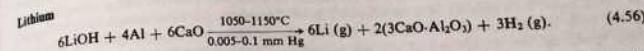
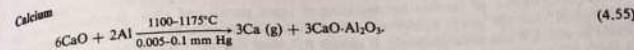
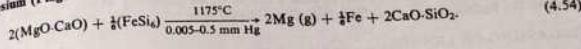
During metalloceramic reduction vacuum would aid the reaction only if there is an increase in the

number of gaseous molecules. Consider the reactions



In reactions (4.52) and (4.53), vacuum would obviously have an adverse effect on the equilibrium. However, some metals have been successfully produced by the metalloceramic reduction of the metal oxide or the oxygen-bearing compound when the reactants are in a condensed state. We now give examples of such metals.

#### Magnesium (Pidgeon Process)



Under vacuum, it is also possible to reduce the oxides of Pb, Zn, Mn, and Bi with silicon. However, the conventional methods are much cheaper than reduction under vacuum.

#### DEGASSING OF SOLIDS

Suppose an iron sample is to be degassed so that it contains only 0.0001 wt % hydrogen at 1000°C. It is given that at this temperature the solubility of hydrogen in iron is 0.0005 wt % at 1 atm. According to Sievert's law, hydrogen dissolves atomically and the equation representing the dissolution of hydrogen (with a different standard state for hydrogen as discussed in Section 2.13) is

$$\text{H}_2(\text{g}) = 2\text{H}_\text{a}, \quad (4.59)$$

where  $\text{H}_\text{a}$  denotes dissolved hydrogen. For reaction (4.59),

$$K = \frac{[\% \text{ H}_\text{a}]^2}{p_{\text{H}_2}}.$$

Since the solubility of hydrogen in iron has been given as 0.0005 wt % at 1 atm, we get

$$K = (0.0005)^2.$$

If  $\rho_{H_2}$  is the partial pressure of hydrogen that is in equilibrium with 0.0001 wt % hydrogen in iron, then

$$K = (0.005)^2 = \frac{(0.0001)^2}{\rho_{H_2}}$$

$$\rho_{H_2} = \frac{0.0001}{0.0005}^2 = \frac{1}{25} \text{ atm} = 30.4 \text{ mm Hg.}$$

Therefore, when the pressure over the iron sample is reduced below 30.4 mm Hg, the hydrogen content can, in principle, be brought below 0.0001 wt %. This pressure can easily be attained by employing a simple vacuum system. In such a situation, the degassing would, however, be slow because the hydrogen has to diffuse through a solid medium.

#### DEGASSING OF LIQUIDS

The required degree of vacuum for degassing of liquid metals and alloys is calculated on the assumption that the gas in equilibrium with the liquid comes from only one source, namely, the liquid in which it has been dissolved. It should be noted that for the solid a uniform pressure throughout the system is assumed. For the liquid, however, the pressure varies along the depth of liquid metal bath because of a metallostatic head. Therefore, the value obtained is valid only if the bath is well-stirred, as would be the case during induction heating. (Stirring would also help speed up the degassing.) If the gas dissolved in the liquid forms compounds such as nitrides, the vacuum must lower the pressure to a value below the decomposition pressure of these compounds.

#### DEOXIDATION OF LIQUID METALS

The deoxidation of liquid metals, in many cases, may be made more efficient by applying a vacuum. For example, consider an iron alloy that contains 0.1 per cent carbon and is melted under a pressure of  $10^{-4}$  atm. If at all deoxidation occurs, it would be according to the reaction



where  $C$  and  $O$  denote dissolved carbon and oxygen, respectively. For reaction (4.60), the equilibrium constant at 1600°C is about 420. Assuming the activity coefficients of the dissolved carbon and oxygen to be unity, we get

$$[\% O] = \frac{10^{-4}}{420[\% C]} = 2.4 \times 10^{-6}.$$

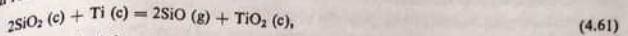
This value of the oxygen content shows that the deoxidation has been very effective.

Vacuum would have no beneficial effect on deoxidation by hydrogen because the number of gaseous molecules would remain unchanged.

#### MELTING

Metals are often melted in an oxide refractory crucible or a furnace lined with an oxide refractory material. The metal-refractory reactions are, therefore, of considerable interest to the process metallurgist. It is, therefore, worthwhile to examine the influence that vacuum can possibly have

on such reactions. Let us consider the reaction



for which the standard free energy change at 1600°C is about +3800 cal. Using the formula,  $\Delta G^\circ = -RT \ln K$ , we get

$$K = \frac{p_{SiO}^2 \cdot a_{TiO_2}}{a_{Ti} \cdot a_{SiO_2}^2} = 0.36,$$

where  $p$  is the equilibrium partial pressure and  $a$  the activity. Now, when an alloy containing titanium ( $a_{Ti} = 0.0014$ ) is melted in a refractory crucible whose lining is a silicate containing  $SiO_2$  ( $a_{SiO_2} = 0.2$ ), then, using the foregoing equation and assuming the activity of the  $TiO_2$  formed to be unity, we get

$$p_{SiO} = (0.36 \times 0.0014 \times 0.04)^{1/2} = 0.0045 \text{ atm or } 3.42 \text{ mm Hg.}$$

Thus, the equilibrium pressure in the system is 3.42 mm Hg. A pressure below this value would result in the constant removal of  $SiO$  from the system as well as the loss of titanium. Vacuum melting, therefore, cannot ensure oxygen-free metal unless a refractory more stable than  $SiO_2$  is found. Even if the pressure were normal, reaction (4.61) would continue to proceed if the system were open and  $SiO$  not allowed to establish an equilibrium pressure, i.e., it is allowed to escape. However, when the same titanium-containing alloy is melted in an alumina crucible, the relevant reaction is



where  $\underline{\underline{Al}}$  denotes titanium in alloy. One of the reaction products, namely,  $Al$  may form a solution and the standard free energy change for reaction (4.62) at 1600°C is found to be about 35 kcal. Therefore,

$$\Delta G^\circ = -RT \ln K = 35 \text{ kcal.}$$

Hence,

$$K = 8 \times 10^{-5} = \frac{a_{TiO_2} \cdot a_{\underline{\underline{Al}}}^{4/3}}{a_{Al_2O_3}^{2/3} \cdot a_{Ti}},$$

which gives  $a_{\underline{\underline{Al}}} = (8 \times 10^{-5} \cdot a_{Ti})^{3/4}$ . We know that the value of  $a_{Ti}$  is 0.0014, therefore,  $a_{\underline{\underline{Al}}}$  works out to be  $6 \times 10^{-6}$ . This value shows that the contamination due to aluminium is very small, and the application of vacuum to this system cannot bring about the metal-refractory reaction. However, the reaction corresponding to a situation where aluminium is continuously removed by evaporation is



where  $\underline{\underline{Al}}$  is aluminium in solution. The equilibrium partial pressure of aluminium over the melt can be estimated. However, this value would be extremely small. A high degree of vacuum would certainly remove aluminium continuously and thus would hinder the attainment of equilibrium, although only marginally. From the foregoing discussion, we conclude that metals can be melted for purification if their reaction with the refractory is avoided.

**4.13 HYDROMETALLURGY**

Hydrometallurgical treatment was generally confined to low-grade ores. However, in recent times, it has been extended to cover concentrates, mattes, speiss, and scrap. The stages involved in hydrometallurgical extraction are as follows.

**PREPARATION OF ORE FOR LEACHING**

The preparation of an ore for leaching includes grinding, the physical concentration of the metallic values or the removal of specific impurities by physical methods, roasting, and special chemical treatment either to render these values soluble in the subsequent leaching operation or to prevent the leaching reagent from being consumed by impurities.

**LEACHING**

In leaching, the metallic values in an ore are selectively dissolved using a suitable liquid reagent. The selectivity in dissolution depends on the nature of the reagent while the rate of leaching depends on various factors including temperature, pressure, the volume of the leaching liquid, the ore particle size, the composition and concentration of the reagent, the pulp density, the duration of the leaching reaction, and the degree of aeration of the leaching reagent.

**SEPARATION OF LEACH LIQUOR**

The leach liquor is separated from the residue left behind after processes such as leaching, settling, thickening, filtration, and washing.

**RECOVERY OF METALLIC VALUES FROM LEACH LIQUOR**

The metallic values are recovered from the leach liquor by employing one of the following processes, namely, precipitation, cementation, electrolysis, ion exchange, and solvent extraction.

**RECYCLING OF LEACH LIQUOR**

The leach liquor is recycled after it has been purified and its composition readjusted.

A typical hydrometallurgical process could have one or more of the objectives now listed:

- (1) To produce a pure compound which can later be processed by pyrometallurgy to yield the metal.
- (2) To produce the metal from either the crude metal or the metal compound which has already been prepared by other methods.
- (3) To produce a metal directly from an ore or concentrate.

A general outline of the various possible steps for achieving these objectives is shown in Fig. 4.11.

**ADVANTAGES OF HYDROMETALLURGY**

At present, hydrometallurgy is a well-established branch of extraction metallurgy. Complete hydrometallurgical processes are now available for the extraction and refining of almost all metals. In many instances, these processes help in achieving a higher degree of purity and a more economical operation.

The most important advantages of hydrometallurgy are:

- (1) Hydrometallurgical methods are ideally suited for lean and complex ores. With the gradual depletion of rich ore deposits, it is becoming increasingly difficult to apply conventional pyrometallurgical methods for metal extraction.

(2) Hydrometallurgical operations ensure greater control than other conventional methods over every step in the processing of ores, resulting in the recovery of valuable byproducts.

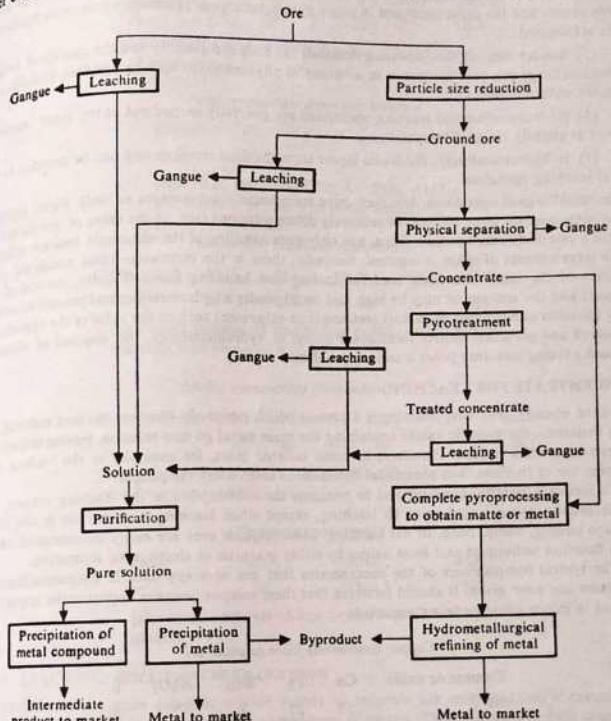


Fig. 4.11 Outline of Various Possible Hydrometallurgical Steps.

(3) The growing constraints within which metallurgical plants must operate due to environmental protection laws make conventional pyrometallurgical process such as roasting and smelting, increasingly difficult to carry out. Hydrometallurgical processing of sulphide minerals eliminates

such processes.

(4) Because of the rapidly increasing cost of metallurgical coke, which is both the main energy source and the main reductant in many pyrometallurgical processes, an aqueous processing route is favoured.

(5) Besides meeting the mounting demands for both the quantity and the quality of metals, hydrometallurgy can produce metals in a variety of physical forms such as powders, nodules, and coherent surface deposits.

(6) Hydrometallurgical leaching operations are generally carried out at the room temperature or at slightly elevated temperatures.

(7) In hydrometallurgy, the waste liquor from the final recovery step can be recycled to the initial leaching operation.

Hydrometallurgical operations, however, have some basic disadvantages as well. First, aqueous processing involves large volumes of relatively dilute solutions (say, of the order of one molar) to obtain a relatively small output. Thus, not only does handling of the chemicals become difficult but a large amount of space is required. Secondly, there is the corrosion—often combined with erosion—of the tanks and ducts used for storing and handling fluids. Thirdly, the cost of the reagents and the equipment may be high and could render a hydrometallurgical process economically unviable unless offset by factors (economic or otherwise) such as the value of the byproducts recovered and pollution control measures. Finally, in hydrometallurgy, the disposal of effluents without causing pollution poses a serious problem.

#### CONCENTRATE FOR LEACHING

We have already seen that leaching is a process which selectively dissolves the feed material. In most instances, the metallic values containing the main metal go into solution, leaving behind the gangue as a solid residue. However, in some isolated cases, for example, in the leaching of a complex ore of thorium, it is sometimes desirable to leach away the gangue.

To facilitate material-handling and to minimize the consumption of the leaching reagent, an ore is usually concentrated prior to leaching, except when leaching is carried out *in situ*, as in solution mining, dump, heap, or vat leaching. Most sulphide ores are easily concentrated using froth flotation techniques and most oxides by either magnetic or electrostatic separation.

The typical compositions of the concentrates that are normally used in hydrometallurgical processes are now given. It should be noted that these compositions are approximate, impurities present in minor amounts being neglected:

#### Copper concentrate from sulphide ore

Element or oxide	Cu	Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	S
wt %	35	25	8	2	30

(also small amounts of Mo, Pb, and Zn and traces of noble metals)

#### Copper concentrate from oxide ore

Element or oxide	Cu	Fe	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>
wt %	0.4	5	50	10	5	20

#### Zinc concentrate from sulphide ore

Element or oxide	Zn	Fe	S	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
wt %	50	8	30	2.5	0.5

(also small amounts of Pb, Cu, and Cd and traces of noble metals)

#### Lead concentrate from sulphide ore

Element	Pb	Zn	Cu	Fe	S
wt %	60	10	2	5	20

(also small amounts of Cd, As, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and traces of Bi, Sb, and noble metals)

#### Aluminium (bauxite) concentrate

Oxide	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	H <sub>2</sub> O
wt %	50–55	2–4	10–20	2–5	25

(also small amounts of manganese oxides, carbonaceous material, and phosphates)

#### Nickel concentrate from sulphide ore

Element or oxide	Ni	Fe	S	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O
wt %	10	40	30	10	3	10

(also small amounts of Cu, MgO, and CaO and traces of Pt and Pd group metals)

#### Zirconium concentrate

Oxide	ZrO <sub>2</sub>	HfO <sub>2</sub>	SiO <sub>2</sub>
wt %	65	0.5–0.2	30

(also small amounts of iron oxides and aluminium oxides)

#### 4.14 LEACHING: SOLUTION PREPARATION

In addition to the main solvents, a wide variety of reagents are employed, on a commercial scale, in the dissolution of the valuable components of an ore. These reagents include chemicals which aid the dissolution process because of their chemical effect on the minerals. For example, these chemicals help in obtaining an oxidized or reduced state of a metal or a metal compound more easily. For this purpose, in some cases, inorganic salts such as ferric chloride and acidified sodium chloride can be used. It should be noted that all solvents are water-based. In some isolated cases, plain water itself can be used as a solvent. However, in most cases, acids or alkalis, in varying degrees of concentration are employed. Generally, an acid is a much stronger

solvent than an alkali, and, as a prerequisite, does not require the fine grounding of the ore or concentrate which an alkali usually does. Further, leaching by an acid is applicable to a wide variety of ores. Alkali leaching is preferable in certain specific areas, for instance, in obtaining a particular type of solution for subsequent treatment or in retaining some ore constituents which may be destroyed by acid leaching.

Some of the common reagents are:

- (1) acids, e.g.,  $H_2SO_4$  (the most common) and  $HCl$ ,
- (2) alkalies, e.g.,  $NaOH$ ,  $Na_2CO_3$ , and  $NH_4OH$ ,
- (3) oxidizing agents, e.g.,  $O_2$ ,  $NaClO_3$ ,  $MnO_2$ ,  $KMnO_4$ , and  $FeCl_3$ , and
- (4) reducing agents, e.g.,  $SO_2$  and  $H_2$ .

Some of the criteria for the selection of an effective reagent are:

(1) Leaching by the reagent must be as selective and as rapid as possible. (While selectivity primarily depends on the nature of both the reagent and the ore, the rate of leaching depends on various parameters, for example, temperature, pressure, volume of the reagent, dilution, stirring, bacterial action, and the degree of aeration.)

(2) It should be possible to dissolve the reagent in order to prepare a sufficiently strong leaching solution which can ensure a fast rate of leaching. (The advantage is that a concentrated solution occupies less volume and, therefore, handling problems are minimized.)

(3) The reagent should not corrode the equipment. (Corrosion may be particularly severe in the case of chloride solutions.)

(4) The reagent should be economical and should preferably allow regeneration.

#### LEACHING OPERATION

There are several techniques used in commercial leaching or dissolution operations. The traditional methods treat the ore body at the mine site itself with the minimum use of equipment. These traditional techniques are divided into three categories. *In situ leaching* is either the leaching of the shattered rock residues left behind in a mine after the major mining operations have been carried out or the direct leaching of the ore deposit. *Dump leaching* is the application of the leach solutions to dumps consisting of off-grade ore rejected during normal mining operation. When higher grades of ore are leached in a predetermined manner using dumps, the process is known as *heap leaching*.

A dissolution operation can be made more efficient by recirculating the solvent and by continuously agitating the solution.

In *percolation leaching*, the leach solution is percolated upward or downward through an ore which has already been crushed and bedded into tanks. Usually, a mixture of coarse and fine ores is used so as to ensure permeability. By subjecting the ore to 10 or more leach cycles, 80 to 90 per cent of the metal values can be recovered.

In *agitation leaching*, stirring is used to aid the dissolution process. There could be variations; for example, atmospheric or high-pressure operation, continuous cocurrent or continuous countercurrent modes, and single-stage or multistage leaching.

*Percolation leaching* has certain advantages because it is operated in batches. For example, since each batch is separate or distinct, operational flexibility is greater, and accidental breakdowns are not that serious. A percolation leaching circuit is more versatile and can be employed in the case of ores for which the leaching rate is very slow.

#### 4.15 THEORY OF LEACHING

During leaching, a mineral (or a combination of minerals) decomposes in an aqueous environment. The mineral may simply dissolve completely, leaving behind the gangue as a solid residue. Sometimes, only some constituents of the mineral may dissolve. During alkali or acid leaching, with or without additional reagents, a metal forms simple or complex ions. We now consider some categories of leaching.

##### Simple Dissolution

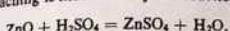
Simple dissolution is illustrated by the reaction



Pyrometallurgical treatment sometimes yields salts (i.e., during sulphating and chloridizing roasting) that can be leached with water.

##### Acid Leaching

Acid leaching is illustrated by the reaction



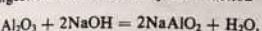
i.e.,



As already mentioned, sulphuric acid is the most commonly used acid; hydrochloric acid is also sometimes used.

##### Alkali Digestion

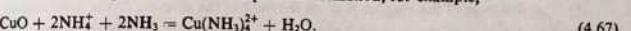
Alkali digestion is illustrated by the reaction



i.e.,



Apart from  $NaOH$ , other sufficiently strong alkalies also bring about a reaction similar to reaction (4.66). Ammonia leaching often leads to complex ion formation, for example,



##### Radical Exchange

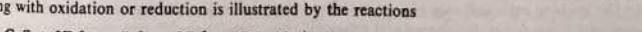
Radical exchange is illustrated by the reaction

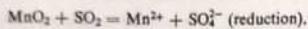


This type of reaction leads to the formation of a new insoluble solid phase which has a lower solubility product than that of the mineral being decomposed.

##### Leaching with Oxidation or Reduction

Leaching with oxidation or reduction is illustrated by the reactions





Many leaching systems of practical interest are combinations of the types given by reactions (4.69) and (4.70).

#### KINETICS OF LEACHING

The concentration gradients involved in mass transport between solids and liquids have been discussed in Chapter 2. Figure 4.12 shows the concentration profile when a mineral surface dis-

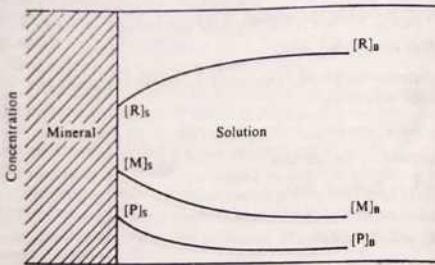


Fig. 4.12 Representation of Mineral Surface Dissolving Completely.

solves in a leaching medium. (Subscripts S and B refer to interface and bulk respectively.) The dissolution steps are explained in detail with reference to a more general case shown in Fig. 4.13. The situation is simple for complete dissolution. However, when the mineral decomposes, and dissolves only partially, then a new solid residue appears. Leaching would continue if this new phase is porous. This situation is shown in Fig. 4.13. (Subscripts I and II refer to the mineral-residue and residue-solution interfaces, respectively.) This figure may be considered as the more general case. The kinetic step that determines the rate of leaching could be one or a combination of the following:

- (1) The diffusion of the reagent R from the bulk of the solution to the solid surface II.
- (2) The diffusion of the reagent R through the porous reaction product layer.
- (3) The reaction of the reagent with the mineral surface I to form a soluble metal species.
- (4) The diffusion of product metal species M or other reaction products P through the porous reaction product layer in the outward direction.
- (5) The diffusion of the product metal species M (or other products P) away from the surface. When there is no porous reaction product layer, then steps (2) and (4) would, of course, be absent.

If we know the rate-determining step(s), then, the appropriate techniques required for speeding up the leaching reaction can be adopted. Such techniques would depend on the surface area exposed to the leaching action. Finely ground material, which has a large surface area, would, therefore, generally leach faster, for example, if either diffusion step (1) or diffusion step (5) is rate-control-

ling, then leaching can be speeded up by stirring the aqueous medium. However, if the chemical reaction step, i.e., step (3) is rate-controlling, agitation would have no effect. The effect of concentration of the reactants and products on the surface reaction would depend on the order of the reaction. Obviously, as the temperature increases, all the foregoing steps would be accelerated.

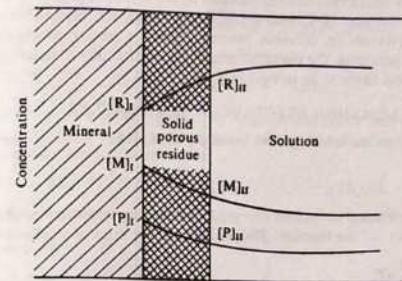


Fig. 4.13 Representation of Mineral Surface Decomposing and Dissolving.

#### INFLUENCE OF STIRRING SPEED

It should be noted that the concentration profiles shown in Figs. 4.12 and 4.13 are valid only for a particular level of agitation. Obviously, these gradients would become steeper as the level of agitation is increased. As a variable in rate determination, stirring can be eliminated only if the level of agitation is sufficiently high. With increasing agitation, the boundary layer gradually decreases to a limiting value and the concentration profiles are stabilized. Figure 4.14 illustrates

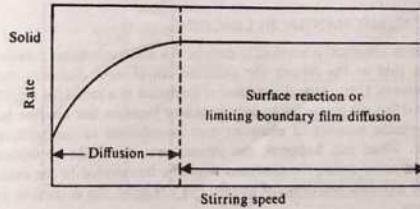


Fig. 4.14 Reaction Rate versus Stirring Speed.

the variation of the rate with stirring speed for the dissolution of a solid. It should, however, be noted that even when agitation ceases to have any effect on the rate, diffusion may still remain the rate-controlling step. In other words, although the boundary layer thickness becomes

independent of agitation, eventually, diffusion across this layer may still constitute the slowest step in the kinetics. Under these conditions, only the activation energy determines whether diffusion through the limiting boundary or the surface reaction is rate-controlling. The activation energy for diffusion through a solution is usually of the order of 5 kcal per mole or less. A dissolution process, in which the chemical reaction is rate-controlling, usually has a much higher activation energy in the range 10–25 kcal per mole. The relatively small variation of the dissolution rate with temperature in diffusion process implies a greater probability of diffusion control at higher temperatures. On the other hand, it is obvious that at these higher temperatures chemical reaction is less likely to be rate-controlling.

#### DEPENDENCE OF LEACHING REACTION ON TEMPERATURE

The effect of temperature on leaching rates is usually expressed in terms of the Arrhenius equation [eq. (2.122)]

$$\ln k = \ln A - \Delta E/(RT),$$

where  $\Delta E$  is the experimental activation energy,  $T$  the absolute temperature,  $R$  the gas constant and  $k$  the rate constant for the reaction. This equation in the form of a differential reads as

$$d \ln k = \frac{\Delta E}{RT^2} dT, \quad (4.71)$$

and on integration between limits the  $T_1$  and  $T_2$  becomes

$$\ln \frac{k_2}{k_1} = \frac{\Delta E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right), \quad (4.72)$$

where  $k_1$  and  $k_2$  are the rate constants at the temperatures  $T_1$  and  $T_2$ , respectively. If the specific rate constant is known for any two temperatures,  $\Delta E$  can be calculated directly by using eq. (4.72). The assumption that both  $A$  and  $\Delta E$  are independent of temperature is valid provided the difference between  $T_1$  and  $T_2$  is not too large. As already mentioned, the identification of the rate-determining step during a leaching reaction must ultimately depend on the activation energy.

#### ELECTROCHEMICAL MECHANISM IN LEACHING

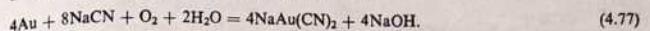
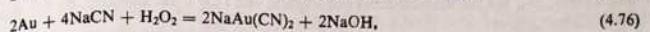
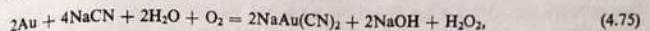
Some leaching reactions are electrochemical in nature. An electrochemical reaction differs from a chemical reaction in that in the former the electrons travel over distances much larger than merely atomic dimensions. During the dissolution or oxidation of a metal (or metallic compounds), the electrons produced are not restricted to any particular location but are free to move through the solid. Thus, a specific number of electrons may be released to the oxidizing medium anywhere on the surface. When this happens, the element would oxidize at certain specific areas called *anodic areas*. At other areas, the electrons would be transferred to the oxidizing agent in a manner similar to the galvanic corrosion of metals. For example, the corrosion of iron is represented by the reactions



Examples of leaching by an electrochemical mechanism are the dissolution of gold and silver in a cyanide solution, copper in ammonia solution, and some oxide and sulphide minerals in acids.

#### Cyanidation of Gold and Silver

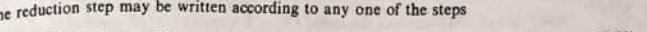
Cyanidation is a process in which gold and silver are leached by a cyanide solution. The commonly used cyanides are sodium cyanide, potassium cyanide, and calcium cyanide. The dissolution of gold by NaCN is represented by the overall reactions



The cyanidation of silver can also be expressed by reactions similar to reactions (4.75) to (4.77). A cyanidation reaction can be considered to be a combination of two steps—an oxidation step and a reduction step. The oxidation step is



while the reduction step may be written according to any one of the steps



corresponding to reactions (4.75), (4.76), and (4.77), respectively. The surface being leached is, therefore, divided into anode and cathode areas, represented, respectively, by  $A_1$  and  $A_2$ . Further,  $A_1$  and  $A_2$  give, respectively, the sum of all the elemental anode and cathode areas. We assume the boundary layer thickness at the anode and cathode areas to be  $\delta$ , as shown in Fig. 4.15.

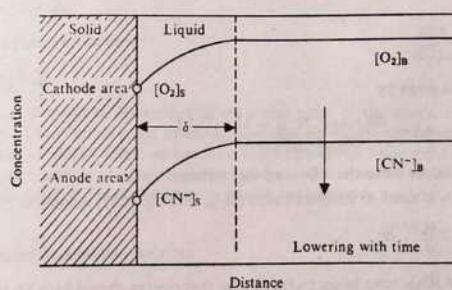


Fig. 4.15 Concentration Profile of  $O_2$  and  $CN^-$  near Metal Surface.

It is assumed that the kinetics of the reactions (4.75)–(4.81) are basically determined by the diffusion of both the dissolved  $O_2$  and the  $CN^-$  ion and not by the chemical reactions at the

surface. The appropriate equation for the diffusion of oxygen from the bulk to the cathode area is

$$\frac{d[\text{O}_2]}{dt} = D_{\text{O}_2} A_1 ([\text{O}_2]_B - [\text{O}_2]_S)/\delta, \quad (4.82)$$

where  $[\text{O}_2]_B$  and  $[\text{O}_2]_S$  are the concentrations of the dissolved oxygen at the bulk and surface, respectively,  $D_{\text{O}_2}$  the diffusion coefficient of oxygen, and  $t$  the time. Similarly, for the diffusion of a  $\text{CN}^-$  ion, we have

$$\frac{d[\text{CN}^-]}{dt} = D_{\text{CN}^-} A_2 ([\text{CN}^-]_B - [\text{CN}^-]_S)/\delta. \quad (4.83)$$

Assuming that the surface reactions proceed very fast,  $[\text{O}_2]_S$  and  $[\text{CN}^-]_S$  can be taken as the equilibrium values. As these values must necessarily be very low,  $[\text{O}_2]_S$  and  $[\text{CN}^-]_S$  can be eliminated from eqs. (4.82) and (4.83), respectively.

If we assume that the overall cyanidation reaction takes place according to eq. (4.75), then

$$\begin{aligned} \text{molar rate of dissolution of the metal } (R) &= 2 \times \text{molar rate of dissolution of oxygen} \\ &= \frac{1}{2} \times \text{molar rate of consumption of cyanide.} \end{aligned}$$

Hence,

$$R = 2D_{\text{O}_2} A_1 [\text{O}_2]_B/\delta, \quad (4.84)$$

that is,

$$A_1 = \frac{R\delta}{2D_{\text{O}_2} [\text{O}_2]_B}. \quad (4.85)$$

Similarly,

$$A_2 = \frac{2R\delta}{D_{\text{CN}^-} [\text{CN}^-]_B}. \quad (4.86)$$

The total area  $A$  is given by

$$A = (A_1 + A_2) = \frac{R\delta(D_{\text{CN}^-} [\text{CN}^-]_B + 4D_{\text{O}_2} [\text{O}_2]_B)}{2D_{\text{O}_2} [\text{O}_2]_B D_{\text{CN}^-} [\text{CN}^-]_B}. \quad (4.87)$$

From eq. (4.87), we make the following observations:

(1) If  $[\text{CN}^-]_B$  is small as compared with  $[\text{O}_2]_B$ , then eq. (4.87) reduces to

$$R = \frac{AD_{\text{CN}^-} [\text{CN}^-]_B}{2\delta}. \quad (4.88)$$

The absence of an  $[\text{O}_2]_B$  term in eq. (4.88) implies that oxygen should have no role to play when  $[\text{CN}^-]_B$  is too low compared with  $[\text{O}_2]_B$  and when the rate of dissolution depends only on the cyanide concentration.

(2) If  $[\text{CN}^-]_B$  is high and  $[\text{O}_2]_B$  is negligible as compared with  $[\text{CN}^-]_B$ , then eq. (4.87) reduces to

$$R = 2AD_{\text{O}_2} [\text{O}_2]_B/\delta. \quad (4.89)$$

Equation (4.89) shows that when the cyanide concentration is high, oxygen plays an important role in cyanidation kinetics. In this case, the diffusion of  $\text{CN}^-$  is already fast because of the high concentration gradient of  $\text{CN}^-$ . Therefore, the rate-determining factor should be the rate of oxygen diffusion. Thus, the rate of dissolution may be accelerated using higher pressures to ensure a higher degree of oxygen solubility in the leaching medium and, consequently, a higher concentration gradient of oxygen.

Experimental verification of the foregoing observations has proved that the diffusion phenomenon did indeed control cyanidation kinetics.

(3) In intermediate ranges of  $[\text{CN}^-]_B$  concentration, both  $[\text{O}_2]_B$  and  $[\text{CN}^-]_B$  influence cyanidation kinetics, as expressed by eq. (4.87). When

$$D_{\text{CN}^-} [\text{CN}^-]_B = 4D_{\text{O}_2} [\text{O}_2]_B, \quad (4.90)$$

eq. (4.87) reduces to

$$R = \sqrt{D_{\text{O}_2} D_{\text{CN}^-} A [\text{O}_2]_B^{1/2} [\text{CN}^-]_B^{1/2}/(2\delta)}. \quad (4.91)$$

In eq. (4.91), the value of  $D_{\text{CN}^-}$  is  $1.83 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$  and that of  $D_{\text{O}_2}$   $2.76 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ . The thickness of the boundary layer varies between  $2 \times 10^{-3} \text{ cm}$  and  $9 \times 10^{-3} \text{ cm}$ , depending on the speed and the method of agitation.

By comparing eq. (4.91) with eqs. (4.88) and (4.89), we conclude that the rate of dissolution changes its greater dependence on  $[\text{CN}^-]_B$  to that on  $[\text{O}_2]_B$  at conditions given by eq. (4.90). If the average ratio of  $D_{\text{O}_2}/D_{\text{CN}^-}$  is taken as 1.5, then the  $[\text{CN}^-]_B/[\text{O}_2]_B$  ratio works out to be 6; actual experimental values range from 4.6 to 7.4 (Wadsworth and Wadia, 1955).

It should be noted that if a surface chemical reaction were rate-controlling, then, too, the equations for the rate would be similar to eqs. (4.88) and (4.89). For an anode reaction, we have

$$R = K_1 A_1 [\text{CN}^-]_B^a, \quad (4.92)$$

and for a cathode reaction, we have

$$R = K_2 A_2 [\text{O}_2]_B^b. \quad (4.93)$$

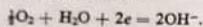
The values of  $a$  and  $b$  would be determined by the actual order of the anode and cathode reactions, respectively. Their values could be unity, depending on the reaction mechanism. In such a situation, therefore, we would obtain an equation indistinguishable from the diffusion equation. As already discussed, a more categorical method of deciding the control mechanism is obtained by considering the dependence of the reaction rate on temperature.

#### Dissolution of Copper in Ammonia Solution

We now discuss the dissolution of copper in an ammonia solution which is electrochemical in nature. In this case, too, some elemental areas on the metal surface are visualized as anodic and some as cathodic. Let  $A_1$  and  $A_2$  represent, respectively, the sum of all the elemental anode and cathode areas. The anode reaction is



and the cathode reaction is



We know that the solubility of oxygen in ammonia solution is low. The rate of reaction (4.95) is, therefore, controlled by the diffusion of dissolved oxygen from the bulk to the cathode areas, unless the ammonia concentration is very low. The rationale behind this conclusion is as follows. If it is assumed that the oxygen reacts on the surface as soon as it reaches it, and that the ammonia solution is sufficiently strong, then the reaction would depend only on oxygen diffusion. The corresponding equation is

$$R = 2k_1 A_1 [\text{O}_2]_B \quad (4.96)$$

where  $R$  is the rate of dissolution and  $k_1$  a constant ( $= D_{\text{O}_2}/\delta$ ). The factor 2 accounts for the fact that two atoms of copper are oxidized by one molecule of oxygen.

By the same rationale, the rate of reaction at the cathode is given by  $k_2 A_2 [\text{NH}_3]_B$ , where  $k_2$  represents either the rate constant for the surface reaction or the mass transfer coefficient for the diffusion of ammonia. Under steady-state conditions, the rates of the anode and cathode reactions must be the same, and since  $(A_1 + A_2)$  is equal to the total area  $A$ , we get

$$2k_1 A_1 [\text{O}_2]_B = k_2 A_2 [\text{NH}_3]_B = R \quad (4.97)$$

$$\frac{R}{A} = \frac{2k_1 k_2 [\text{O}_2]_B [\text{NH}_3]_B}{2k_1 [\text{O}_2]_B + k_2 [\text{NH}_3]_B} \quad (4.98)$$

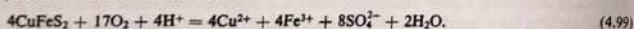
Equation (4.98) shows that the rate of reaction depends on  $[\text{O}_2]_B$  when  $[\text{NH}_3]_B$  is large compared with  $[\text{O}_2]_B$ . On the other hand, if  $[\text{NH}_3]_B$  is very small compared with  $[\text{O}_2]_B$ , then the rate would depend only on  $[\text{NH}_3]_B$ . In practice, ammonia solutions are not dilute, and hence  $[\text{NH}_3]_B$  does not control the reaction rate.

The electrochemical mechanism of dissolution is not restricted to metals; it can also be applied to semiconductors such as sulphides or oxides.

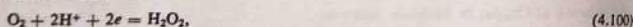
#### Electrochemical Dissolution of Sulphide Minerals

The dissolution of various sulphide minerals in a leaching medium is interpreted as an electrochemical reaction similar to the corrosion of metals. Oxygen is reduced at the cathode areas and at the anode areas, sulphides are dissolved, liberating electrons to complete the couple. The reduction of oxygen may occur through a series of steps involving peroxide intermediates.

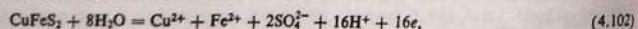
As an example, consider the leaching of chalcopyrite ( $\text{CuFeS}_2$ ) in an acid solution under oxygen pressure. The overall reaction is



The cathode reactions are



and the anode reactions are



It should be noted that the electrochemical dissolution mechanism involves the diffusion of various ions in the aqueous medium as well as the transfer of the electrical charge across the solid-electrolyte interface. The kinetics of a charge-transfer reaction is influenced by the potential gradient at the electrode surface. Thus, in the areas where the charge-transfer reactions are slow, the leaching rate can be influenced by applying an external voltage. Accordingly, attempts have been made to accelerate the leaching rate of some sulphide minerals by applying suitable potentials externally.

#### 4.16 ROLE OF OXYGEN IN LEACHING OPERATIONS

Oxygen plays an important role in many leaching operations. In most reactions, it is directly involved as a reactant; for example, in the cyanidation process (discussed in Section 4.15) for the dissolution of gold and silver. The reaction in this instance cannot proceed unless oxygen is made available. The equilibrium of this reaction would depend on the partial pressure of oxygen. The kinetics of leaching also would depend on the oxygen pressure if the rate-controlling mechanism were to involve the diffusion of oxygen either in the gas phase or in the aqueous solution. Oxygen pressure would also influence the diffusion processes in an aqueous solution by controlling the concentration of the dissolved oxygen. In some leaching processes, oxygen may have an indirect role, for example, in bacterial leaching, micro-organisms serve as catalysts. Since these organisms necessarily need oxygen for survival, all catalytic activity would cease in the absence of oxygen.

We now briefly discuss some leaching operations which directly involve oxygen.

#### Cyanidation of Gold and Silver

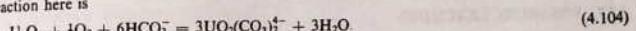
We have discussed the cyanidation of gold and silver in Section 4.15, and shown that the partial pressure of oxygen governs the kinetics of dissolution when the cyanide concentration is high.

#### Dissolution of Copper in Ammonia

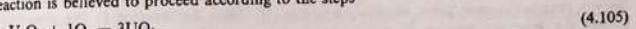
The dissolution of copper in ammonia, too, has been discussed in Section 4.15, and, in this case also, it has been shown that the partial pressure of oxygen determines the rate when the concentration of the dissolved oxygen is low and that of ammonia is high.

#### Carbonate Leaching of Uranium Ore

The reaction here is



This reaction is believed to proceed according to the steps

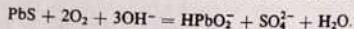


It is also believed that reaction (4.105) is a slow one, and, therefore, rate-determining. Accordingly, the rate of dissolution of the oxide should be proportional to  $[\text{O}_2]_B^{1/2}$ .

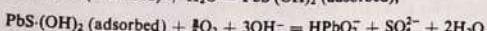
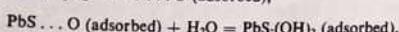
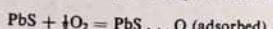
#### Leaching of Sulphides

The chemistry of the leaching of metal sulphides is usually more complicated than that of metals and oxides because a greater variety of products are involved.

We now consider the leaching of PbS by an NaOH solution that contains oxygen. (The leaching of other sulphides and oxides is discussed in Section 4.17.) The reaction is



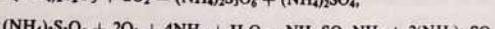
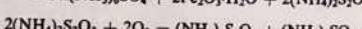
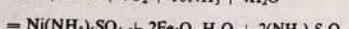
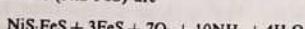
According to one theory, the steps in this reaction are



These steps are intended to account for the experimentally observed facts that the leaching rate is almost independent of the OH<sup>-</sup> concentration and it is proportional to [O<sub>2</sub>]<sup>1/2</sup>.

#### Ammonia Leaching of Pentlandite Under Pressure

Forward and Mackiw (1955) have suggested that the principal reactions in the ammonia leaching of pentlandite (NiS-FeS) are



During the early stages of the reaction, i.e., when fresh sulphides are abundant in the pulp, a high quantity of oxygen is required for the oxidation of the sulphide and for that of the thiosulphate and thionate to sulphate and sulphamate, respectively. Under these conditions, the concentration of oxygen in the leaching solution is depleted, and the leaching rate is determined by the dissolution of oxygen at the gas-solid interface which, in turn, depends on the oxygen pressure. As the reaction proceeds, the oxygen requirement decreases. As a result, the oxygen pressure, as a rate-controlling factor, may be eventually superseded by other factors such as the outward diffusion of the sulphide ions through the oxide layer surrounding the unreacted sulphide cores.

#### 4.17 PRESSURE LEACHING

When a solid is dissolved in a leaching reagent, the change in the total volume of the mixture, from a thermodynamic point of view, is negligible. Thus, an increase in the pressure hardly affects the leaching process. Pressure would, however, become an influential parameter if a gaseous substance is introduced simultaneously along with the solid so as to take part in the dissolution reaction. Reactions of this type have been discussed in Section 4.16. For these reactions, it should be noted that an increase in the pressure necessarily shifts the equilibrium in favour of better dissolution. However, it is not necessary that the actual rate of dissolution change. This rate would become dependent on the pressure only if oxygen transport, either in the gas phase or in the liquid, were rate-determining.

Besides the reason just mentioned, in many leaching processes, an increased pressure is advantageous for entirely different reasons. We know that the rate of dissolution is increased by leaching

at a high temperature. Some leaching processes are carried out at a temperature as high as 200°C, and the operator has to use a high pressure in autoclaves to prevent the water from becoming steam. Thus, in many instances, a high pressure is applied only so that a high temperature can be attained and the boiling away of the solvent can be suppressed, for example, the leaching of bauxite by a sodium hydroxide solution. Moreover, a high pressure becomes necessary when highly volatile and gaseous reagents are used in leaching. By increasing the partial pressures of such reagents, their concentrations in aqueous solutions can be maintained at sufficiently high levels to ensure their efficient utilization. For example, all leaching operations involving ammonia are aided by a high pressure.

#### KINETIC CONSIDERATIONS

Generally, the thermodynamics of a leaching reaction is very favourable, and the limitations are only of a kinetic nature. In most leaching operations, a heterogeneous reaction occurs at the solid-liquid interface. As already discussed, a leaching reaction may be viewed as a combination of several steps, the slowest of which becomes rate-determining if, by comparison, the other step are much faster. We know that when a liquid absorbs a gas, the reaction proceeds very rapidly. Such a reaction could be rate-determining if a large reacting vessel is employed because, as the size of the reactor increases, the ratio of the gas-liquid interface to the volume of the liquid correspondingly decreases. The rate of gas absorption may be accelerated

(1) by increasing the partial pressure of the gas,

(2) by increasing the area of the gas-liquid interface relative to the volume of the liquid, and

(3) by increasing the efficiency of agitation.

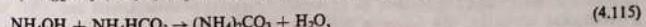
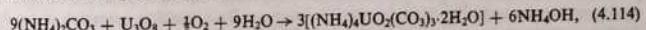
For obvious reasons, it would be difficult to carry out successfully the latter two methods; however, the first method can be manipulated to a great extent.

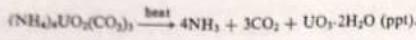
The transport of the reactants dissolved in a leaching liquid from the bulk to the interface relates to the transport of a number of reacting species. For example, in cyanidation, it involves the transport of CN<sup>-</sup> and the dissolved oxygen. The transport of the latter is often the rate-determining step, especially if the CN<sup>-</sup> concentration is high. In such a case, an increase in the pressure would accelerate the transport of oxygen by correspondingly increasing the solubility limit of oxygen.

Reactions at the interface may become rate-controlling if the diffusion steps are sufficiently speeded up by agitation. However, pressure rarely influences the interface reactions. We now consider examples of high-pressure leaching.

#### LEACHING OF OXIDES

High pressure has been effectively applied to the leaching of the oxides of metals such as Al, V, Ti, and U. In the dissolution of the first three metals, a gaseous reagent does not take part. In the case of uranium, however, where the ore usually contains U<sub>3</sub>O<sub>8</sub>, dissolution by an alkali is very slow, unless the oxide has already been oxidized to a higher valence state, namely, UO<sub>3</sub>. Here, atmospheric oxygen is the gaseous oxidizing agent at a high pressure. Consequently, the rate of dissolution depends on the partial pressure of O<sub>2</sub>. A high pressure can also be applied to the ammoniacal leaching of U<sub>3</sub>O<sub>8</sub>. The reactions are





#### LEACHING OF SULPHIDE ORES

Sulphide minerals such as ZnS, PbS, MoS<sub>2</sub>, FeS<sub>2</sub>, FeS, CuFeS<sub>2</sub>, FeS-NiS, and CuS and the mixed concentrates of these minerals are rapidly oxidized, under pressure at an elevated temperature, in aqueous solutions of sulphuric acid, ammonia, or sodium hydroxide. In some cases, a prior heat treatment of the ore at an elevated temperature renders it more suitable for leaching.

In nature, ores of Ni, Co, and Cu are often found mixed with each other, and considerable difficulty has been experienced in separating a sulphide or a metal from the bulk concentrate of the mixed sulphides. A recently developed commercial process for the mixed sulphides allows the approximate composition (per cent by weight) Ni 2-16, Cu 1-2, Fe 30-40, Co 0.5, S 28-34. Autoclave leaching in the presence of ammonia produces a solution containing ammines of Ni, Cu, and Co, free ammonia, and a number of ammoniacal salts including thiosulphates, thionates, sulphamates, and sulphates.

A diagrammatic representation of the leaching of a pentlandite particle is shown in Fig. 4.16.

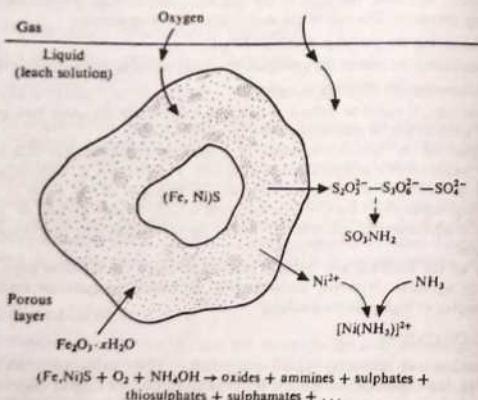


Fig. 4.16 Leaching of Pentlandite Particle (Forward and Mackiw, 1955).

During the early stages of the leaching process the dissolution of gaseous oxygen by the solution limits the leaching rate, while, in the subsequent stages, the diffusion of oxygen through the iron oxide coating around the sulphide particles does so. This leaching operation is regulated to produce a pregnant liquor containing an appreciable quantity of thiosulphate and other salts. In a subsequent operation, this liquor is boiled in order to reduce its ammonia content to a point

where the thiosulphate and other salts are decomposed and react to precipitate the copper (present as chalcocite associated with pentlandite) as a sulphide.

In the foregoing process, the pentlandite is leached in preference to copper sulphide. However, we should not conclude on the basis of separate dissolution kinetic studies for individual sulphides that a particular sulphide dissolves at a given rate even if other sulphides are present. To determine the optimum conditions of leaching we have to study the rate of dissolution of the ore mixture.

It has been shown that CuS dissolves less easily than NiS and that it is very difficult to dissolve CoS if associated with sulphides of Ni and Cu.

#### LEACHING OF SULPHIDES OF Zn AND Pb

Various processes have been developed to separate Zn and Pb from complex low-grade sulphide concentrates such as those produced by the flotation of the disseminated pyrite ore concentrate. In one process, the bulk concentrate is pressure leached in autoclaves using a sulphuric acid solution. This yields a ZnSO<sub>4</sub> solution and a residue containing PbSO<sub>4</sub>, elemental sulphur, and pyrite. To separate the pyrite, sulphur, and PbSO<sub>4</sub> from each other, the leach slurry is heated to a temperature above the melting point of elemental sulphur. As a result, pellets of pyrite and elemental sulphur are formed, which can be separated from PbSO<sub>4</sub> by screening. The advantages of such a process are as follows:

- (1) Zinc is not lost as zinc ferrite (which is formed during roasting).
- (2) The zinc producer is not committed to the recovery of sulphur as sulphuric acid from roaster gases.
- (3) Sulphur is produced in an elemental form and not as SO<sub>2</sub>, and is sold as such or converted to H<sub>2</sub>SO<sub>4</sub>.

#### ARSENIC EXTRACTION BY PRESSURE LEACHING OF SPEISS

One of the products obtained from a lead blast furnace is speiss, which is a solution of iron and arsenic [it may contain the compound Fe(As)<sub>4</sub>]. Arsenic can be recovered from speiss by leaching it with an NaOH solution (concentration 225 gm/litre) for 4 hours at an oxygen partial pressure of 20 atm, the speiss-NaOH ratio being 0.1. It may be noted that as much as 98 per cent of the arsenide can be recovered.

#### LEACHING OF MATTES WITH HIGH NICKEL CONTENT

During the matte smelting of nickel ores, a matte containing 60-75 per cent Ni along with Cu and Fe is produced; As and Sb may also be present. Ni, Cu, and As can be extracted by leaching the finely ground matte ( $\approx$  325 mesh) at 120-125°C under an oxygen partial pressure of 1.5-7 atm in a slightly acidic medium (pH 4.5-5). The residue is separated from the leaching solution, slurried with H<sub>2</sub>O to obtain a solid-liquid ratio in the range 0.2-0.4, and leached again under the same conditions, except that the pH is now in the range 1.5-2.5. In less than 3 hours, the Ni can be completely extracted.

#### ZINC EXTRACTION USING HIGH-PRESSURE LEACHING

Zinc can be extracted from sphalerite when the latter occurs as a complex sulphide along with ores such as chalcopyrite and pyrite. The complex ore is leached for 4 hours in concentrated H<sub>2</sub>SO<sub>4</sub> at 110°C and 6 atm partial pressure of O<sub>2</sub>. While the percentage recovery of Zn is about 98, that of Cu is only about 55.

#### 4.18 BACTERIAL OR MICROBIAL LEACHING

In nature, many sulphide minerals form water-soluble sulphates in mine waters. In fact, the presence of soluble metal values containing sulphide minerals has been known for several centuries. In the past, cementation was used to recover the metal from such solutions.

Natural processes are, however, very slow, and take years to produce a solution suitable for commercial exploitation. However, in the early part of the twentieth century, it was accidentally discovered that certain types of bacteria could considerably speed up the natural conversion processes. The mineral sulphides that leach faster in the presence of a suitable type of bacteria are arsenopyrite ( $\text{FeS}_2$ ,  $\text{FeAs}_2$ ), bornite ( $\text{Cu}_3\text{FeS}_4$ ), chalcopyrite ( $\text{CuFeS}_2$ ), covellite ( $\text{CuS}$ ), enargite ( $3\text{Cu}_2\text{S}$ ,  $\text{As}_2\text{S}_3$ ), galena ( $\text{PbS}$ ), marcasite ( $\text{FeS}$ ), molybdenite ( $\text{MoS}_2$ ), orpiment ( $\text{As}_2\text{S}_3$ ), pyrite ( $\text{FeS}_2$ ), stibnite ( $\text{Sb}_2\text{S}_3$ ), sphalerite ( $\text{ZnS}$ ), tetrahedrite ( $\text{Cu}_3\text{Sb}_2\text{S}_3$ ). Bacterial leaching not only leads to an enhanced dissolution rate but also to an effectively greater extent of recovery. Figure 4.17 shows how the presence of bacteria may influence both the leaching rate and the extent of recovery.

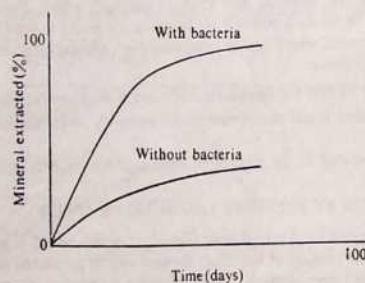
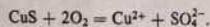
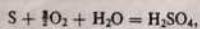
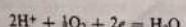
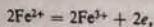


Fig. 4.17 Influence of Bacteria on Leaching.

The three most important types of bacteria from the viewpoint of leaching are *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, and *Ferrobacillus ferrooxidans*. They are capable of growing in purely inorganic media, obtaining their energy by oxidizing inorganic substances such as sulphur and thiosulphate to sulphate and ferrous iron to ferric ion. A biological catalyst, called enzyme, is synthesized by the bacteria and helps in accelerating the rate of oxidation reaction. The oxidation of sulphide minerals can be expressed by the reactions



Iron oxidation is given by the reactions



It should be noted that iron sulphide is a common impurity in many sulphide minerals. During leaching, ferric iron acts as a good oxidant and attacks the metal sulphide as shown by the reaction

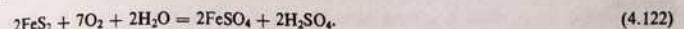


One of the functions performed by the bacteria is to rapidly reoxidize the ferrous ion to the ferric ion. The mechanism of leaching of the metal sulphide in reaction (4.121) is, therefore, indirect compared with the direct mechanism given in reaction (4.118).

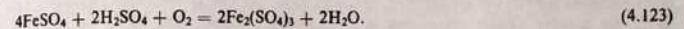
Since iron is found in most leach solutions, in practice, both the direct and indirect mechanisms operate simultaneously; their relative importance being largely dependent on both the type of mineral being leached and the type of bacteria being employed. Thus, while *Thiobacillus ferrooxidans* oxidize ferrous ion, *Thiobacillus thiooxidans* do not. Both oxidize sulphur and thiosulphate. Despite such differences in their nature, their morphological and nutritional characteristics are so similar that it is difficult to separate them. Consequently, they are generally classified as belonging to the *Thiobacillus ferrooxidans* group.

#### OXIDATION MECHANISM OF PYRITE AND COPPER SULPHIDE MINERALS

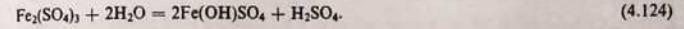
It is generally believed that the process of oxidation is initiated by the oxidation of pyrite in the presence of moisture according to the reaction



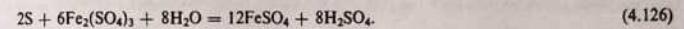
This reaction is slow and is not influenced by bacteria. Under slightly alkaline or acidic conditions, ferrous sulphate oxidizes to ferric sulphate, as given by the reaction



This reaction is fast and is influenced by bacteria. The resultant ferric sulphate hydrolyzes, and sulphuric acid is liberated as shown by the reaction



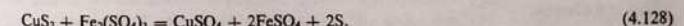
Ferric sulphate can also react with the pyrite:



Sulphur too may be oxidized by the bacteria to sulphuric acid according to the reaction

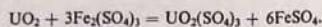


It has been observed that the reactions which result in the production of sulphuric acid are conducive to the growth of iron-oxidizing bacteria. The ferric sulphate that is regenerated by bacterial action can attack sulphide minerals in a manner similar to that given in reaction (4.125). For example, the dissolution of  $\text{CuS}_2$  can be written as



Ferric iron can also help in dissolving oxide minerals. For example, the reaction for the leaching

of  $\text{UO}_2$  is



From reactions (4.125), (4.126), (4.128), and (4.129), we see that ferric sulphate is the basic ingredient in the dissolution of sulphide and oxide minerals. The mechanisms described for the oxidation of the metal sulphide, however, are valid only over a limited pH range. Under alkaline conditions, the reactions are different, and the products are ferric oxide, alkali sulphide, and alkali thiosulphate.

Chalcopyrite ( $\text{CuFeS}_2$ ), covellite ( $\text{CuS}$ ), bornite ( $\text{Cu}_3\text{FeS}_4$ ), and tetrathydrate ( $\text{Cu}_4\text{Sb}_3\text{S}_9$ ) are oxidized and the copper liberated is dissolved by bacterial action. The fact that even reagent-grade  $\text{CuS}$  is attacked by bacteria shows that the intermediary action of ferric sulphate is supplementary to direct leaching. Although a large number of sulphide minerals are sensitive to bacterial action, copper and uranium appear to be the only two metals which are, at present, recovered on a reasonably large scale using bacterial leaching methods.

#### EFFECT OF VARIOUS FACTORS ON BACTERIA

In recent years, extensive investigations have been carried out in the laboratory to determine the operating conditions which are the most conducive to the catalytic action of the bacteria. Although most work has been done on copper and uranium ores, some general observations may be made.

##### Effect of Temperature

Temperature has a marked effect on the rate of bacterial conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , i.e., maximum bacterial activity occurs between  $30^\circ\text{C}$  and  $35^\circ\text{C}$ . As the temperature increases, i.e., above  $50^\circ\text{C}$ , the activity almost stops, and at a temperature higher than  $70^\circ\text{C}$ , the bacterial micro-organisms become sterile and are destroyed. As the temperature decreases, i.e., below  $30^\circ\text{C}$ , the activity also decreases, and, at a temperature below  $18^\circ\text{C}$ , it is negligible from a commercial point of view.

##### Effect of Nutrients

The addition of bacterial nutrients such as  $\text{FeSO}_4$ ,  $\text{FeS}_2$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{Fe}_2(\text{SO}_4)_3$  to the leaching solution increases the concentration of ferrous ions present. Consequently, the bacteria become more active so that both the rate and the extent of extraction are increased.

##### Effect of Particle Size and Bed Depth

The bacterial oxidation rate depends on the surface of the solid material present because the bacteria concentrate at the solid surface that is in contact with the solution and build up colonies there. Finely ground particles can cover a great surface area, leading to an increased leaching rate. However, very finely ground particles inhibit leaching because both the permeability of the solution and the air supply are reduced. Further, experimental observations show that a shallow bed enhances the leaching rate.

##### Effect of Radiation

When exposed to direct sunlight, a bacterial culture becomes inactive, but is not destroyed. As this culture is extremely sensitive to ultraviolet light, even a short exposure completely sterilizes it.

##### Effect of Acidity and Aeration

Oxidizing bacteria are active only in acid media. In general, it has been observed that bacterial oxidation is highly pronounced in a medium having a pH value between 2.0 and 3.5. Both above and below these pH values, the rate of bacterial oxidation decreases. At a pH value around 6, the oxidation is almost completely inhibited. It should be noted that these bacteria are destroyed in an alkaline medium.

The supply of oxygen to living micro-organisms is vital. Generally, oxygen is supplied by aerating a portion of the bacterial solution and subsequently transferring the aerated solution to the site of bacterial activity.

##### SCOPE FOR BACTERIAL ACTIVITY IN INDIA

There is a good scope for bacterial leaching operations in India where the sulphide ores are often lean, and, consequently, must be exploited by hydrometallurgical methods. The climate, often hot and humid, is ideally suited for bacterial activity. Although most of the foregoing observations have been based on work carried out in the West, they can be held valid for India too. This is because bacteria, like most living organisms, can, to a considerable extent, acclimate themselves to varying climates.

#### 4.19 CONTACT REDUCTION OF METALS IN AQUEOUS SOLUTIONS (CEMENTATION)

The leaching of an ore results in two distinct products, namely, a leach liquor containing the metallic values and a solid residue containing the gangue. The separation of the leach liquor from the residue is achieved by a variety of techniques. A discussion of these techniques is beyond the scope of this work. Here, we assume that separation has already been brought about and that a clear leach liquor from which the metallic values are to be recovered is available. The reduction of the metallic ions in solution to the elemental form of the metal is generally accomplished by three methods, namely, cementation or contact reduction, gaseous reduction, and electrolysis. We first consider contact reduction and then gaseous reduction. (Electrolytic reduction is dealt with in Section 4.25.)

The reduction of metals from a solution is a complex process as far as the overall stoichiometry is concerned. The reducible ions may be present as hydrated cations such as  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  or as complex ions such as  $\text{Ni}(\text{NH}_3)_6^{2+}$  and  $\text{Au}(\text{CN})_4^-$ . These ions are involved, respectively, during electrolysis of copper, hydrogen reduction of nickel ammines, and the zinc precipitation of gold from cyanide solutions. It may be noted that these reduction reactions are electrochemical in nature.

##### ELECTRODE POTENTIAL AND CEMENTATION

In cementation, a more reactive metal dissolves in a solution to precipitate a less reactive metal from the solution. Here, the electrochemical series (given in Table 3.2) can be used to determine the reactivity of a metal. For example, aluminium or zinc can be added to a gold cyanide solution to precipitate gold. Aluminium and zinc are placed high in the series (greater oxidation potential) while gold is placed towards the bottom (low oxidation potential). Aluminium or zinc dissolves because the conversion of the metal to metal ion involves a greater free energy decrease than that in the case of gold. It should, however, be noted that the elements in the electrochemical series have been arranged for a certain specific temperature ( $25^\circ\text{C}$ ) and solution

concentration (i.e., taking the metallic ion concentration as unity). The sequence of elements is not necessarily valid for arbitrary solution concentrations. For example, in precipitation of copper from  $\text{CuSO}_4$  solution by iron, since the oxidation potential of iron ( $\text{Fe} \rightarrow \text{Fe}^{2+}$ ) is 0.44 volts while that of copper ( $\text{Cu} \rightarrow \text{Cu}^{2+}$ ) is -0.344 volts, iron would normally be expected to reduce  $\text{Cu}^{2+}$  according to the overall reaction



However, the oxidation potentials taken from the standard electrochemical series are valid only for unit ion concentrations. The actual  $M/M^{2+}$  potential depends, among other factors, on the actual concentration of  $M^{2+}$ . Thus, if the  $\text{CuSO}_4$  solution is sufficiently dilute, then the  $\text{Cu}/\text{Cu}^{2+}$  potential may become higher. When iron is immersed in  $\text{CuSO}_4$ , the initial  $\text{Fe}/\text{Fe}^{2+}$  potential is high because of the absence of  $\text{FeSO}_4$ . As the reaction proceeds, the  $\text{FeSO}_4$  concentration builds up and the  $\text{CuSO}_4$  in the solution gets depleted. Accordingly, the  $\text{Fe}/\text{Fe}^{2+}$  potential gradually decreases from an initial high value and the  $\text{Cu}/\text{Cu}^{2+}$  potential increases from an initial low value. After a certain period, the two potentials become equal, and the reaction attains equilibrium. Obviously, the reaction never proceeds to completion unless some means is devised to continuously remove  $\text{FeSO}_4$  and  $\text{Cu}$  as they are formed.

The precipitation of copper from copper sulphate solution by metallic iron can also be visualized as an electrochemical process as shown by the reactions



The cementation reaction is shown schematically in Fig. 4.18. Iron dissolves at the anode, and each copper ion picks up electrons at the cathode to deposit metallic copper.

The general reaction for the reduction of a metal ion  $M_1^{Z_1+}$  by a metal  $M_2$  to form  $M_2^{Z_2+}$  ions is written as



The appropriate equations for the electrode potentials of metals  $M_1$  and  $M_2$ , respectively, are

$$E_1 = E_1^0 + \frac{RT}{Z_1 F} \ln C_1, \quad (4.134)$$

$$E_2 = E_2^0 + \frac{RT}{Z_2 F} \ln C_2, \quad (4.135)$$

where  $E_1^0$  and  $E_2^0$  are, respectively, the standard potentials of  $M_1$  and  $M_2$ ,  $F$  is the Faraday constant, and  $C_1$  and  $C_2$  are, respectively, the bulk concentrations of the ions  $M_1^{Z_1+}$  and  $M_2^{Z_2+}$ .

In practice, the system is short-circuited, and it is not possible to separate the anode reaction from the cathode reaction. Due to the continuous flow of electrons from the anode area to the cathode area, this system has a unique electrode potential  $E$ —known as the ‘compromise potential’—which is less than the equilibrium potential  $E_1$  of the cathode but greater than the equilibrium potential  $E_2$  of the anode. If the slow discharge is controlled by diffusion or reaction at the cathode, that is, by a cathodic process, the anode reaction will essentially be at equilibrium. In such a situation, the compromise potential will be equal to the anode equilibrium

potential  $E_2$ . This situation implies that the overpotential at the anode would be negligible, which is indeed the case in most contact processes.

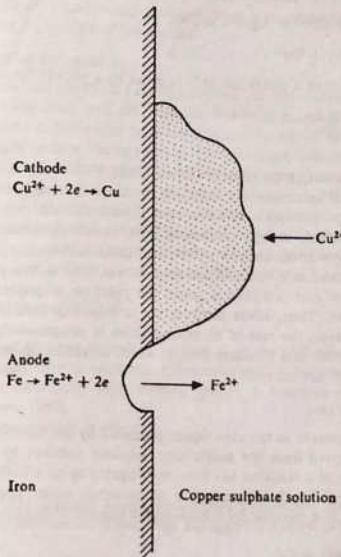


Fig. 4.18 Cementation Reaction (Power and Ritchie, 1975).

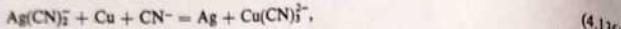
A higher driving force for the cementation reaction is obtained by using a reactive metal which would give an anode potential as high as possible. From a practical point of view, however, such a procedure may not be advisable. For example, aluminium, although placed higher than zinc in the electrochemical series, is not preferred in the cementation of gold because the precipitate of gold always traps some of the reductant within it. Further, while zinc can be easily eliminated by volatilization, it would be very difficult to remove aluminium.

#### Kinetics of Cementation Processes

In recent years, a number of kinetic studies have been carried out to gain a better understanding of cementation reactions. We now briefly discuss some of the reactions to highlight their general characteristics.

#### Silver cementation on copper

The kinetics of silver cementation has been studied using an alkaline cyanide solution containing silver ions and rotating copper strips immersed in perchloric acid. The reactions are



The rate of cementation of a metal ion  $M^{Z+}$  is given by a pseudo-first-order rate equation

$$-\frac{d[M^{Z+}]}{dt} = kA[M^{Z+}], \quad (4.138)$$

where  $k$  is the rate constant,  $t$  the time,  $A$  the area, and  $V$  the volume. It should be noted that eq. (4.138) is valid for all heterogeneous reactions in solutions, regardless of whether the rate is controlled by ionic transport across a diffusion layer adjacent to the metal surface, by chemical reaction at the metal surface, or by a mixture of both. A rate equation similar to eq. (4.138) is valid for the cementation of silver on iron and that of palladium on copper.

The metal deposit formed as a result of cementation can lead to complications. For example, if the deposit is coherent and continuous, then the reaction is gradually retarded and may eventually stop altogether. Thus, silver cementation in a cyanide solution is gradually retarded. In perchloric acid, however, the rate of silver deposition is progressively enhanced. This effect is attributed to the formation of a powdery deposit which increases the effective cathodic area on which adsorbed silver ions are reduced.

#### Cadmium cementation on zinc

Cadmium is invariably present in the zinc liquor produced by the leaching of roasted sphalerite. The metal is usually removed from the acidic zinc sulphate solution by cementation on zinc. (In this case, the kinetics of a reaction has been investigated using a buffered sulphate solution.) When a zinc sheet is used for the cementation of cadmium under appropriate conditions of temperature and acidity, it is covered by a high-purity deposit of cadmium. The reaction is



This deposit floats up to the liquid surface along with the hydrogen bubbles produced during the dissolution of zinc. Since the cathode area on the zinc sheet is limited, the reaction proceeds slowly. The reaction rate can be speeded up by using zinc powder and by stirring the solution. However, this may produce a low-grade cadmium precipitate with some unreacted zinc trapped in it.

The rate of cementation in the foregoing system has been experimentally determined, and the general rate equation is the same as eq. (4.138).

The rate of cementation is found to be dependent on the degree of agitation, indicating that the diffusion processes are rate-controlling. From the magnitude of the activation energy measured, it has been concluded that the rate of cementation is controlled by the diffusion of ions through the aqueous layer on the metal.

#### Effect of Impurities on Cementation

The impurities present in the reductant or in the solution often have a marked effect on cementation. For example, if the zinc metal that is used to precipitate cadmium contains as little as 0.9 per cent lead, the rate of cementation may be lowered by as much as 50 per cent. For the aforesaid cementation process, the copper and arsenic ions present in solution may increase the rate, while the cobalt ions may retard it. Apart from influencing the reaction rate, impurity ions often adversely affect the quality of the deposit.

#### Diffusion Mechanism During Cementation

A large number of cementation reactions basically depend on the diffusion of ions through the boundary layer between the solid and the solution. For example, in the precipitation of copper by iron, the kinetics follows a first-order equation [similar to eq. (4.138)] and increases as the speed of agitation increases up to a limiting value. The maximum obtainable rate of cementation is in close conformity with the theoretical values obtained by using, as a basis, the diffusion of an aqueous solution through a limiting boundary layer.

Let us next consider the diffusion of  $\text{Cu}^{2+}$  ions to a metallic iron surface on which they are precipitated. If the concentration of the copper ions at the surface is denoted by  $[\text{Cu}^{2+}]_s$  and in the bulk solution by  $[\text{Cu}^{2+}]_b$ , and if the boundary layer thickness is  $\delta$ , then the rate of transport across the diffusion boundary, written according to Fick's first law, is

$$\frac{dn}{dt} = -DA_2\{[\text{Cu}^{2+}]_b - [\text{Cu}^{2+}]_s\}/\delta, \quad (4.140)$$

where  $n$  is the number of  $\text{Cu}$  ions deposited in time  $t$ ,  $D$  the diffusion coefficient, and  $A_2$  the cathode area. As the rate of stirring increases,  $\delta$  decreases until a limiting boundary layer thickness is approached. At sufficiently high stirring speeds,  $\delta$  becomes constant (for details, see Nadkarni and Wadsworth, 1967).

The rate of the surface reaction is given by

$$\frac{dn}{dt} = -A_2k_1[\text{Cu}^{2+}]_s, \quad (4.141)$$

where  $k_1$  is the reaction rate constant. Under steady-state conditions, the mass transport kinetics becomes equal to the surface kinetics. Thus, from eqs. (4.140) and (4.141), we get

$$\frac{dn}{dt} = -\frac{A_2[\text{Cu}^{2+}]_b}{\frac{1}{k_1} + \frac{\delta}{D}}. \quad (4.142)$$

For a given concentration, if the surface reaction proceeds much more rapidly than the diffusion reaction, then

$$\frac{1}{k_1} < \frac{\delta}{D}. \quad (4.143)$$

Hence,

$$\frac{dn}{dt} = -AD[\text{Cu}^{2+}]_b/\delta. \quad (4.144)$$

The empirically determined rate equation for the diffusion model is

$$\frac{d[\text{Cu}^{2+}]_b}{dt} = -Ak[\text{Cu}^{2+}]_b, \quad (4.145)$$

where the constant  $k$  includes the diffusion coefficient, the boundary layer thickness, and the kinematic viscosity of solution. Since

$$\frac{1}{A} \frac{dn}{dt} = \frac{V}{A} \frac{d[\text{Cu}^{2+}]_B}{dt}, \quad (4.146)$$

$$\frac{dn}{dt} = -VAk[\text{Cu}^{2+}]_B. \quad (4.147)$$

Comparing eq. (4.147) with eq. (4.144), we find

$$D = V k \delta. \quad (4.148)$$

In eq. (4.148),  $V$  (volume of the solution) and  $k$  can be experimentally determined and  $\delta$  can be estimated. Kortum and Bockris (1951) have found the theoretical value of  $\delta$  to be approximately  $10^{-3}$  cm. Thus, the value of  $D$  can be calculated to determine if its magnitude is in consonance with the solution diffusion model, on the basis of which eq. (4.148) has been derived. In the Cu-Fe system, the value of  $D$  was worked out to be  $1.2 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>, which is considered sufficiently reasonable to validate the diffusion model. Further corroboration can be obtained by determining the activation energy of the cementation reaction. As already stated, a diffusion controlled process has a much lower activation energy than a process controlled by chemical reaction.

#### 4.20 GASEOUS REDUCTION OF METALS IN AQUEOUS SOLUTIONS

Of the many recent developments in the hydrometallurgical processes for metal recovery that are based on the properties of metal ions in aqueous solutions, the gaseous reduction process is noteworthy. Gaseous reduction processes have already produced more than half a million tons of high-purity metal powders mainly of copper, nickel, and cobalt. The products of gaseous reduction processes, i.e., metallic powders, find application in powder metallurgy, catalysis, dispersion strengthening of metals, plasma-arc and flame-sprayed coatings.

It may be noted that hydrometallurgical processes in which the final metal recovery step is carried out by either cementation (e.g., Au, Ag, and Cu) or electrolysis (e.g., Cu, Zn, Ni, and Cd) have been widely used in the past. The possibility of employing reducing gases such as SO<sub>2</sub>, CO, and H<sub>2</sub> under pressure to effect the final precipitation of metals directly from their solutions had been considered for a long time. However, this process first found commercial application only in the early nineteen fifties in Canada and the U.S.A.

#### THERMODYNAMIC PRINCIPLES OF GASEOUS REDUCTION

When a piece of zinc is dropped into a copper sulphate solution, the zinc dissolves to form a soluble sulphate, and copper is precipitated as free metal. The reaction in this case can be explained in terms of the positions of Cu and Zn in the electrochemical series (given in Table 3.2). Zinc dissolves because it is more electropositive than copper. Similarly, zinc displaces hydrogen from an acid solution because the oxidation potential of Zn is higher than that of hydrogen. For example, the reaction of Zn with sulphuric acid is



The concept of the standard oxidation potential, as listed in the electrochemical series, may,

however, be misleading (see Section 4.19). For example, reaction (4.149) tends to reverse its direction if the hydrogen pressure is high and the H<sup>+</sup> acidity low. These two factors must be taken into account for a rigorous thermodynamic analysis.

The general reaction when a metal is precipitated from its state of solution, as M<sup>Z+</sup> ions, by hydrogen may be written as



where  $Z$  is the number of electrons taking part in the reaction. Reaction (4.150) may be viewed as the result of two opposing reactions, namely,

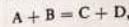


The free energy change  $\Delta G$  for a reaction is related to the potential obtainable in an electrochemical cell by the general equation

$$\Delta G = ZFE, \quad (4.153)$$

where  $F$  is the Faraday constant. From eq. (4.153), we see that a greater potential implies a higher negative free energy change, i.e., the likelihood of a reaction is greater. Therefore, the metal would be liberated from its solution, provided  $E_{H^+}$  is greater than  $E_M$ .

For a reaction



$\Delta G$  is given by

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}, \quad (4.154)$$

where  $\Delta G^\circ$  is the standard free energy change. Using eq. (4.153), we can rewrite eq. (4.154) as

$$E = E^\circ - \frac{RT}{ZF} \ln \frac{a_D \cdot a_C}{a_A \cdot a_B}, \quad (4.155)$$

where  $E^\circ$  is the standard potential for the reaction and  $a_A$ ,  $a_B$ ,  $a_C$ , and  $a_D$  are the activities of A, B, C, and D, respectively. Assuming the activity of a metal to be unity and applying eq. (4.155) to reactions (4.151) and (4.152), we obtain

$$E_{H^+} = E_H^\circ - \frac{2.303RT}{F} \log a_{H^+} + \frac{2.303RT}{2F} \log p_{H_2}, \quad (4.156)$$

$$E_M = E_M^\circ - \frac{2.303RT}{ZF} \log a_{M^{Z+}}. \quad (4.157)$$

It should be noted that the activity of hydrogen is taken as identical with its partial pressure. From eqs. (4.156) and (4.157), we find that the hydrogen potential is dependent on three factors, namely, the standard potential (a constant), the hydrogen ion concentration in the solution, and the hydrogen gas pressure. By definition,  $E_{H^+}^\circ$  is zero at 25°C, and  $-\log a_{H^+}$  can be taken as the pH of the solution. Using compatible units for  $R$  and  $F$ , we have

$$E_{H^+} = 0.05916 \text{ pH} + 0.02958 \log p_{H_2}, \quad (4.158)$$

for a temperature of 25°C only. Equation (4.158) shows that the hydrogen potential is more sensitive to changes in pH than in  $p_{H_2}$ . As long as the metal remains in an unalloyed state (unit activity), the general equation for the metal potential remains as shown in eq. (4.157). However, when the activity coefficient  $\gamma_{M^{Z+}}$  is introduced into eq. (4.157), this equation is rewritten as

$$E_M = E_M^0 - \frac{2.303RT}{ZF} \log [M^{Z+}] - \frac{2.303RT}{ZF} \log \gamma_{M^{Z+}} \quad (4.159)$$

where  $[M^{Z+}]$  is the molar concentration. In most practical situations in hydrometallurgy where the solutions are dilute, the activity coefficient may be taken as unity. Thus, eq. (4.159) now becomes

$$E_M = E_M^0 - \frac{2.303RT}{ZF} \log [M^{Z+}] \quad (4.160)$$

For accurate calculations, the exact values of the activity coefficient must be used.

Figure 4.19 shows the plots corresponding to the hydrogen and the metal electrode potentials (in volts) at different metal ion concentrations and at different hydrogen pressures according to

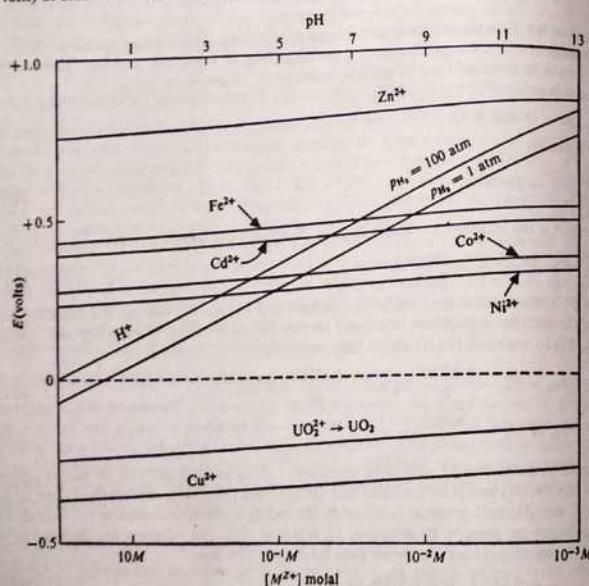


Fig. 4.19 Hydrogen and Metal Electrode Potentials at 25°C.

eqs (4.158) and (4.160). (It should be noted that all these values are for 25°C only.) Hydrogen can reduce a solution containing metal ions when the potential of the hydrogen reaction given by eq. (4.158) is greater than that of the metal reaction given by eq. (4.160). The hydrogen overpotential and metal overpotential are ignored.

The general observations that we can make from Fig. 4.19 are:

(1) The effect of the concentration of the metallic ions, within the limits usually observed in hydrometallurgy, on the metal potential is very small.

(2) The effect of pressure on the hydrogen potential is also very small. (Even a hundred-fold increase in the pressure increases the potential very slightly. The hydrogen potential, however, is very sensitive to pH.)

(3) The plots give the value of pH at which the potential of hydrogen exceeds that of the metal, making gaseous reduction possible. An increase in pressure slightly lowers this limiting pH value by shifting the point at which the metal line and the hydrogen line intersect.

From Fig. 4.19, we see that the hydrogen potential is always greater than that of copper. Thus, hydrogen can reduce and displace copper ions in solutions at all pH values, even at low pressures. This is possible because copper is placed very low in the electrochemical series. From Fig. 4.19, it is also evident that the reduction of  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cd^{2+}$ , and  $Fe^{2+}$  is favoured only at high pH. In a situation, where the equilibrium partial pressure of  $H_2$  is 1 atm at 25°C and when  $E_H = E_M$ , we have

$$E_{H_2} = 0.05916 \text{ pH} = E_M^0 - \frac{0.05916}{Z} \log [M^{Z+}] = E_M \quad (4.161)$$

$$-\log [M^{Z+}] = Z \text{ pH} - \frac{ZE_M^0}{0.05916} \quad (4.162)$$

In commercial hydrometallurgy, a metal concentration below  $10^{-2}$  molal is not of significant interest. Hence, it is worthwhile to solve eq. (4.162) when  $\log [M^{Z+}] = 2$  and then tabulate the pH values obtained. These values are given in Table 4.2. It should be obvious that if a 1.0 molal

Table 4.2 Equilibrium pH Values at  $[M^{Z+}] = 10^{-2}$  Molal at  $H_2$  Pressure 1 atm and Temperature 25°C (after Meddings and Mackiw, 1969)

Ion	$E$ (V)	pH
$Zn^{2+}$	0.762	13.9
$Fe^{2+}$	0.440	8.5
$Cd^{2+}$	0.403	7.8
$Co^{2+}$	0.267	5.5
$Ni^{2+}$	0.241	5.1
$Cu^{2+}$	-0.337	-4.7
$Ag^{2+}$	-0.799	-11.5

solution is to be reduced to  $10^{-2}$  molal by hydrogen, then adequate precautions must be taken to prevent the number of moles ( $Z$ ) of  $H^+$  ions produced from decreasing the pH value of the solution below the equilibrium values given in Table 4.2. For metals having high potentials (i.e., high  $E$  values), the addition of neutralizing agents to maintain the pH value above the required equilibrium value becomes essential. From eqs. (4.161) and (4.162) it is also possible to calculate the hydrogen pressure necessary to reduce a given metal at a given pH. Consider a solution whose pH is 6 at 25°C. At this pH, the metal potential is normally greater than the hydrogen potential. The theoretical potentials required to reduce  $Zn^{2+}$ ,  $Fe^{2+}$ , and  $Cd^{2+}$  are, respectively, 0.83, 0.50, and 0.47 volts. These values are, respectively, nearly 0.47, 0.14, and 0.11 volts above the hydrogen potential when the pH is 6, pressure 1 atm, and temperature 25°C. Obviously, then, hydrogen will not reduce the metal ions unless its potential is made to increase sufficiently. From eq. (4.158), we see that the potential change is related to the pressure by the relation

$$\Delta E = 0.02958 \log p_{H_2} \quad (4.163)$$

For the reduction of zinc ions at a pH value of 6, we have

$$0.47 = 0.02958 \log p_{H_2} \\ \log p_{H_2} = 15.9. \quad (4.164)$$

Thus, if the hydrogen pressure is increased to a value of about  $10^{16}$  atm, then the reduction of the metal is possible. A pressure of this order is, however, considered to be beyond practical limits. The pressure required for metal reduction remains very high even in highly alkaline solutions, i.e., when the pH is high. We may thus conclude that it is almost impossible to reduce zinc ions by hydrogen even at high values of pH and  $p_{H_2}$ . The corresponding pressures for the reduction of iron (ferrous) and cadmium at a pH of 6 are  $5.4 \times 10^4$  atm and  $5.2 \times 10^3$  atm respectively. Since these pressures are still beyond practical limits, we conclude that pressure is not an effective parameter in changing the potential required for reduction.

#### PRACTICAL ASPECTS OF GASEOUS REDUCTION

It should be remembered that the foregoing discussion can provide only guidelines for gaseous reduction derived from the theoretical treatment pertaining to idealized conditions. The practical potential requirements would be somewhat different because, for an observable rate of reduction, the hydrogen potential must be somewhat greater than the metal potential to provide the driving force for the reaction. The kinetic aspects of hydrogen reduction processes with respect to some particular systems are discussed in Section 4.21.

In hydrogen reduction, hydroxide precipitation could lead to serious problems. It is seen from the electrode potential plots (see Fig. 4.19) that hydrogen reduction is more favourable at higher pH values. However, several metal ions become unstable at high pH values and precipitate as insoluble hydroxides. The solubility products of some metal hydroxides and sulphides, at 25°C, are shown in Table 4.3. This table shows that the solubilities of metal hydroxides vary widely. Some hydroxides, therefore, tend to precipitate at the pH values required for hydrogen reduction. This should be prevented or sufficient agitation provided to keep the hydroxide in suspension.

#### PRODUCTION OF NICKEL AND COBALT BY HYDROGEN REDUCTION: COMPLEX FORMATION

$Ni^{2+}$  and  $Co^{2+}$  ions tend to get hydrolyzed and then precipitated as hydroxides or oxides around

Table 4.3 Solubility Products\* ( $K_{SP}$ ) of Some Metal Hydroxides and Sulphides at 25°C (after Feifknecht and Schindler, 1963)

Metal hydroxide	$\log K_{SP}$	Metal sulphide	$\log K_{SP}$
$Ca(OH)_2$	-5.4	$MnS$	-12.55
$Mg(OH)_2$	-9.2	$FeS$	-17.31
$Mn(OH)_2$	-12.8	$NiS$	-20.55
$\beta\text{-Cd(OH)}_2$	-13.7	$CoS$	-21.64
$Fe(OH)_2$	-14.0	$ZnS$	-24.05
$Ni(OH)_2$	-14.7	$CdS$	-26.15
$Co(OH)_2$	-14.8	$PbS$	-27.03
$Zn(OH)_2$	-15.6	$CuS$	-37.05
$Cu(OH)_2$	-18.8	$Cu_2S$	-47.70
$\alpha\text{-Be(OH)}_2$	-21.1	$Ag_2S$	-49.10
$\alpha\text{-Al(OH)}_3$	-33.8	$HgS$	-51.89
$Fe(OH)_3$	-38.7	$Co_2S_3$	-125.90

\*Solubility product  $K_{SP}$  is the product of ionic concentrations which are in equilibrium with the precipitate.

a pH value of 7 or higher. If such a precipitation does take place, then sufficient metallic ions would not be available for hydrogen reduction. The situation can be rectified by forming complex ions of Ni and Co which can resist hydrolysis. Thus, if ammonia is added to a solution containing Ni and Co ions, then, not only does the solution become alkaline, with a high pH value (a condition favourable to reduction) but the metal ion may also form a series of stable soluble complex ammines. In the case of  $Ni^{2+}$ , several sequential reactions take place. For example,



and so on. The final composition of the nickel complex ion is  $Ni(NH_3)_6^{2+}$ , the maximum coordination number of  $Ni^{2+}$  being 6. The complex ions are stable and prevent precipitation of the hydroxide. An increased stability of the complexes, however, also implies that gaseous reduction can take place only at a potential higher than that theoretically required for the reduction of simple  $Ni^{2+}$  ions. It is, therefore, necessary to increase the pH accordingly. In such a situation, there would be two opposing factors: increased amounts of  $NH_3$  ensure a higher alkalinity, which would tend to make reduction easier and increased amounts of  $NH_3$  produce higher ammines having greater stability, which would tend to make reduction more difficult.

The most favourable condition for reduction, as demonstrated by thermodynamic calculations as well as experiments, is achieved at an  $\text{NH}_3/\text{Ni}^{2+}$  ratio of approximately 2.2. At this ratio value, the difference between the hydrogen potential and the metal potential (see Fig. 4.20) has the maximum value. The reaction, therefore, achieves the maximum driving force. A similar situation exists for a solution containing cobalt ions.

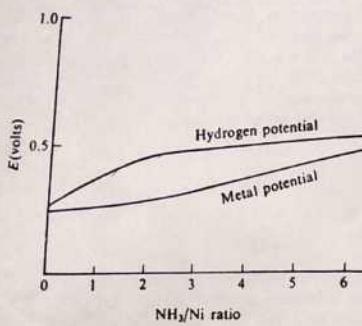


Fig. 4.20 Variation of Potential with  $\text{NH}_3/\text{Ni}^{2+}$  Ratio.

It should be noted that at any particular  $\text{NH}_3/\text{Ni}^{2+}$  ratio, various orders of complex ions exist simultaneously. As the ratio ( $n$ ) of the ammonia to nickel (in all forms) increases, intermediate complex ions are formed. Their concentration gradually increases and then decreases as the higher ammines are formed. This process is shown in Fig. 4.21.

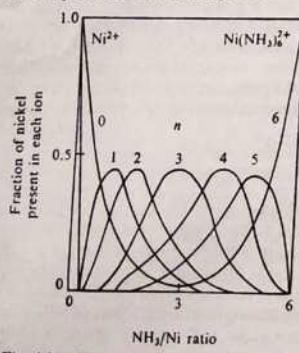


Fig. 4.21 Formation of Nickel Ammines.

The potential required for the reduction of the individual complex ions can be calculated from the data for the complex formation reactions. The reduction potential values required for Ni and Co are now tabulated:

$n$	0	1	2	3	4	5	6	
Ni	$-E(V)$	0.241	0.324	0.390	0.441	0.477	0.499	0.500
Co	$-E(V)$	0.267	0.329	0.378	0.409	0.431	0.436	0.418

If the solution is not sufficiently alkaline to have all the  $\text{Ni}^{2+}$  ions in the  $\text{Ni}(\text{NH}_3)_6^{2+}$  form, then several complexes coexist, the potential for each complex depending on the concentration. The aforementioned reduction potential values have been calculated by using the value of  $E$  for each complex and for the composition of the solution. It may be noted that the potential values are the lowest for any ammonia/nickel ratio.

The foregoing discussion on nickel reduction is more or less valid for cobalt too. For instance, ammine formation is necessary for the gaseous precipitation of ions of Co and Ni. Similar complexes in the case of other metal cations have yet to find practical application.

It is interesting to note that in the case of metals such as tin, the problem of hydroxide precipitation cannot be tackled by complexing. In the electrochemical series, tin lies below cobalt and nickel, and, theoretically, should be obtained at a lower pH value. However, tin tends to precipitate as either hydroxide or oxide at a rather low pH value, i.e., much below the pH required for the reduction of  $\text{Sn}^{2+}$  ions. There are very few complexing reagents which can form a cationic complex with tin. Some reagents can form anionic complexes (i.e., negatively charged) which obviously cannot be reduced by hydrogen. In the case of metals such as tin, hydrogen reduction cannot precipitate the metal from the solution.

#### 4.21 KINETIC ASPECTS OF GASEOUS REDUCTION

A gaseous reduction reaction involves two distinct kinetic steps:

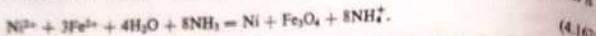
- (1) The nucleation of a metal in a clear solution or on a solid substrate. (The former is known as homogeneous nucleation and the latter as heterogeneous nucleation.)
- (2) The growth of metal particles by the deposition of metal on its own surface.

Homogeneous nucleation during gaseous reduction is difficult to achieve. For example, nickel and cobalt do not precipitate from an ammoniacal solution within a reasonable period unless seeding is resorted to. This is also true in the precipitation of some oxides, e.g., uranium and vanadium oxides from carbonate and sulphate solutions, respectively, and chromium oxide from dichromate solutions. There are some exceptions. For example, copper, silver, mercury, and some platinum metals can be precipitated from their clear solutions by hydrogen reduction.

The difficulty associated with homogeneous nucleation during hydrogen reduction is attributed to the inhibition of the hydrogenation reaction in the absence of a solid phase. A solid surface often absorbs and activates hydrogen. Consequently, immediate nucleation can be achieved by adding substances such as metal powder, colloidal graphite, red phosphorus, and sulphides. Nucleation can be further increased by adding some organic compounds to act as surface-active reagents. For example, the addition of anthraquinone to a solution containing

$\text{Ni}^{2+}$  ions can activate even insulating surfaces such as oxides, refractories, glass, plastic, and textiles. Consequently, nickel can be plated on these surfaces by hydrogen reduction.

The addition of ferrous sulphate helps the nucleation of nickel and cobalt. This phenomenon has been explained as follows. Iron oxide initially precipitates as  $\text{Fe(OH)}_2$  or  $\text{Fe}_3\text{O}_4$  and the resulting solid acts as a heterogeneous nucleation catalyst. It has also been observed that as a reducing agent,  $\text{Fe}^{2+}$  is considered stronger than hydrogen. The initial nucleation powder is generated by the  $\text{Fe}^{2+}$  reduction reaction. This powder acts as the seed for further reduction. It should be noted that the reaction involving  $\text{Fe}^{2+}$  that is capable of chemically reducing nickel is



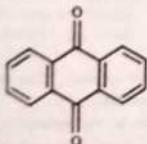
In reaction (4.167),  $\text{Fe}_3\text{O}_4$  is simultaneously produced along with the other products. Thus, in both instances, iron oxide is homogeneously nucleated and nickel is heterogeneously nucleated on the iron oxide.

It should be noted that all the aforementioned addition agents are employed mainly to eliminate the induction time for precipitation. In the absence of an additive, the quantum of reaction at the beginning may be negligible for an hour or so. However, after a sufficiently long period, nucleation and growth are triggered off. The rate at this point is identical with that which can be achieved right at the beginning by using an additive.

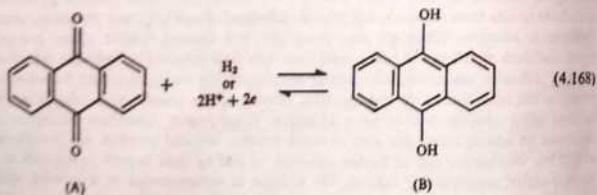
#### EFFECT OF ANTHRAQUINONE ADDITION

Anthraquinone is extremely useful in the reduction of a nickel solution by hydrogen, whereas it has no effect on cobalt reduction by the same gas. Anthraquinone accelerates the deposition of nickel on a variety of surfaces, eliminates surface irregularities, and controls particle shape and size.

The structure of anthraquinone is



The doubly bonded oxygens react with hydrogen on a catalytic surface. The reaction is



Thus, a surface site at which an anthraquinone molecule is immediately adsorbed becomes a site where hydrogen molecules can react to form structure (B) that is shown in eq. (4.168). This new structure promotes the electrochemical reduction of the metal ion by making electrons available to the metal ion and simultaneously discharging  $\text{H}^+$  ions and transforming itself to structure (A). The regenerated anthraquinone molecule activates one fresh molecule of hydrogen. Highly active surfaces such as reactive nickel powder seed and platinum are not significantly catalyzed by anthraquinone because the bare metal itself readily activates hydrogen by adsorption.

#### RATE EQUATION FOR REACTION KINETICS

The thermodynamic data presented in Fig. 4.19, though sufficient for indicating the feasibility of reducing a metal by hydrogen, do not give any idea regarding the rate or the mechanism of reduction. To achieve a fast reaction rate, it is necessary to work at elevated temperatures. However, there are practical limitations to this because the vapour pressure of the system increases, necessitating high operating pressures. Moreover, an increase in the temperature can accelerate undesirable side reactions and can drive the complexing agent into the vapour phase, causing the precipitation of the metal hydroxides.

Quite a few reduction reactions take place at a catalytically active solid surface. Hence, their rate can be increased by increasing the surface area of the catalyst. Alternatively, catalytic activity of the surface available can be increased by adding surface-active agents. The rate of reduction is also enhanced by agitation because reduction takes place in a heterogeneous system involving solids, liquids, and gases. A high level of agitation not only keeps the solids in suspension but also ensures that the mass transfer of hydrogen does not become the rate-controlling factor.

Equations (2.112)–(2.115) can be used to derive the rate of the reaction



We now discuss some systems of the type represented by reaction (4.169).

#### Precipitation of Copper

From Fig. 4.19, it is evident that metals such as copper and nickel can be precipitated at 1 atm by hydrogen from aqueous solutions of their salts. However, the reactions are found to be extremely slow. High activation energies exist for these reactions in which molecular hydrogen is one of the reactants. This is due to the very stable electron configuration of molecular hydrogen, leading to a large dissociation energy of about 103 kcal/mole. Metals such as nickel, cobalt, and iron and the oxides of chromium and zinc catalyze such reactions by lowering the activation energies. In the case of copper, the cupric ion in solution is believed to act as a homogeneous hydrogenation catalyst, forming intermediary substances as given by (Halpern *et al.*, 1956)



The  $\text{CuH}^+$  ion then reduces a cupric ion, that is,



The cuprous ion formed rapidly disproportionates to give the metal according to the reaction



By applying the steady-state concepts to this sequence of reactions, i.e., reactions (4.170)–(4.172), we get the rate as

$$\text{rate} = -\frac{d[\text{H}_2]}{dt} = \frac{k_r [\text{Cu}^{2+}][\text{H}_2]}{[\text{Cu}^{2+}] + \frac{k_r}{k_b} [\text{H}^+]}. \quad (4.173)$$

For an alkaline solution with a sufficiently low concentration of hydrogen ions, eq. (4.173) reduces to the simple form

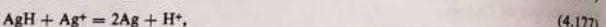
$$-\frac{d[\text{H}_2]}{dt} = k_r [\text{Cu}^{2+}][\text{H}_2]. \quad (4.174)$$

The reduction of copper salts in an alkaline medium is too complex for detailed kinetic analysis because various insoluble species may be precipitated. Moreover, the process is of little practical interest because copper leach liquors are usually acidic.

Reaction (4.172) shows the relative instability of cuprous ions in water. In the presence of a sufficiently high concentration of ammonia, which stabilizes the cuprous ions by forming complexes, the disproportionation reaction may not occur. From such ammoniacal solutions, copper will not be precipitated by hydrogen. Therefore, ammoniacal solutions containing cuprous ammine should be treated by acid to precipitate copper.

#### Precipitation of Silver

During the precipitation of silver from aqueous solutions, several bimolecular or trimolecular sequential reactions may take place, some of which involve short-lived intermediaries. The relevant reactions are



Reactions (4.175) and (4.176) essentially determine the rate. Accordingly, the reaction for silver is either second order or third order, i.e.,

$$-\frac{d}{dt} [\text{Ag}^+] = k_2 [\text{Ag}^+] p_{\text{H}_2} \quad (4.179)$$

or

$$-\frac{d}{dt} [\text{Ag}^+] = k_3 [\text{Ag}^+]^2 p_{\text{H}_2}, \quad (4.180)$$

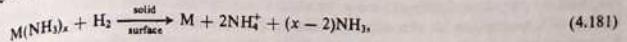
where  $k_2$  and  $k_3$  are the rate constants for the second- and third-order reactions, respectively.

Equation (4.179) is valid when the silver concentration is low and the temperature high and eq. (4.180) is valid when the concentration is high and the temperature low.

#### Precipitation of Nickel and Cobalt

As already noted (in Section 4.20), nickel and cobalt, in ammoniacal solutions, readily reduce

only at a solid surface. The reactions are strictly heterogeneous. The overall reduction reaction may be written as



where  $x$  is maintained between 1.9 and 2.2 for the reasons mentioned in Section 4.20. At a constant hydrogen pressure, the rate of reduction remains independent of the metal concentration up to as high as 85 per cent reduction. The reaction rate can, therefore, be considered constant. This rate is of the first order with respect to both the hydrogen pressure and the nickel seed surface area, and is given by

$$\text{rate} = -\frac{d[\text{Ni}^{2+}]}{dt} = -\frac{d[\text{H}_2]}{dt} = k A p_{\text{H}_2}, \quad (4.182)$$

where  $A$  is the nickel surface area. It is assumed that the surface of the Ni powder is covered by a strongly adsorbed layer of nickel ions (or nickel ammine ions) and that these ions are so strongly adsorbed that the number of adsorbed ions begins to decrease appreciably only when more than about 85 per cent of the metal ions originally present in the solution has been reduced. Obviously, in such a situation, the reaction rate would be governed by the rate at which hydrogen molecules are adsorbed. This rate would vary directly with both the surface area available for adsorption and the gas pressure. Catalysts such as anthraquinone are added to increase the number of active sites at which the adsorbed nickel (ammine) ion would react with the adsorbed hydrogen molecule. Although the rate equation or the activation energy would remain unaltered, the actual reaction rate would increase.

#### 4.22 RECOVERY OF METAL VALUES FROM LEACH LIQUOR BY ION EXCHANGE, SOLVENT EXTRACTION, AND ELECTROLYSIS

In an ion exchange process, when the leach liquor is percolated through a column containing a resin, the metal ions are preferentially adsorbed at active sites on the resin. The adsorbed ions are subsequently removed by elution and the metal values recovered.

In solvent extraction, the metal ions in the aqueous leach liquor are complexed by an organic reagent. The complex is subsequently dissolved in an organic solvent (e.g., paraffin) which is insoluble in water and the metal values are recovered from the organic solvent.

The principles of ion exchange and solvent extraction are discussed in greater detail in Chapter 5. We now discuss the electrometallurgical extraction of metals.

#### 4.23 ELECTROMETALLURGY

Electrometallurgy includes all metallurgical processes which utilize electricity and electrical effects. Thus, a large number of operations can be considered electrometallurgical in nature. A classification scheme of various electrometallurgical processes is shown in Fig. 4.22. It should be obvious that not all the processes given in Fig. 4.22 fall under the scope of process metallurgy. Only a limited number of processes that use electricity supplied from external sources are considered here, namely, *electrowinning*, *electrorefining*, and *electrodeposition*.

Electrowinning refers to a process that produces a metal by the electrolysis of an aqueous solution or a fused salt; electrorefining is a refining process based on electrolytic phenomena; and electrodeposition refers to the technique of depositing one metal on another at the cathode.

Nowadays some metals are produced exclusively by electrolysis, whereas in the case of some others, a substantial percentage of the total production is by electrowinning. The approximate percentages (by electrolysis) of some important metals are: aluminum 100; sodium 100; lithium 100; magnesium 80; chromium 70; cobalt 50; cadmium 50; zinc 10; copper 10; nickel 10; Electrolysis can be used, among other methods, to obtain other metals, for example, Be, Ta, Nb, rare earths, Ga, Ti, Tl, In, Zr, Hf, and B.

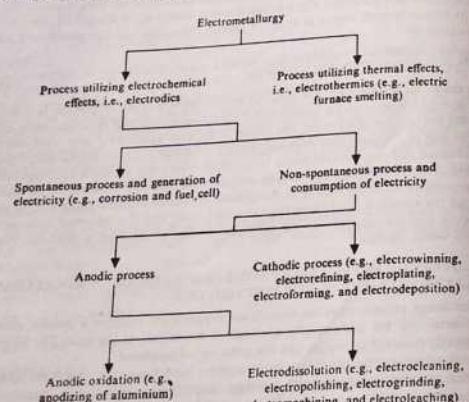


Fig. 4.22 Classification of Electrometallurgical Processes.

#### ELECTROLYTIC DECOMPOSITION

Electrolytic decomposition is used in both the extraction and the refining of metals. In both processes, the electrolyte is an aqueous solution or a mixture of fused salts. Of late, some organic media containing dissolved organometallic salts have also been electrolytically decomposed in the laboratory.

In an extraction process, the anode is either an insoluble conductor or an electrical conductor such as copper matte or nickel matte, while, in electrorefining, it is the impure metal itself. The electrolyte in both cases is a solution with a sufficiently high electrical conductivity and a reasonably high metal ion concentration. The cathode could be the pure metal built up as a pure 'starting sheet' or, sometimes, it could be built up on a blank of another metal.

In electrolytic operations, the selection of a proper electrolyte is the most important requirement. The basic conditions that an electrolyte must satisfy are:

(1) It must have a sufficiently high ionic conductivity, and conduction must be entirely due to ions. (Any electronic contribution to the total conduction would short-circuit the electrodes and lead to a wastage of electricity.)

(2) It must be chemically inert towards the electrodes, the container material, and the electrolysis products.

(3) It must be stable at the temperature of operation.

(4) When a solution containing the metal to be extracted is being used, then it must be chemically more stable than the solute. (In other words, the metal compound should dissociate at a voltage appreciably lower than that required for the dissociation of the solvent.)

Common metals such as Cu, Zn, Sn, Au, and Mn can be produced by aqueous electrolysis, whereas reactive metals such as Ti, Zr, Th, Na, K, Mg, and Al cannot. To obtain reactive metals, their fused salts must be electrolyzed at a high temperature. In recent years, interesting developments have been reported in the electrolysis of nonaqueous inorganic and organic systems, often below 100°C. Some of these are considered later in this chapter.

#### 4.24 STRUCTURE OF SOLVENT MEDIA

The electrolytic phenomena depend on the structure of the solvent media. Therefore, we first briefly discuss the salient features of the structure of aqueous and nonaqueous media.

##### AQUEOUS SOLUTIONS

We know that valence compounds such as alkali chlorides readily dissociate in water to give rise to ionic solutions. This is commonly attributed to the high dielectric constant of water.

Water is made up of associated molecules because of the polar nature of its molecule. In 'association', the asymmetric molecules cling to each other by means of hydrogen bonds, as shown in Fig. 4.23. This figure shows the hydrogen bond between a slightly negatively charged oxygen atom of one molecule and a slightly positively charged hydrogen atom of another. The

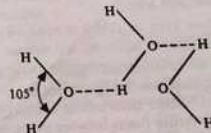


Fig. 4.23 Associated Water Molecules.

result of such association is a liquid having a high dielectric constant which helps cause the breakdown of the crystal lattice of ionic compounds. In water, the unlike charges in the dissolved compounds are no longer strongly bound because the attractive force between them is inversely proportional to the dielectric constant of the medium.

Apart from its ability to break up ionic lattices, water also forms hydrated complexes of the

metal ions. A stable complex, shown in Fig. 4.24, is formed when water molecules are linked with the metal ion through coordinate bonds.

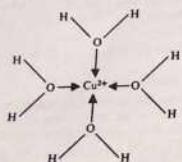
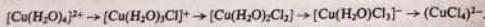


Fig. 4.24 Hydrated Cupric Ion  $[Cu(H_2O)_4]^{2+}$  (arrows represent coordinate bonds formed when each oxygen atom donates an electron pair to cupric ion and stabilizes configuration).

In general, most aqueous solutions of metal compounds contain complexed metal ions. Complexes may be formed by  $NH_3$ ,  $Cl^-$ ,  $Cu^{2+}$ ,  $OH^-$ , and  $P_2O_5^{4-}$ . For example, in an ammoniacal solution, nickel ions form a series of ammines written as  $Ni(NH_3)_x^{2+}$ , where  $x$  varies from one to six. If  $HCl$  is added to an aqueous solution of cupric sulphate, the solvated (in water) cupric ion progressively loses water molecules to finally form a complex containing only  $Cl^-$ . The step-wise change may be expressed as



Any analysis of the electrolytic phenomena in aqueous solutions must take into account the existence and stability of these complex ions.

#### MOLTEN SALT ELECTROLYTES

Molten salts are ionic melts, some of which are liquids at temperatures up to  $3000^\circ C$  at 1 atm. They form the largest class of nonaqueous inorganic solvents. An empirical classification of inorganic melts is shown in Fig. 4.25. Ionic melts consist of charged particles, namely, anions and cations, in intimate contact. The attractive forces between particles having opposite charges and the repulsive forces between similarly charged particles are very strong. Therefore, a cation has anions as its closest neighbours and vice versa. To determine energy change required to form this arrangement of the ions, we estimate the energy needed to break up the arrangement of ions. For a compound such as sodium chloride, the transfer of a cation from a position where it is surrounded by anions to a position where it is surrounded by cations requires an energy of the magnitude of 200 kcal/mole, as indicated by electrostatic considerations. This value is very large compared with the heat of fusion, which is about 7 kcal/mole and with the heat of vaporization, which is about 41 kcal/mole. This is why we assume that the arrangement of the ions in an ionized melt is

such that the ions are surrounded by other ions having an opposite charge, and, over a short range, we can identify two main positions, one for cations and the other for anions.

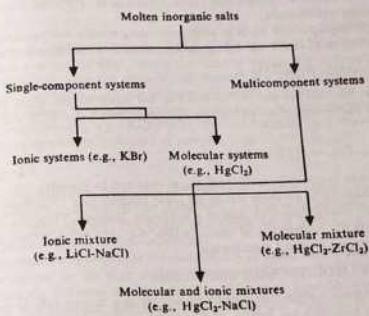


Fig. 4.25 Molten Salt Systems Classified in Order of Increasing Phase Rule Complexity.

#### TEMKIN'S MODEL

In the earliest models of ionic melts, a completely random mixing of anions and cations was assumed, irrespective of the nature of the charge of the ion. Thus, it was theoretically possible to have a segregation of charges on a macroscopic scale, one part of the solution being negatively charged and another positively charged.

According to the model given by Temkin (1945), in pure molten salts and in salt mixtures, the ions arrange themselves in a manner similar to the arrangement in a crystal lattice, i.e., each cation is always surrounded by anions and vice versa. Accordingly, the structure can be represented by two interlocked sublattices, one for cations and the other for anions. The ionic liquid exhibits a short-range order over a few ionic diameters, especially at a temperature close to the melting point of the salt.

According to Temkin's model, the activity of a salt  $M_nZ_x$  dissolved in an ideal fused salt mixture is given by

$$a_{M_nZ_x} = (X_M)^m (X_Z)^x \quad (4.183)$$

where  $X_M$  and  $X_Z$  are the ionic fractions of cations and anions, respectively. It should be noted that

$$X_M = \frac{n_M}{\sum n_M}, \quad X_Z = \frac{n_Z}{\sum n_Z}$$

where  $n$  is the number of moles. This definition of ionic activity implies that the cations and anions present in the solution are randomly distributed within their respective sublattices, regardless of the number of electrical charges they carry. Equation (4.183) is not arbitrary, but can be derived using entropy calculations.

Temkin's definition of activity leads to some interesting results. For example, consider a one mole : one mole solution of NaCl and KBr, and assume that the solution is ideal. By definition,

$$a_{\text{NaCl}} = X_{\text{Na}^+} X_{\text{Cl}^-} = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right) = \frac{1}{4}. \quad (4.184)$$

From eq. (4.184) we see that the activity of NaCl is not equal to the mole fraction, although ideality is assumed. However, for an equimolar mixture of NaCl and KCl, the activity of NaCl is given by

$$a_{\text{NaCl}} = X_{\text{Na}^+} X_{\text{Cl}^-} = \left(\frac{1}{2}\right)\left(1\right) = \frac{1}{2}. \quad (4.185)$$

In this case, the activity is equal to mole fraction, as required by Raoult's law.

Statistically, the activity of an ionic salt in an ionic mixture can be defined as the probability of finding the right configuration of ions at a particular location. Thus, the activity of sodium chloride simply implies the probability of finding a  $(\text{Na}^+ \cdot \text{Cl}^-)$  ion pair together. The term activity, therefore, has only a vague physical significance.

#### REGULAR TYPES OF MOLTEN SALT SOLUTIONS

The Temkin model presents a simplified picture of activity in a molten salt. In general, there is a change in energy when two salts are mixed. As explained in Section 2.12, a solution formed by a change in energy can be termed 'regular' if the distribution of the ions is ideal, as in Temkin's model. The activities in a mixture of salts, say, AX and BY can be calculated from Flood's equation (see Flood *et al.*, 1953) given by

$$RT \ln \gamma_{AX} = X_B X_Y \Delta G^\circ, \quad (4.186)$$

where  $X_B$  and  $X_Y$  are the ionic fractions and  $\Delta G^\circ$  is the free energy for the reaction



The assumption that both cations and anions are randomly distributed in their respective lattice sites cannot be true unless the energy change for reaction (4.187) is small. When this energy change becomes appreciably large, a quasi-chemical distribution of the ions is to be expected, and eq. (4.186) has to be modified.

#### CONDUCTANCE OF MOLTEN SALTS

The ionic nature of most molten salts and salt mixtures makes them relatively good conductors of electricity. The electrical conductivity depends on the transport of the mobile ions whose mobility is governed by ionic size, ionic interaction, and temperature.

In general, the conductivity-temperature relationship is given by

$$\kappa = A \exp [-E/(RT)], \quad (4.188)$$

where  $\kappa$  is the conductivity,  $E$  the activation energy of conduction, and  $A$  a constant.

A salt with an ionic lattice, e.g., alkali halide, forms a melt with a high conductivity, the

conductivity increasing as the size of the cation or anion decreases. An exception is the fluoride of Na or K. For instance, it is believed that NaF forms a 'dimer', namely,  $\text{Na}_2\text{F}_2$ , which dissociates according to the reaction



In this case, the cation is bulky, and sharply decreases the conductivity.

When a salt has a molecular lattice where the elements of the salt structure are not ions but molecules, the fused salt does not conduct any current (e.g.,  $\text{HgCl}_2$ ). The conductivity of salts such as  $\text{HgCl}_2$ ,  $\text{InCl}_3$ , and  $\text{InBr}_3$  decreases as the temperature increases. This is believed to be due to a decrease in the degree of their electrolytic dissociation. In salt systems having a marked tendency to form compounds, e.g.,  $\text{KCl}-\text{PbCl}_2$ , the conductivity may show marked decrease at certain compositions due to the formation of complex ions.

#### ORGANIC MEDIA

Relatively recent investigations have indicated that some alkali metals can be obtained from simple salts dissolved in various organic solvents. However, most of these investigations appear to be of theoretical interest only; the exceptions which seem promising are those employing organometallic aluminium and boron compounds.

It has already been mentioned that the dissociation of metal compounds in aqueous solutions is commonly attributed to the high dielectric constant of water. This concept can, however, be misleading because the dielectric constant is not a satisfactory general criterion for the selection of an electrolyte. For example, whereas diethyl ether, whose dielectric constant is 4.5, is a good solvent in several nonaqueous plating processes, anhydrous HCN with a high dielectric constant of 95 is not. The conductivity of a pure solvent is not an index of the value of a solvent. For example, it is possible to conduct electrodeposition in ether which has a conductivity of only  $4 \times 10^{-13}$  ohm cm $^{-1}$ , i.e., about a million times lesser than that of water. It is also interesting to note that the ionic character of a solute alone is not a suitable criterion in electrolysis. Several organic compounds form conducting solutions in ammonia but not in water. Further, some compounds such as diethyl beryllium, beryllium borohydride, and diethyl zinc do not conduct in a pure state but conduct in an ether solution. It can be concluded that the ionic nature of a solution is a result of the interactions between the solute and the solvent, neither of which needs to be very ionic in character.

The predominant forces of interaction existing between the molecules of a solute and those of a solvent are a result of coordinate bond formation between the metal and the complex ionic species. When a metal salt  $\text{MX}_n$  dissolves in a solvent S, an addition compound is initially formed as the first solute species according to the reaction



The subsequent reactions depend on the interaction between the metal and the solvent. If the coordination number of the metal in the addition compound is retained in the products too, the reaction that ensues is



If the coordination number of the metal is variable, then a loose coordination compound of the type  $\text{MS}_i \text{X}_{(n-i)}$ , in which  $(i + j)$  is less than  $(p + n)$ , may be formed. Examples of a loose coordinate

nation compound are a metal alkyl ( $\text{NaCH}_3$ ) dissolved in diethyl ether and aluminium chloride dissolved in aromatic hydrocarbons.

#### 4.25 ELECTROLYSIS OF AQUEOUS SOLUTIONS

The fact that water can dissolve relatively high concentrations of salt renders it suitable for electrolysis. It may be noted that aqueous solutions have a high conductivity at ambient temperatures, especially when acidic.

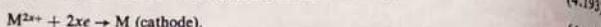
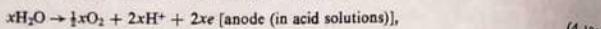
The stages involved in the overall extraction process leading to the electrowinning of metals from aqueous solutions are:

(1) Leaching of a roasted ore (e.g., an oxide) to a form soluble in an acid



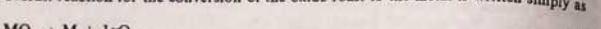
(2) Purification and concentration of the leaching liquor.

(3) Anode and cathode reactions during electrolysis



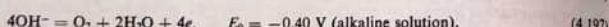
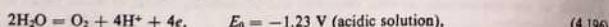
(4) Recirculation of the acid liberated at the anode for leaching purposes.

The overall reaction for the conversion of the oxide roast to the metal is written simply as



Reaction (4.195) indicates that there should be no overall consumption of water or acid when the anode product is oxygen. Sulphuric acid favours the evolution of oxygen, while in a hydrochloric acid solution, chlorine would probably be evolved.

During electrolysis, the reactions take place at two distinct regions, namely, at the cathode and at the anode. At the cathode, the metal ion is discharged and the metal deposited. At the anode, the reactions depend on the nature of the electrolyte. For example, the reactions in acidic and alkaline aqueous solutions, respectively, are



As just stated, the anode reaction favours the evolution of oxygen.

The decomposition potential is the difference between the reversible potentials for the anode and cathode reactions. The operating voltage of a cell should be greater than this difference because it must also include additional terms such as activation and concentration overpotentials at the electrodes, the voltage loss due to the resistance offered by the electrolyte and due to resistance to the circuit and contacts. Generally, the operating voltage varies between 2 and 5 volts and the current efficiency between 80 and 90 per cent. In a cell, when the anode is unstable, the cathode is either a Pb-Sb-Ag alloy or graphite. The metal is deposited on a variety of cathode surfaces (see Table 4.4). The purity of the metal is usually higher than 99.95 per cent.

During electrowinning, an impure anode is corroded and the purified metal is deposited at the cathode. The theoretical voltage for a reversible condition is, of course, zero. Under normal

Table 4.4 Typical Data for Electrowinning from Aqueous Systems (after Steele, 1971)

Metal	Purity (%)	Current efficiency (%)	Current density (mA/cm <sup>2</sup> )	Cell voltage (V)	Temperature (°C)	Concentration in electrolyte (gm/l)	Power consumption (kWh/kg)	Anode, cathode
Cu	99.5	80-90	10	2.2	30-35	Cu: 20-70 Free acid: 20-70	2.2	Anode: Pb-Sb-Ag
Co	93-99.9	75-90	30-40	5.0	50-70	Co: 15-50		Anode: Pb-Sb-Ag Cathode: mild steel, stainless steel
Zn	99.9	90	30	3.5	35	Zn: 100-220 H <sub>2</sub> SO <sub>4</sub> : 100-200	3.3	Anode: Pb-Ag Cathode: Al
Cd	90	8	2.5-2.7	20-35	Cd: 100	H <sub>2</sub> SO <sub>4</sub> : 100	1.5	Anode: Pb-Ag Cathode: Al
Cr	99.8	45	70	4.2	50	Cr <sup>III</sup> : 150 Fe: 0.2 NH <sub>3</sub> : 43 H <sub>2</sub> SO <sub>4</sub> : 3	18.0	Anode: Pb-Ag Cathode: stainless steel
Mn	40-60	5.1				Mn (as MnSO <sub>4</sub> ): 30-40 (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> : 125-150 SO <sub>4</sub> : 0.10 Glue: 0.01	9.0	Anode: Pb-Ag Cathode: stainless steel, Ti

operating conditions, only a small voltage is required, mainly to overcome the resistance of the electrolyte. Consequently, the power consumption is low. The energy required for electrorefining is usually about one-fifth of that required for electrowinning.

In Chapter 2, it has been shown that during the actual electrolytic process, the potential at an electrode deviates from equilibrium due to the effect of the activation overpotential and the concentration overpotential. In fact, in practice, no deposition or solution process can proceed at the reversible electrode potential of the system. Hydrogen evolution on a platinized platinum electrode, however, comes close to equilibrium conditions.

The electrolytic behaviour of metals is mainly of two types. Normal metals, when immersed in their salt solutions, rapidly establish a reversible potential. Since the activation overpotential is low, the displacement behaviour exhibits a good correlation with the electrochemical series of standard electrode potentials. Examples of this type are, Cu, Zn, Ga, Cd, Sn, Au, and Bi. These metals are deposited with a high current efficiency. Some other metals, for example, the transition metals, are deposited with a high activation overpotential and a low current efficiency.

The hydrogen overvoltage decreases as the temperature and the current density increase. The practical effect of hydrogen overvoltage, as already pointed out, is to make possible the electrowinning of metals such as zinc which, because of the hydrogen overpotential, do not displace hydrogen from an acid solution as long as the current flow is maintained.

Some typical operational data for the electrowinning and electrorefining of a few metals in aqueous solutions are given in Tables 4.4 and 4.5.

#### ANODIC DISSOLUTION OF METAL SULPHIDES

The anodic dissolution of metal sulphides in an aqueous medium has received considerable attention recently. The reaction at a sulphide anode in an aqueous electrolyte is



Sulphide electrodes can be made from mattes. Commercial plants based on the anodic dissolution of nickel sulphide are presently being operated successfully.

#### 4.26 ELECTROLYSIS OF FUSED SALTS

The emf series—in which the electrode potentials are arranged with respect to the potential of the standard hydrogen electrode—indicates that the metals placed above hydrogen should not normally be amenable to electrolytic deposition. Nevertheless, due to polarization phenomena, some metals, although placed above hydrogen, become stable in aqueous solutions during the passage of a current. However, the polarization phenomena can be exploited only in the case of metals up to manganese. Metals placed above manganese are too reactive to be produced from aqueous solutions, and are produced by electrolyzing water-free fused salt mixtures.

Theoretically, any metal can be obtained by the direct electrolysis of one of its salts, for example, a pure halide. In practice, however, it is often advantageous to dissolve a compound such as a halide in a mixture of more stable halides such as sodium chloride and potassium chloride. This procedure improves the conductivity of the melt, lowers the melting point of the medium, and reduces the possibility of dissolution of the metal in the salt.

Operations in high-temperature media such as molten salts have some distinct advantages, for example, a reactive metal may be readily obtained in the absence of hydrogen ions. The conditions are favourable for attaining a more complete heterogeneous equilibrium because all

Table 4.5 Typical Data for Electrorefining from Aqueous Systems (after Steele, 1971)

	Copper	Nickel	Cobalt	Lead	Tin	Silver	Gold
Electrolyte concentration (gm/l)	Cu: 40-50 H <sub>2</sub> SO <sub>4</sub> : 175-225 Cl: 55-60 H <sub>3</sub> BO <sub>3</sub> : 10-20 Na: 35	Ni: 50-60 SO <sub>4</sub> : 90-95 Cl: 10 H <sub>3</sub> BO <sub>3</sub> : 10-20 Na: 40	Co: 50-60 SO <sub>4</sub> : 150-200 Cl: 10 H <sub>3</sub> BO <sub>3</sub> : 10-20 Na: 40	Pb: 60-90 H <sub>2</sub> SiF <sub>6</sub> : 50-100 H <sub>2</sub> SO <sub>4</sub> : 75 H <sub>3</sub> BO <sub>3</sub> : 10-20	Sn: 30-40 HNO <sub>3</sub> : 0-10 HCl: 100	Ag: 30-150 HNO <sub>3</sub> : 0-10 HCl: 100	Au: 100
Slime impurity	Ag, Au, Ni, Sb, Pb	Ag, Au Pt metals		Bi, Ag, Sn, Sb	Pb, Sb	Au	Ag
Major electrolyte impurity	Ni, As, Fe	Cu, Co	Ni, Cu		Cu	Pt metals	
Current density (A/m <sup>2</sup> )	100-200	150-200	150-200	150-200	100	200-500	600-1500
Cell	Simple	Diaphragm	Diaphragm	Diaphragm	Simple	Diaphragm	Simple
Temperature (°C)	60	60	60	30-40	20-30	25-45	60
Cell voltage (V)	0.15-0.3	1.5-3	1.5-3.0	0.3-0.6	0.3-0.6	1.5-5.0	0.5-2.0

the reactions are accelerated. The metal produced, if molten, may be easily removed. Overvoltages on molten metals are often small enough to allow high current densities and, therefore, greater throughput. Further, at high temperatures, diffusion rates are high and, therefore, during some electrorefining processes, impurities can be transferred from the anode to the cathode so as to purify the metal. In such processes, only very small amounts of metal impurities need to be transferred electrochemically.

The use of high temperatures, however, has some disadvantages too. The efficiency is lowered due to the increased possibility of side reactions taking place, for example, between the products of electrolysis and the electrodes. In most molten salt electrolytic processes, the anode material is graphite, which leads to formation of CO and CO<sub>2</sub>, unless inert gases are used. Sometimes, CO may diffuse through the melt or the gas phase to reach the metal and seriously contaminate it, affecting its mechanical properties.

In most fused salt electrolytic processes, several side reactions may take place apart from the desired decomposition reaction. These reactions and other diverse factors are responsible for an apparent deviation from Faraday's laws. Consequently, the current efficiency is far below the optimum value of 100 per cent. Theoretically calculated current consumption values hold good only in very simple systems, such as in silver halide electrolysis using inert electrodes. In some cases, for example, during the electrolysis of CdCl<sub>2</sub> or BiCl<sub>3</sub>, the initial cathode current efficiency may even be zero, which means that, in the initial stages, no metal is deposited on the cathode. Further, the magnitude of current lost is very high in some systems, for example, in a Pb-PbCl<sub>2</sub> system. We now summarize the factors that lead to a lower current efficiency and state how these can be avoided.

(1) Mechanical losses (handling losses) of the substances formed at the electrodes. These losses can be minimized by using improved operational techniques.

(2) The evaporation of the metal from the cathode. This may take place during the electrolytic liberation of sodium from fused sodium chloride because the operating temperature would be close to the boiling point of the metal. The problem can be solved by dissolving the sodium chloride in a suitable medium to form a low melting mixture, thus lowering the operating temperature.

(3) Chemical side reactions. The unwanted side reactions can be controlled by choosing the proper electrolyte and using a lower operating temperature.

(4) The formation of lower valency compounds at the cathode. For example, in the electrolysis of SnCl<sub>4</sub>, in the initial stages, tin reacts with the electrolyte to form SnCl<sub>2</sub>, and the cathode current efficiency is zero. In most instances, the melt is soon saturated with the lower valency compounds, and after a while, the metal starts depositing on the cathode.

(5) The formation of higher valency compounds at the anode. This reduces to zero the anode current efficiency in the initial stages of electrolysis. For example, during the electrolysis of SnCl<sub>2</sub>, in the initial stages, the chlorine liberated at the anode reacts to produce SnCl<sub>4</sub>. However, after some time, the melt becomes saturated with SnCl<sub>4</sub>, and further reaction would cease.

(6) The dissolution of the metal in the fused salt. This drawback can be eliminated to a great extent by dissolving the metal salt in a more stable salt to form a relatively dilute solution. (For details, see Section 4.27.)

(7) The recombination of the electrolysis products with the original salt. (This problem assumes serious proportions in the production of reactive metals such as magnesium. During the

electrolysis of MgCl<sub>2</sub>, the liberated metal and gas should never be allowed to come in contact.) Recombination can be eliminated by the immediate and complete isolation of the electrolysis products by employing an electrolytic cell with a special design.

(8) Current losses due to the presence of moisture. This problem is not serious in the case of fluorides because they can be prepared and stored in a dry state without much difficulty. Most chlorides, however, are extremely hygroscopic, and precautions have to be taken to completely eliminate the moisture. To do so, chlorides are produced *in situ* in the electrolytic cell, by feeding the metal oxide slowly into the cell. The hot gases formed in the cell are used to eliminate all traces of moisture, and the chlorine evolved is used to chlorinate the oxide inside the cell.

#### SOLUBILITY OF METALS IN FUSED SALTS

We now consider the interaction of a metal with a fused salt to form the following solutions:

(1) A solution of a metal M in a salt M'X<sub>n</sub>, where M' is another metal which is less noble than M. In this case, there is no measurable reaction, and is not discussed here.

(2) A solution of a metal M in a salt M'X<sub>n</sub>, where M' is another metal which is more noble than M. Here, since MX<sub>n</sub> is more stable than M'X<sub>n</sub>, the reaction is nothing but a displacement reaction where M displaces M' from M'X<sub>n</sub> to form MX<sub>n</sub>.

(3) A solution of a metal M in its own salt MX<sub>n</sub>. In this case, since the solubility is very high, and thus of great significance in fused salt electrolysis, the dissolution of the metal in the electrolyte not only causes an apparent metal loss but the dissolved metal may also react, at the anode, with the halide. Such a back reaction would cause a further decrease in the current efficiency. Moreover, an excess of metal in solution could introduce electronic conduction in the melt.

We next consider the electrolysis of some systems where a metal shows measurable solubilities in their halides. The phase diagrams of systems having measurable solubilities, for example, Cd-CdCl<sub>2</sub> and Bi-BiCl<sub>3</sub> systems, are shown in Fig. 4.26a and Fig. 4.26b, respectively. In the phase diagram of Cd-CdCl<sub>2</sub>, the homogeneous liquid phase, which is a solution of Cd in fused CdCl<sub>2</sub>, is demarcated by AEb. The broken lines correspond to the separation of the liquid phase into two immiscible phases—one rich in CdCl<sub>2</sub> and the other rich in Cd. Suppose that electrolysis takes place at 600°C. Initially, the metal that is formed at the cathode continues to pass into solution (liquid phase L<sub>1</sub>) for a prolonged period of time. When a sufficient quantity of current is passed in order to liberate enough Cd so that the Cd content of the solution exceeds 25 mole per cent (point on line b), a second liquid phase (L<sub>2</sub>) appears, which consists primarily of cadmium (composition given by c). From this point onward, the amount of metal deposited at the cathode begins to continuously increase, and the electrolysis proceeds, as usual, with a measurable cathodic current efficiency.

In the electrolysis of BiCl<sub>3</sub>, the products formed can be explained in the light of the phase diagram, i.e., Fig. 4.26b. Chlorine is evolved at the anode, whereas no metal is formed at the cathode even on prolonged electrolysis. Bismuth forms the lower compound BiCl with BiCl<sub>3</sub>. At a temperature above the melting point of BiCl<sub>3</sub>, metallic bismuth added to BiCl<sub>3</sub> dissolves in it. When a specific concentration of bismuth in BiCl<sub>3</sub> is attained, BiCl begins to crystallize out, as shown by EF. Above 320°C, the separation of BiCl is no longer observed, instead, two immiscible liquid layers are formed: one a solution of BiCl<sub>3</sub> and BiCl and the other that of BiCl and Bi, as shown by the broken line abcde.

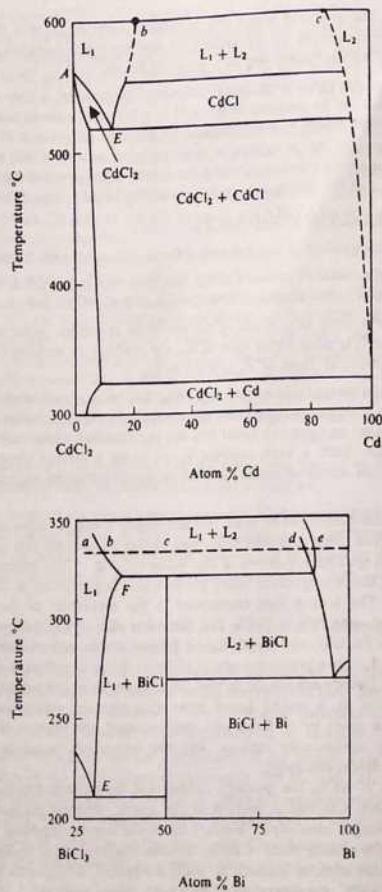
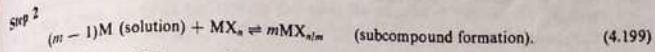
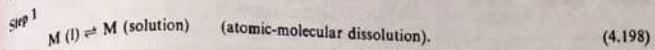


Fig. 4.26 Cd-CdCl<sub>2</sub> and Bi-BiCl<sub>3</sub> Binary Phase Diagrams Showing Metal Solubilities (after Delimarskii and Markov, 1961).

#### Mechanism of Metal Dissolution

It is believed that the dissolution of a metal in its own salt is a two-step process.



In reaction (4.199), M is a metal whose normal valency is n, m is the number of atoms of M, and X any halogen. Since monovalent alkali metals cannot have a subhalide, their solubilities in molten salts are often very limited. However, metals with a higher normal valency (e.g., a heavy transition metal) can have one or more subhalides. In this case, the solubilities are high.

On slow cooling of the molten salt containing the metal, the latter separates out because of the decomposition of the subcompound or because of the decrease in the solubility of the metal. The separated metal is often in a highly dispersed state and appears colloidal when the melt is solidified. The metal may, however, be retained in solution by employing a very fast rate of cooling.

In general, the solubility of a metal increases with temperature, but, sometimes, there is a maximum limit beyond which the solubility decreases. This may be due to the instability of the subcompound of the metal at high temperatures.

The relationship between the solubility of a metal and the nature of the cation and anion of a melt is not exactly known. As already mentioned, the solubility is appreciable only when a metal dissolves in its own salt. When a fused salt of a metal is diluted with the salt of a less noble (i.e., more reactive) metal, the solubility of the former metal decreases rapidly. This fact is important in industrial electrolytic processes and is explained by the activity of the solvent salt being lowered. It is also explained by complex formation between the two different salts. These complexes cannot form subcompounds easily. For example, the solubility of Al in cryolite ( $\text{Na}_3\text{AlF}_6$ ) is greatly reduced by adding NaF and that of Pb in  $\text{PbCl}_2$  by adding KCl.

From the foregoing discussion, we observe that the solubility of a metal can be minimized by using the lowest possible operating temperatures and a mixture of fused salts instead of pure salts. Such a mixture also facilitates the attainment of low temperatures by the formation of low melting compositions.

#### MOLTEN SALT PROCESSES

Electrowinning is presently being used for extracting a large number of metals from their molten salts. The most outstanding example is the electrolysis of alumina that has been dissolved in a cryolite bath. Generally, however, it is not possible to dissolve oxides in molten salts so as to produce ionic solutions suitable for electrolysis. Oxides, of course, dissolve in silicate solutions, but the latter are not suitable for electrolysis because of their high viscosity and high melting points. They may, however, find application in refining operations such as the electroslag refining process for steel. (For details on electrowinning processes using molten salts, the reader is referred to the chapters dealing with the extraction of individual metals.) Typical operational data for electrowinning are given in Table 4.6. These may be compared with the data for electrowinning of metals from aqueous solutions (given in Table 4.4).

Table 4.6 Typical Data for Electrowinning from Molten Salts

Metal	System	Cell voltage (V)	Temperature (°C)	Current efficiency (%)	Current density (A/cm²)	Other data
Al	Al <sub>2</sub> O <sub>3</sub> in NaAlF <sub>3</sub> , CaF <sub>2</sub> , and NaF	4.5-5	960-1000	85	0.5-1.2	Carbon anode (consumable), 0.5 kg/kg Al; energy efficiency, 35%; cell body, steel ceramic
Mg	MgCl <sub>2</sub> in NaCl-KCl	6.5-7.5	700-750	75-90		Cell body, steel ceramic; carbon anode (theoretically inert); maximum consumption, 100 kg/ton metal; energy required, 18.5 kWh/kg Mg
Ti	TiCl <sub>4</sub> in Li-Na-K-Cl eutectic	6-8	500	90	0.5	Graphite anode; metal screen cathode
Be	BeCl <sub>2</sub> in KCl-NaCl	6-9	900		1.0	Graphite anode; stainless steel cathode

#### 4.27 ELECTROLYSIS OF LOW-TEMPERATURE NONAQUEOUS SYSTEMS

In this section, *nonaqueous systems* refer to organic solutions in which metals can be deposited and dissolved at the anode. We now list the general advantages of such systems:

(1) In some instances, the organic medium is better suited than other media for plating purposes. For example, aluminium and zinc can be coated by deposition from organic solutions to give more coherent coatings than those usually achieved in aqueous solutions.

(2) Reactive metals cannot be plated in aqueous media, therefore, nonaqueous media must be used. For example, uranium, which requires plating for corrosion resistance, can be plated with zinc by employing an organic medium.

(3) Reactive metals may be produced electrolytically at low temperatures using solutions of various salts in organic media.

Processes based on electrolytic decomposition in organic baths are yet to find wide commercial application mainly because of their poor conductivity. However, we mention in this section some baths where some measure of success has been achieved. Baths suitable for reactive metals, which cannot at all be produced from aqueous solutions, are listed in Table 4.7.

It should be noted that although the electrolytes listed in Table 4.7 have been used for metal deposition, various problems remain unresolved, for example, problems relating to electrode side reactions and to the poor nature of the deposits. In fact, little success has been achieved in the electrolytic production of elemental Zn, Ti, Ge, the rare earths, and the reactive metals belonging to groups V and VI of the periodic table.

Table 4.7 Electrolytes for Nonaqueous Class of Metals

Metal	Electrolyte
Sodium	Molten compounds NaAl(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> (melting point 130°C) and NaB(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> (melting point 140°C) (Electrolysis may be carried out at around 150°C; however, in this case, the process is perhaps similar to fused salt electrolysis)
Lithium	LiCl in acetone, pyridine, or aliphatic alcohols (AlCl <sub>3</sub> + LiCl) in propylene carbonate
Beryllium	BeCl <sub>2</sub> in dimethyl beryllium and beryllium borohydride in ether
Magnesium	MgBr <sub>2</sub> and magnesium borohydride in diethyl ether
Aluminium	Anhydrous AlCl <sub>3</sub> in ether with lithium hydride or lithium aluminium hydride Also molten sodium triethyl aluminium fluoride [NaF·2Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ]

Copper, lead, and zinc can be deposited from solutions of their chlorides, nitrites, or oxides, in formamide. Zinc, cadmium, tin, nickel, and copper can also be obtained from formamide by dissolving their thiocyanates in it. Chlorides of some other metals, for example, Cr, Ni, Fe, Bi, and Mn, can also be electrolyzed in formamide.

In general, metals having high melting points, when deposited from liquids at low temperatures often yield powdery nonadhesive deposits with unsatisfactory physical properties. This is one of the most serious disadvantages of electrolysis of organic solutions. Further, there is the possibility of large-scale contamination of metals by organometallic compounds. Because of these drawbacks, none of the foregoing processes seems practicable on a large scale.

#### 4.28 CELL DESIGN

A variety of cell designs have been evolved after a great deal of trial and experimentation. Although the design of one cell differs greatly from that of another, it is possible to make some general observations.

The electrolytic cell is essentially a 'box' in which the arrangement of the electrodes and the electrolyte allows cell reactions to proceed smoothly. Appropriate provision should also be made for the removal of gases and other products formed as a result of the cell reactions. The accumulation of gases may result in problems such as the polarization of electrodes, 'gas locking' (which may cause the electrolyte to spill out), and contamination of the electrodes by impurities. The design would, therefore, depend on the nature of the electrodes, the electrolyte, and the cell reactions.

The electrodes are usually solid metal, graphite, or metallic sulphides. In some fused salt processes, the cathode is the molten metal that remains submerged. For aqueous solution processes, the physical form of the electrode has been endlessly varied in an attempt to decrease

polarization. Cells have been designed with variations such as fast-flowing electrolytes, rotating electrodes, and wiped electrodes. In some designs, the electrodes have been employed in particulate or fluidized forms. The aim of these modifications has been to achieve the maximum surface area per unit volume. The results have, however, not been very encouraging, and rigid and massive electrodes still remain the most functional. Rigidity ensures the maintenance of a uniform interelectrode gap and massiveness ensures the low resistance of the electrode. Most electrodes are placed vertically to facilitate their removal.

Another factor to be borne in mind is that the material employed to fabricate the cell must be able to withstand the chemical attack of the electrolyte. For aqueous solutions, materials such as wood lined with Pb or Pb-Sb alloys, rubber-lined steel, and cast iron find application. Mild steel is the best material, if it can withstand the cathodic potential. Of late, the tendency is to go in for plastics or glass fibre resin-bonded materials. For molten salts, both refractory-coated steel and stainless steels have been found useful.

#### PERFORMANCE CRITERIA

The performance of an electrolytic cell is decided by two main criteria, namely, current efficiency and cell voltage. In general, the current efficiency is far better for low-temperature processes in aqueous solutions than for high-temperature processes in fused salts. The various factors which lower current efficiency have been discussed in Section 4.26. From the viewpoint of design, the most important factor is the possibility of recombination of the products, which may take place outside the electrolyte or inside it. To improve the design, special hoods can be incorporated in a cell to withdraw the gaseous products. Further, diaphragms can be introduced to prevent recombination by diffusion. (A diaphragm is a chemically inert, nonconducting rigid wall that separates the cathode and anode compartments.) Diaphragms allow only ions to permeate but not molecules and thus prevent the combination of the molecular reaction products. Diaphragms should have a void fraction in order to minimize the electrical resistance. At the same time, they should have a small mean pore size to prevent the passage of gas bubbles and to minimize molecular diffusion. A small pore size, however, leads to greater electrical resistance. In practice, therefore, a compromise has to be made between pore size, i.e., quality of the diaphragm, and the resistivity.

According to Faraday's first law of electrolysis, the metal output as a result of electrolysis depends on the total current passed through the cell. This output is, however, independent of the cell voltage. It is, therefore, necessary to minimize to the extent possible the voltage required for electrolysis. The cell voltage is, in fact, a summation of several terms, namely, the voltage required to overcome the reversible decomposition potential of a salt, the ohmic resistance of the bath (which would include the resistance of the diaphragm, if there is one), the contact resistances, and the overpotentials. While it is not possible to change the reversible decomposition potential, it may be possible to bring about a limited change in the overpotentials by adopting the special electrode designs already mentioned. The internal resistance and contact resistance terms can be decreased by suitably altering the design. The internal resistance usually comprises the resistances of the electrolyte, of the gas bubble layer on the electrode, of the diaphragm, and of the electrode itself. The resistance of the electrolyte is minimized by increasing its conductivity by various additions, by raising the temperature, and by minimizing the space between the electrodes. The resistance of the electrode is minimized by employing massive electrodes having a high conductivity. The resistance of the gas bubble layer can be eliminated by employing special electrode designs.

Contact resistances may sometimes consume as much as 20 per cent of the total energy requirement. These resistances are minimized by including as many permanent connections as possible, by minimizing contact points, and by using a better quality of material and improved techniques for temporary connections.

#### 4.29 ELECTROPLATING

Electroplating is a process in which an object, usually metallic, is coated with one or more relatively thin but adherent layers of some other metal or alloy. This process is used to impart better surface characteristics and protection against corrosion. A detailed analysis of the physicochemical principles underlying electroplating is beyond the scope of this work. However, some popular electroplating baths are listed to highlight the variety of electrolytes that are commercially used.

At the outset, it should be remembered that since the aim of electroplating is to produce only a thin coating layer, the characteristics of the surface to be coated must be taken into account. For example, in chromium plating, if the underlying metal has already been polished, then, the chrome will retain this polish if a thin layer is deposited.

The potential ( $E_d$ ) required for the electrodeposition of a metal is given by a modified form of the Nernst equation as

$$E_d = E_0 - \frac{RT}{ZF} \ln a + P, \quad (4.200)$$

where  $E_0$  is the decomposition potential,  $a$  the activity of the depositing cation on the cathode film, and  $P$  a rate factor expressed as the additional potential that must be provided to maintain a uniform rate of deposition. It is possible to achieve codeposition of two metals by adjusting values of  $a$  and  $P$ .

The principal metals used in electroplating are nickel, silver, chromium, copper, zinc, gold, cadmium, iron, lead, cobalt, and tungsten. Of the alloys, brass is the most common. The electroplating process may use either soluble or insoluble anodes. Some common electroplating baths are listed in Table 4.8.

Table 4.8 Electroplating Baths (after Mann and Barns, 1970)

Metal	Electrolyte	Remarks
Aluminium	Diethyl aluminium iodide, ethyl aluminium diiodide, ether solutions of $\text{AlCl}_3$ with $\text{LiH}$ , ...	No aqueous plating solution
Antimony	Potassium antimony tartarate, fluorides, fluoroborates, fluosilicates, and sulphides	Brittle coating
Arsenic	$\text{As}_2\text{O}_3$ in concentrated HCl or in NaOH	Grey or greyish black finish
Bismuth	Bismuth oxide in $\text{HClO}_4$ solution in water with glue and cresol as addition reagents	Similar bath can also be used for codepositing Pb-Bi alloys

Table 4.8 Electroplating Baths (after Mann and Barns, 1970) (cont.)

Metal	Electrolyte	Remarks
Cadmium	$\text{Cd}(\text{CN})_2$ in water or Cd in $\text{CdCN}$ with relatively large amounts of addition agents such as glue, casein, and molasses	
Chromium	$\text{CrO}_3$ plus small amount of sulphate in dilute acid	Coating is good for resistance to oxidation; it allows mirror-like finish, but does not prevent corrosion of iron because it is porous
Copper	Acid sulphate, alkaline cyanide, fluoborate, and pyrophosphate solutions	Good as base for ornamental or other finishes by additional plating with other metals
Gold	Cyanide with $\text{KAu}(\text{CN})_2$ in water (Gold deposits of 14 carat shades are produced from solutions with copper salts; green gold by addition of $\text{AgCN}$ ; red gold by addition of $\text{CuCN}$ or $\text{Cu}(\text{C}_2\text{H}_5\text{O}_2)_2$ ; white gold by addition of double nickel cyanide)	Codeposition of alloys of various compositions allow coloured coatings
Lead	Fluosilicate, fluoborate, and perchlorate	
Nickel (cobalt)	$\text{NiSO}_4$ , $\text{NiCl}_2$ , $\text{H}_3\text{BO}_3$ , $\text{CoSO}_4$ , $(\text{NH}_4)_2\text{SO}_4$ , and some formaldehyde in hot acidic medium	Lustrous deposits of Ni-Co alloys
Silver	Cyanide solutions containing $\text{KAg}(\text{CN})_2$ or $\text{NaAg}(\text{CN})_2$	
Tin	Sodium stannate along with an oxidizing agent such as $\text{H}_2\text{O}_2$ or sodium perborate to maintain tin in the stannous form and sodium acetate as a buffer	
Copper-zinc alloys	Solutions containing cyanide salts of copper and zinc	
Lead-tin alloys	Fluoborate solutions	

#### 4.30 ROLE OF ENERGY IN METAL EXTRACTION

Having made a survey of various metal extraction processes, it would be appropriate at this stage to discuss the role of energy in metal extraction. The primary energy for all purposes, including metal extraction, is generated mainly by coal, oil, and gas. Electricity is a secondary energy source, and, on a world-wide basis, about 75 per cent of the electric power is generated by burn-

ing fuel (fossil or nuclear) and only 25 per cent by water power (Kellogg, 1977). The fossil fuel resources are getting rapidly depleted, and the recent escalations in the price of oil has focused attention on the role of energy in metal extraction. Energy costs will play a larger role than ever before in the selection of a metal extraction process. In future, metallurgical processes will have to be designed to achieve the maximum conservation of energy resources.

The energy requirements for the production of some metals from their concentrates are presented in Table 4.9. Most of these metals are produced from their concentrates which range in

Table 4.9 Energy Requirement for Production of Metals from Their Concentrates (after Kellogg, 1977)

Metal	Process energy ( $10^6$ kcal/ton)	Free energy ( $10^6$ kcal/ton)	Process efficiency (%)
Titanium sponge	90.4	4.0	4.4
Magnesium ingot (sea-water process)	85.4	5.1	5.9
Aluminium ingot	49.6	6.4	12.9
Ferrochrome low carbon	31.5	2.2	7.0
Sodium metal	22.9	1.8	7.8
Nickel cathode	22.4	0.8	3.5
Ferrochrome high carbon	13.9	2.2	15.8
Ferromanganese (arc furnace)	12.1	1.8	14.8
Copper refined	12.1	0.45	3.7
Zinc (electrolytic)	12.1	1.1	9.0
Ferromanganese (blast furnace)	10.8	1.8	17.0
Steel slab	5.5	1.4	26.0
Tin ingot	4.8	1.0	20.0
Lead ingot	4.5	0.2	4.4

grade from 40 per cent to 70 per cent metal (except Ni 8 per cent and Cu 25 per cent), so that their process energies are comparable with each other.

In Table 4.9, Column 2 gives the total process energy required to extract a particular metal less the energy spent in mining and concentration. In each case, the metal concentrate is considered the starting point for determining the energy requirement. For example, with reference to magnesium and aluminium, the concentrates considered are  $\text{Mg}(\text{OH})_2$  filter cake and pure alumina, respectively. Column 3 lists the values of the free energy of formation of the stable oxide per ton of the metal at 25°C. These values represent the theoretical energy required for the reduction of the respective stable oxides to the metal under ideal (reversible) conditions. The last column gives the efficiency of the process, i.e., (free energy  $\times 100$ /process energy). In each case, there is a

large difference between the process energy and the theoretical free energy. Titanium is the most energy-intensive and lead the least energy-intensive among the metals listed in Table 4.9. Yet, both have the same efficiency, showing that no correlation exists between the efficiency and the process energy or free energy. As is evident from Table 4.9, titanium, magnesium, and aluminium have the highest process energy values. This is to be expected because on thermodynamic grounds, the reduction of their oxides, which have high free energies of formation, requires the expenditure of more energy. For the same reason, lead is the least energy-intensive metal.

The large variations in the process efficiency values, as evident from the last column of Table 4.9, can be attributed to a number of reasons, some of which are now listed. For titanium, the process efficiency is low, as compared with the exceptionally high process energy, because another energy-intensive metal, namely, sodium, is employed to reduce  $TiCl_4$  to Ti. For copper and nickel, the process efficiency values are low because the metal content in their concentrates is significantly lower than that of the other metals given in Table 4.9. Metals which are produced by expending a large amount of electrical energy either for heating or for electrolysis will have low process efficiencies. This is because of the low efficiency with which the electrical energy is generated from fuel resources.

Steel, tin, and ferromanganese (blast furnace) have very high process efficiencies because their production does not require much electrical energy. Factors such as operation on a small scale, the need for controlled atmospheres, and the use of gas-tight equipment also lead to a low process efficiency.

Since the high-grade ores are getting rapidly depleted, the process energies required for the extraction of a metal are bound to increase substantially in the future. The need to develop new metal production processes with a high degree of efficiency can hardly be overemphasized.

Secondary metals are obtained by recycling scrap, and it is estimated that in future a large proportion of the metals produced will come from such recycling. In Table 4.10, the unit energies

secondary metal requires a much smaller amount of energy than that of a primary metal. In fact, 20 tons of secondary aluminium can be produced by using the same energy as for 1 ton of primary. (The recycling of secondary metals from scrap is discussed in detail in Chapter 10.)

#### 4.31 ENVIRONMENTAL PROBLEMS

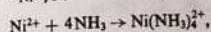
In the past, very few basic metal extraction designs paid adequate attention to the discharge of pollutants into the surroundings. For example, almost all copper reverberatory furnaces release waste gases containing about 1 per cent sulphur dioxide into the atmosphere. The effluents from hydrometallurgical extraction processes may contain pollutants such as heavy metals, chlorides, ammonia, and acid, and their disposal can create serious problems. Over the years, biologists and ecologists have been working out a strong case for environmental protection, and, as a result, most countries have passed strict laws against industrial pollution.

In future, the metal production industry will have to adopt process designs that would minimize the energy consumption and, at the same time, protect the environment. Such designs would have to incorporate, on a broad basis, the use of oxygen in smelting, the use of flash and pneumatic smelting techniques, the use of a countercurrent shaft furnace, and make the fullest possible use of waste heat.

#### QUESTIONS

- During leaching, the formation of an insoluble product may decrease the rate of the leaching reactions. The temperature and the concentrations of the leaching reagents used influence the magnitude of the change in the rate of leaching. Discuss the reasons for such behaviour.
- Compare electrodeposition and precipitation with hydrogen as methods for producing metals from aqueous solutions of their salts. Illustrate your answer with the relevant potential versus pH diagrams.
- The equilibrium molal concentrations of the nickel ammines present in an ammoniacal solution in which, at 25°C, the overall  $Ni/NH_3$  ratio is 4 and the total nickel concentration is 1 M are as follows:  $Ni(NH_3)^{2+}$ , 0.003;  $Ni(NH_3)_2^{2+}$ , 0.050;  $Ni(NH_3)_3^{2+}$ , 0.27;  $Ni(NH_3)_4^{2+}$ , 0.418;  $Ni(NH_3)_5^{2+}$ , 0.235, and  $Ni(NH_3)_6^{2+}$ , 0.025. Prove that hydrogen at this temperature and at a pressure of 100 atm can precipitate nickel from the solution, assuming its pH to be 8.5 and given that

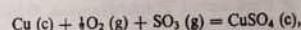
$$E_{Ni^{2+}, Ni}^{\circ} = -0.241 \text{ V}$$



$$K_{eq} = 9.12 \times 10^7$$

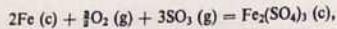
Assume that the activity coefficients of ammonia and those of nickel ammines in the solution are unity.

- A mixture of ferric oxide ( $Fe_2O_3$ ) and cupric oxide ( $CuO$ ) is heated to 650°C in an atmosphere containing  $SO_3$  gas. At what values of  $p_{SO_3}$  will  $CuO$  be converted to soluble  $CuSO_4$ , leaving  $Fe_2O_3$  unchanged at the given temperature? The relevant reactions are



$$\Delta G_T^{\circ} = -94,375 - 5.01T \log T + 86.9T \text{ cal}$$

required for the production of some primary metals are compared with those required for the production of the secondary metals. From Table 4.10, it is obvious that the production of a



$$\Delta G_f^\circ = -223,370 + 111.04T \text{ cal.}$$

5. Describe the main features of a typical flowsheet for the recovery of copper by a heap leaching cementation process. What role do bacteria play in this process and how can their action be made more beneficial?
6. (a) What are the advantages and disadvantages of electrolytic methods of winning metals?  
 (b) In electrolysis what are the advantages offered by molten salts as solvents?  
 (c) What are the problems encountered in winning (i) a liquid metal and (ii) a solid metal from molten salt solvents?
7. What are the essential features of a successful hydrometallurgical process? Under what conditions would it be preferred to a pyrometallurgical process?
8. Certain metals can be deposited from aqueous solutions, whereas for others the use of molten electrolytes is necessary. Discuss the reasons for this and also describe the properties of molten electrolytes desirable for successful extraction.

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## 5 General Methods of Refining

### 5.0 INTRODUCTION

Every metal or alloy is evaluated in terms of some useful properties, for example, mechanical strength, hardness, ductility, specific gravity, melting and boiling points, thermal and electrical properties, resistance to corrosion, and chemical reactivity. All these properties are influenced by the presence of the impurity elements. In some cases, even traces of an impurity may significantly change a specified property. Sometimes, the impurities themselves may have an appreciable commercial value. It is, therefore, often necessary to remove impurities and refine the metal so as to improve its properties and to recover the valuable byproducts which are often present in the bulk metal as impurities.

The 'purity' of a metal is an ambiguous term unless it is defined in terms of the intended use of the metal. An impurity may be negligible from the point of view of one property but may be significant from the point of view of another. For example, traces of oxygen would hardly change the specific gravity of copper, and, if weight were the criterion of any particular use, the presence of oxygen could be ignored. The dissolved oxygen could, however, drastically affect the electrical conductivity of copper. Pure copper from the point of view of use as a conductor must, therefore, necessarily have a very low oxygen content. The effect of metallic impurities on the properties of copper depends largely on the type of copper, whether OFHC (oxygen-free high conductivity) or tough pitch copper (0.01–0.03 per cent oxygen). The presence of oxygen influences the effect produced by the metal impurity through its oxidizing power. For example, about 0.01 per cent oxygen causes iron and tin to precipitate as oxides and thereby eliminates the deleterious effect of these impurities, namely, iron and tin, on electrical conductivity when they are present in a solid solution in copper.

Another good example of the effect of a trace impurity is provided by hafnium in zirconium. It is well known that the property which makes zirconium valuable in a nuclear reactor is its low neutron absorption cross-section (0.18 barn/atom) by virtue of which the metal absorbs only a very small number of neutrons. The corresponding value for hafnium is very high (115 barns/atom). Therefore, even a small amount of hafnium is undesirable if zirconium is to be used in a reactor. The tolerable limit of hafnium is set at a value as low as 200 ppm.

One of the reasons why an impurity element, even in small amounts, can often affect mechanical, electrical, or other properties is its tendency to concentrate in certain areas of the crystalline structure of the matrix. For example, if the impurity happens to be insoluble in the bulk metal, it tends to accumulate in the grain boundaries where the liquid metal is the last to freeze during cooling and crystallization. The impurity concentration is thus felt more strongly than if it were scattered uniformly throughout the mass. A detailed discussion of this topic is, however, beyond the scope of this work.

It is interesting to note that since a gm atomic weight of a metal contains  $6 \times 10^{23}$  atoms of the element, it is conceivable that numerous atoms of each of the other elements may be present

to some degree in this quantity, regardless of any purification treatment. Any impurity at a concentration of one part per billion (ppb), which is far below the detection limit for most elements by normal analytical means, could equal roughly  $6 \times 10^{14}$  atoms in 1 gm atomic weight of the metal. It can, therefore, be concluded that purity has no absolute scale. It must be defined in terms of the intended use of the metal. It should be noted that the refining method itself is not the final answer to contamination; additional impurities may be introduced from the environment during storage and handling.

### PRINCIPLES OF REFINING

A pure phase is said to be thermodynamically unstable with respect to its environment, i.e., entropy works against the refiner. The fact behind this statement can be understood from the treatment that follows. Consider the formation of a binary solution when two elements A and B are mixed according to the equation (see Section 2.8)

$$X_{AA} + X_B B = AB \text{ (solution).}$$

The integral molar free energy of mixing  $\Delta G_M$  is given by

$$\Delta G_M = \Delta H_M - T(\Delta S_M + \Delta S_M^{\text{ex}}),$$

where  $\Delta S_M$  is the configurational entropy of mixing and  $\Delta S_M^{\text{ex}}$  is the excess entropy of mixing due to nonconfigurational factors. Assuming a random distribution of atoms, we get

$$\Delta S_M = -R(X_A \ln X_A + X_B \ln X_B),$$

$$\Delta G_M = X_A \Delta H_A + X_B \Delta H_B + RT(X_A \ln X_A + X_B \ln X_B) - TX_A \Delta S_A^{\text{ex}} - TX_B \Delta S_B^{\text{ex}}. \quad (5.1a)$$

Now, assume that B is the impurity atom and A the element to be purified. Since

$$X_A + X_B = 1, \quad dX_A = -dX_B,$$

we get

$$\frac{\partial \Delta G_M}{\partial X_B} = -\Delta H_A + \Delta H_B + RT \ln \frac{X_B}{1-X_B} + T\Delta S_A^{\text{ex}} - T\Delta S_B^{\text{ex}}. \quad (5.1b)$$

As  $X_B \rightarrow 0$  and  $X_A \rightarrow 1$ ,

$$\Delta H_A = 0, \quad \Delta S_A^{\text{ex}} = 0.$$

Therefore, as  $X_B \rightarrow 0$ , we have

$$\frac{\partial \Delta G_M}{\partial X_B} = \Delta H_B + RT \ln X_B - T\Delta S_B^{\text{ex}}. \quad (5.1c)$$

Moreover, in  $X_B \rightarrow -\infty$  as  $X_B \rightarrow 0$ .

In eq. (5.1c),  $\Delta H_B$  and  $\Delta S_B^{\text{ex}}$  are always finite quantities. Therefore, irrespective of their sign,  $\Delta G_M$  will always be negative in the region where  $X_B \rightarrow 0$  because of the configurational entropy term. The free energy of a pure phase is always lowered by the introduction of an impurity atom, even when the enthalpy term and the nonconfigurational entropy term are not favourable for solution formation and the impurity dissolves to form a solution. The final steps of a refining process are always very difficult to carry out because the pure materials produced tend to become impure by absorbing impurities from the environment.

In all refining operations, the creation of the most satisfactory thermodynamic and kinetic conditions is highly desirable. Many refining processes developed by empirical methods have been improved by the application of thermodynamic and kinetic data.

It is known that the lower the chemical potential at which an impurity is held in a metal, the more difficult is the task of removing it. In principle, refining of the metal is done by bringing the impure metal into contact with an extracting phase which is designed to hold the impurities at a lower chemical potential. In many cases, this extracting phase is a silicate slag or a vacuum, as in the vacuum degassing of metals. So, a knowledge of the metal and impurity activities in the metal and extracting phases should be of use to the refiner. As the impurity content decreases, its chemical potential also decreases, rendering the final steps of a refining process extremely difficult. Hence, it is essential to know how the impurity activities vary with concentration at very low concentrations.

If a metal contains more than one impurity, the influence of one solute on the chemical potential of another is important in refining, as it may determine the order in which the impurities can best be removed. It is advantageous to extract the impurities under conditions where their activity coefficients are raised by the presence of other dissolved elements. If data on the activities in multicomponent solutions are not available, they can be estimated with the help of interaction parameters, as explained in Section 2.14.

In the refining of metals which are very reactive, their reactivity poses a problem. Therefore, it is advantageous to remove the impurities associated with the metals in the ore by chemical separation while the metals themselves are in the form of suitable compounds such as oxides, halides, and oxalates. After the compound has been purified to the maximum possible extent, it is reduced to the metal. Another problem with such metals is the choice of a suitable container material for carrying out high-temperature operations. Graphite is commonly used for holding reactive metals although it is considered unsuitable on thermodynamic grounds because most reactive metals form stable carbides. It is believed that the reaction between the metal and carbon to form carbides proceeds so slowly that graphite containers can be used for melting metals such as zirconium and uranium at temperatures of 1900°C and 1200°C, respectively (see Richardson, 1959).

### 5.1 BASIC APPROACHES TO REFINING

There are two basic approaches to the refining of pure metals. In the first approach, the aim is to produce high-purity metal compounds, which are subsequently reduced to produce the metal in a very pure form. The purity of the metal in this approach essentially depends on the purity of the raw material. The physical and chemical methods available for the purification of metal compounds are discussed later in this chapter. The reduction to metal of the purified compound can, however, lead to contamination by the reductants. This approach is useful in the case of very reactive metals which are difficult to handle in the pure state without being contaminated.

In the second approach, the objective is to first produce the bulk metal from the metal ore, ensuring maximum recovery and then devise ways and means to purify the metal.

### 5.2 PREPARATION OF PURE COMPOUNDS

We first discuss the methods used for the preparation of pure metal compounds. These methods can be classified into two broad categories, namely, physical methods and chemical methods.

## PHYSICAL METHODS OF PURIFICATION

### Purification by Sublimation

Sublimation is resorted to if a solid compound of the metal having a high vapour pressure is available. The sublimation method is specially advantageous if sublimation occurs at low temperatures because the decomposition of heat-sensitive impurities is avoided and corrosion is minimized. After sublimation, nonvolatile particles are left behind unless they are present as very small particles, which tend to get carried away by the vapours.

Several halides which sublime are conveniently produced by chlorination. Thus,  $ZrCl_4$  can be produced by the chlorination of  $ZrO_2$  in the presence of carbon. All oxides, except  $HfO_2$ , are thus eliminated from  $ZrO_2$ .

### Purification by Distillation

Consider a liquid solution of A and B. A can be separated from B by partial vaporization, followed by the recovery of the vapour and residue. One of the factors that determines the efficiency of separation is the relative volatility of the components expressed in terms of their partial pressures  $p_A$  and  $p_B$  of A and B, respectively, over the solution.

If  $a_A$  and  $a_B$  are the activities of A and B in the solution, then

$$a_A = \frac{p_A}{p_A^0}, \quad a_B = \frac{p_B}{p_B^0}$$

where  $p_A^0$  and  $p_B^0$  are the vapour pressures of A and B, respectively, in the pure state at the same temperature. Also,  $a_A = \gamma_A X_A$  and  $a_B = \gamma_B X_B$ , where  $\gamma_A$  and  $\gamma_B$  are the activity coefficients and  $X_A$  and  $X_B$  the mole fractions of A and B, respectively. Therefore, the partial pressure ratio of the components over the solution is given by

$$\frac{p_A}{p_B} = \frac{\gamma_A X_A p_A^0}{\gamma_B X_B p_B^0}$$

i.e.,

$$\frac{p_A}{p_B} \cdot \frac{X_A}{X_B} = \frac{\gamma_A p_A^0}{\gamma_B p_B^0} = \alpha, \quad (5.2)$$

where  $\alpha$  is the relative volatility. It is evident that  $\alpha$  is a direct measure of the ease with which the components can be separated by distillation. Since temperature changes have an almost similar influence on the vapour pressures of both elements,  $\alpha$  usually does not vary with temperature. From eq. (5.2), we see that  $\alpha$  is influenced by the relative values of  $\gamma_A$  and  $\gamma_B$ .

Let us assume that the binary phase diagram is as shown in Fig. 5.1. Here, A, which has a lower melting point than B, is likely to have a higher vapour pressure over the liquid mixture and is, therefore, more amenable to selective distillation. Suppose a liquid having an overall composition C is being distilled at a distillation temperature  $T_D$ . At this temperature, we obtain an equilibrium mixture of a A-rich vapour (composition E) and a B-rich liquid (composition F). When the vapour is removed and condensed, the resulting liquid phase is richer in A than in B. Separation by distillation would be particularly effective when the relative volatility has a large value.

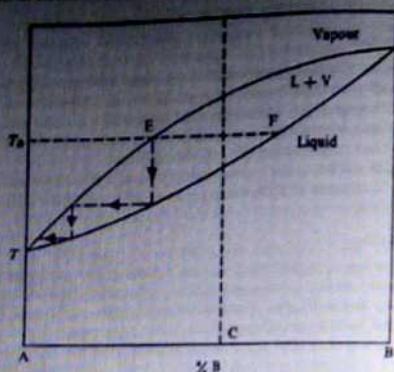


Fig. 5.1 Binary A-B Phase Diagram.

**Influence of  $\gamma_A$  and  $\gamma_B$  on distillation**

With reference to Fig. 5.1, consider a solution of a liquid B that contains small amounts of A as an impurity which is to be removed by distillation. Since  $X_A$  is close to unity, the activity of the solvent B is likely to lie within Raoult's law range, and the value of  $\gamma_B$  is unity. The higher vapour pressure of A permits its separation by distillation. Further, if  $\gamma_A$  is greater than unity, the separation of A by distillation is made more efficient. On the other hand, a negative deviation from ideality of the activity of A in solution makes separation less efficient.

Next, consider a solution of A that contains small amounts of B from which A is to be separated by distillation. Here,  $\gamma_A = 1$ , and the separation of A by distillation is made less efficient by  $\gamma_B$  values greater than unity, because the vapour pressure of B increases.

Differential distillation requires the continuous removal of the vapour. Obviously, only the initial fractions of the vapour are richer in A than in B, and, with the passage of time, the liquid becomes richer in the less volatile component B than in A. As the liquid becomes richer in B, the subsequent fractions of the vapour become less rich in A. In other words, the mole fraction of the more volatile compound in the distillate decreases as the fraction of the liquid that is vaporized increases. Evidently, a high degree of separation is not possible unless the recovery of the distillate is restricted to a very low value or the relative volatility is exceptionally large.

The separation of A from B by distillation can be best achieved if distillation is repeated a large number of times, the condensate of one stage becoming the feed for the next. During repeated distillation, the composition of the condensate follows the path shown by the arrows (leading away from E) in Fig. 5.1. The path shows that the condensate becomes richer in A after every stage. By knowing the phase diagram and the relative volatility, we can calculate the minimum number of differential distillation steps that would be necessary to produce a vapour product of a predetermined purity from a given initial binary mixture.

The effect of relative volatility on separation by distillation is shown in Fig. 5.2. This figure shows that for any given liquid feed composition, a prescribed purity can be attained more

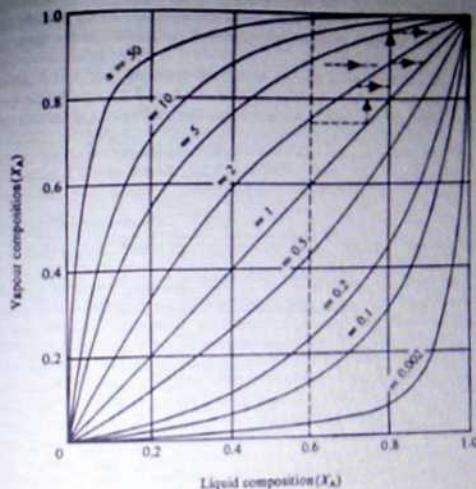


Fig. 5.2 Effect of Relative Volatility on Separation.

easily by using a lesser number of stages if the relative volatility is higher. We can also use this figure to graphically determine the number of steps required to obtain a preset vapour composition. However, this graphical method becomes highly insensitive when the number of steps becomes very small. A more precise procedure would be to apply the appropriate formula. We can show that the composition of the vapour in equilibrium with the liquid feed, at any stage, is given by the equation

$$X_{A(1)} = \frac{\alpha X_{A(0)}}{1 + (\alpha - 1)X_{A(0)}} \quad (5.3)$$

Assuming  $\alpha$  to be constant, in the next immediate stage, this composition of the vapour becomes the composition of the liquid.

Repeated distillation, in sequential steps, however, suffers from the inherent problem that enhanced purity must necessarily be achieved at the cost of reduced recovery. Theoretically, the amount of pure vapour obtainable after an infinite number of steps is zero.

#### Rectification or fractional distillation

Rectification is a distillation technique for separating two components that is conducted as a continuous countercurrent process. The distillation and condensation of the individual phases (fractions) are repeated several times with the vapours continuously moving upward through the liquid stream. Rectification ensures both a high degree of purification and a large amount of recovery.

The basic principle of rectification can be understood from Fig. 5.3, which shows a long column with an assembly of a large number of trays. Each tray is in fact a flat vessel with a hole at the bottom. The vapours move upward through the tray against a stream of dripping

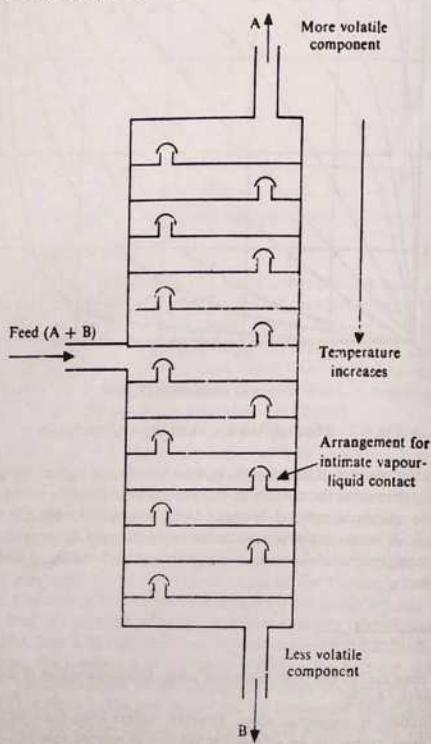


Fig. 5.3 Fractionating Column for Rectification.

liquid. On contact with the liquid, the vapours condense and transfer the latent heat to cause an overflow and lead to the partial vaporization of the liquid. Since the column is heated only at the bottom, a temperature gradient is developed, which further helps the separation. Apart from the column design just discussed, there are several other designs, but all of them incorporate the same basic features, namely, intimate countercurrent flow and repetitive liquid-vapour contact.

We now consider examples of rectification refining. First example is the removal of silicon tetrachloride ( $\text{SiCl}_4$ ) from titanium tetrachloride ( $\text{TiCl}_4$ ). Commercial  $\text{TiCl}_4$  (boiling point  $136^\circ\text{C}$ ) contains up to 2.5 per cent  $\text{SiCl}_4$  (boiling point  $57^\circ\text{C}$ ). In a liquid state both the chlorides are completely soluble in each other.  $\text{TiCl}_4$  can be almost completely separated from  $\text{SiCl}_4$  in a stainless steel fractionating column. As a second example, a complex halide mixture that has been obtained from an oxide ore and containing about 40 per cent  $\text{TaCl}_5$  can be distilled to yield about 75 per cent of pure  $\text{TaCl}_5$  with an impurity content of less than 10 ppm.  $\text{TaCl}_5$  can be separated from a chemically similar halide, namely,  $\text{NbCl}_5$ , because the latter has a lower vapour pressure.

#### Purification by Crystallization

The aim of both crystallization and precipitation is to separate a solid phase from a liquid solution. The solid phase may selectively accumulate either the metallic values or the impurities.

Purification by crystallization is based on the differences between the solubility values of various compounds dissolved in a solvent, usually water. A solute is precipitated from a solution when its concentration exceeds the solubility limit. During crystallization, this can be achieved by either evaporating the solution to increase the concentration or, better, by lowering the temperature so that the value of the solubility limit is decreased below the actual concentration.

Let us consider an example. If an aqueous solution saturated with potassium chloride and sodium chloride at  $100^\circ\text{C}$  is cooled to room temperature, then both salts tend to crystallize. In practice, however, the crystals consist mainly of potassium chloride. Very pure potassium chloride can be obtained by adjusting the concentration of the solution so that the sodium chloride concentration remains below the solubility limit. Significant amounts of impurities are occasionally trapped either in the crystals themselves or in the liquid film adhering to crystals. These impurities are effectively eliminated by repeated crystallization.

#### CHEMICAL METHODS OF PURIFICATION

Chemical methods of purification include chemical precipitation, ion exchange, and solvent extraction. In these methods, suitable chemical equilibria are selectively employed to concentrate the desired compound in a solid or liquid phase, thus eliminating the impurities.

#### Chemical Precipitation

A striking example of the completeness with which an ion can be precipitated is provided by the bismuth phosphate process that is used to separate plutonium from irradiated uranium. In this process, irradiated uranium is first dissolved in nitric acid to give a solution containing uranyl nitrate plus plutonyl nitrate and fission products. Next, the plutonium is reduced to the quadrivalent state and bismuth is added to the solution. Next, bismuth phosphate is precipitated by adding phosphoric acid, plutonium being completely coprecipitated along with it. The precipitate is removed and plutonium oxidized to the hexavalent state. The subsequent reprecipitation of bismuth phosphate leaves plutonium in solution. By repeating the precipitation of bismuth phosphate, we can achieve more than 90 per cent recovery of plutonium, and the radioactive fission products are reduced to less than  $10^{-7}$  of their original amount.

Another example of chemical precipitation pertains to the monazite leach liquors. In this case, uranium and the rare earths are first eliminated from the leach liquors by precipitation prior to the precipitation of thorium. In fact, all the three main constituents, namely, uranium, the rare earths, and thorium, are differentially precipitated.

#### Ion Exchange

When a solution of ammonium sulphate is percolated through a layer of soil, the resulting effluent is found to contain numerous calcium ions but no ammonium salt. This is the result of an exchange of ions between the solution and the solid. In ion-exchange methods, which can be used in the preparation of pure compounds, the solid phase is made to initially absorb a suitable ion of the desired metal through an ion-exchange reaction. The absorbed ion is subsequently taken into solution by once again employing an ion-exchange reaction. This is called *elution*, i.e., a method by which the absorbed ion is brought into solution. The metal is finally recovered from the solution by precipitation through further treatment of the leach solution. An ion-exchange medium that is commonly used consists of synthetic resins which are marketed in the form of small but hard porous beads so that they can be easily packed in long columns.

Resins are complex organic acids or bases which are insoluble in water. The salts of resins are also insoluble in water. Basically, resins are large molecules that comprise interconnected and cross-linked chains. The resin structure contains a large number of basic and acidic groups which are capable of ionization and exchange reactions. Figure 5.4 shows a cation-exchange

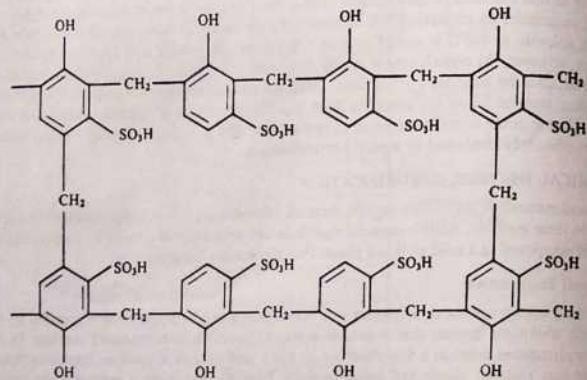
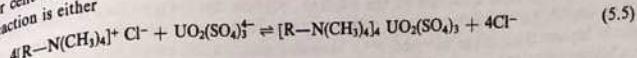


Fig. 5.4 Structure of Cation-Exchange Resin.

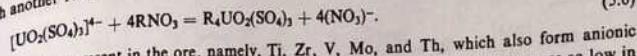
resin structure. For simplicity, the structure may be written as RX, where R is the polymer backbone and X is the ion-exchange site, represented in Fig. 5.4 by the sulphonate group  $\text{SO}_3\text{H}$ . When a cation-exchange resin reacts with solutions containing suitable cations, the H in the sulphonate group is replaced by the cation. For example,



In anion-exchange resins, the formula of the resins may be  $\text{RNO}_3$  or  $\text{RCI}$ , depending on whether the ion-exchange site contains  $\text{NO}_3^-$  or  $\text{Cl}^-$ . When anion-exchange resins react with a solution containing suitable anions,  $\text{NO}_3^-$  or  $\text{Cl}^-$  can be replaced by an anion. For example, in the recovery of uranium from sulphuric acid leach solutions, low-grade ores containing only about 0.2 per cent  $\text{U}_3\text{O}_8$  can be leached by anion-exchange resins for subsequent uranium recovery. The reaction is either



or with another resin



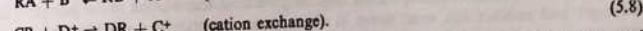
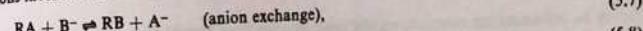
The other metals present in the ore, namely, Ti, Zr, V, Mo, and Th, which also form anionic sulphate complexes in the leach liquor, either form weakly absorbed complexes or are so low in concentration that they become important enough to be taken into account only on repeated cycling. When the resin cannot absorb any more of these complexes, the uranium is obtained from it by an elution operation. The resin is washed or eluted with an acidified solution of any mineral salt, e.g., nitric acid solution containing ammonium nitrate. The solution takes up uranium as a result of reactions which are the reverse of absorption, and the resin can be reused. Another application of ion exchange is in the recovery of gold and silver from cyanide leach liquors. Normally, zinc is used to precipitate gold. In this exchange process, the clear filtrate containing the metallic values is passed through a column of a suitable anion exchanger in the form of a chloride which absorbs the cyanide complexes of the metal. These absorbed complexes are later removed by selective elution. Gold and silver are finally recovered by distilling off the acid-organic mixture.

The degree or extent of the ion-exchange phenomenon depends on several factors such as

- (1) the size and valence of the ions taking part in the exchange,
- (2) the concentration of the ions in water or the solution,
- (3) the physical and chemical nature of the ion-exchange resin, and
- (4) the temperature.

#### Ion-exchange equilibrium

Most ion-exchange reactions, in practice, represent almost true equilibrium states. The reversible reactions involved are written as



The thermodynamic equilibrium constant  $K$  for reaction (5.7) may be expressed in terms of activity as

$$K = \frac{a_{\text{RB}}a_{\text{A}^-}}{a_{\text{RA}}a_{\text{B}^-}}. \quad (5.9)$$

The more practical index of affinity of the resin for the ions  $\text{A}^-$  and  $\text{B}^-$  is the *selectivity coefficient*

$K_s$  which is given by

$$K_s = \frac{[RB][A^-]}{[RA][B^-]} \quad (5.10)$$

where the brackets represent the concentrations of the various species.  $K_s$  remains almost constant over a range of conditions in the solution. In practice, the ion-exchange problems encountered are often concerned with achieving a separation of two species, say,  $M^+$  and  $N^+$  (which may be present in low concentrations in the solution). Suppose that the resin itself is associated with a third ion  $A^+$ . ( $A^+$  is often hydrogen which may also be present in the solution at concentrations much higher than those  $M^+$  and  $N^+$ .) In such a situation, the selectivity coefficient is approximately equal to the distribution coefficients  $D$  of  $M$  and  $N$ , namely  $D_M$  and  $D_N$ , respectively. In other words,

$$D_M = \frac{[RM]}{[M^+]}, \quad D_N = \frac{[RN]}{[N^+]} \quad (5.11)$$

It should be noted that  $D_M/D_N$  is known as the separation factor and indicates the ease with which the two ions can be separated from each other.

The selectivity coefficient is sometimes also written in terms of concentrations in the two phases, i.e., of the resin and the liquid. For example, eq. (5.10) may be rewritten as

$$K_s = \frac{B_r}{A_l} \cdot \frac{B_l}{A_r} \quad (5.12)$$

where  $r$  and  $l$  denote, respectively, the resin and the liquid.

We now make some general observations on the conditions under which ion exchange is rendered more effective:

(1) At low concentrations of the aqueous solutions, the extent of ion exchange increases as the valency of the exchanging ion increases (e.g.,  $Na^+ < Ca^{2+} < Al^{3+} < Th^{4+}$ ).

(2) At low concentrations and for the elements having the same valency, the efficiency of ion exchange increases as the atomic number increases (e.g.,  $Li < Na < K < Rb < Cs; Mg < Ca < Sr < Ba$ ).

(3) The differences in the efficiencies of ion-exchange processes seem to disappear at higher solution concentrations and at higher temperatures.

(4) Organic ions having high molecular weights and complex metallic anionic complexes are usually better suited to ion exchange.

#### Ion-exchange kinetics

During an ion-exchange reaction, an ion must migrate from the solution to the interior of the ion exchanger and another ion must move in the opposite direction in a stoichiometric equivalent amount so as to maintain electroneutrality. The various steps in the reaction are as follows:

(1) The transport of an ion from the solution across a liquid film boundary surrounding a resin which is in the form of a bead.

(2) The diffusion of the ion to the interior of the resin.

(3) The main chemical exchange reaction.

(4) The diffusion of the outgoing ion to the surface of the resin bead.

(5) The diffusion of the outgoing ion across the liquid film boundary. Since the chemical exchange reaction itself is usually rapid, the overall reaction rate is controlled by one of the diffusion stages.

#### Ion-exchange plants

In ion-exchange processes, several types of resin columns are used. A simple scheme is shown in Fig. 5.5. The resin beads contained in Columns A and B are initially used for absorption, while

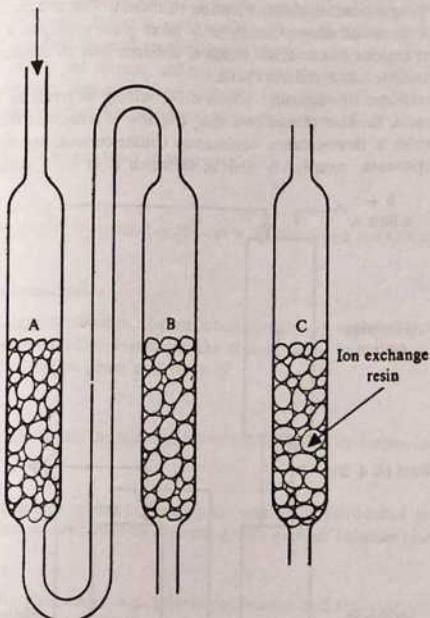


Fig. 5.5 Ion-Exchange Columns.

those in Column C are used for elution. When Columns A and B get sufficiently saturated with the metallic values, a volume of water is introduced through Column A. The pregnant liquor feed is now introduced into Column B and then passed through Column C. When this is done, Columns B and C are used for absorption and Column A for elution. Gradually, when Column C also gets saturated with the metallic values, another change-over is done. This time, Columns C and A are placed on absorption and Column B on elution. Such change-overs can be repeated endlessly.

Two basic techniques find application in ion exchange through resin columns. In the *frontal analysis technique*, the feed solution containing the metallic values and the impurity ions is passed through a resin column at an appropriate rate. This column absorbs, in varying degrees, a variety of ions. Thus, unabsorbed impurity ions come out of the column, followed immediately by weakly absorbed ions. Finally, even the desired ions begin to leak through the column as a result of the saturation of the resin. It is thus necessary to choose operating conditions that lead to the maximum selectivity. In the *elution analysis technique*, an eluting agent is chosen so as to displace, at different rates, the ionic species absorbed by the column. It should be noted that the rate for each ion is inversely proportional to the distribution coefficient. This technique is best applied by using a long column in which absorption initially takes place mainly in a narrow band at the top, leaving the lower regions free to allow bands of different ions to separate from each other as they are eluted from the top at different rates.

In industrial operations, ion exchange plants differ widely in terms of factors such as the arrangement of columns, the flow of feed or eluant, the flow of resin, and the sequence of operations. Figure 5.6 shows a three-column continuous countercurrent arrangement suitable for separating two components, namely, A and B, of which A is more selectively absorbed. In

Fig. 5.6, the resin passes down Column I and then into Column II, while the two aqueous solutions are pushed upward. The main feed solution enters at the base of Column I and meets the scrub solution coming up through Column II. The flow rates of the feed solution and the scrub solution are adjusted so that the resin leaving the base of Column II contains virtually only species A. This resin is eluted in Column III by a countercurrent flow of the eluant. The product A is thus transferred to the eluate and the resin is passed back to Column I for reuse.

#### Solvent Extraction

Solvent extraction or liquid-liquid extraction is the separation of one or more components from a liquid by preferential dissolution in an extracting solvent. Solvent extraction methods were first used around 1945 for metallurgical applications in the processing of nuclear fuels which demanded a high degree of purity. At present, solvent extraction is commercially employed to separate tantalum from niobium, zirconium from hafnium, vanadium from uranium, cobalt from nickel, fission products from irradiated material and to purify compounds of copper, uranium, thorium, and the rare earths.

We now discuss the basic stages in solvent extraction.

#### Dissolution

In dissolution, the impure compound or the ore is dissolved in a suitable acid or alkaline aqueous medium.

#### Extraction and decontamination

In extraction and decontamination, the extractant, usually an organic liquid, is brought into contact with an aqueous solution containing the desired metal ions as well as impurity ions. The metal ions enter the organic phase preferentially.

#### Partition

In partition, the organic and the aqueous layers are separated by employing suitable techniques.

#### Stripping

After partition, the loaded solvent containing the product is introduced into another extracting unit where the values are removed by contacting with another aqueous phase.

#### Auxiliary processes

A number of auxiliary processes, e.g., solvent purification and recirculation, are used in solvent extraction.

The important basic stages in solvent extraction are illustrated in Fig. 5.7. For better selectivity and recovery of the metallic values as well as for the better utilization of the solvent, multistage contacting and the countercurrent principle are usually made use of.

A good example of solvent extraction is provided by the recovery of uranium (anion exchange). The main steps are:

- (1) The uranium ore is first leached with sulphuric acid to form the sulphate ion  $\text{UO}_2(\text{SO}_4)_2^{2-}$  in the solution.

- (2) Next, the organic extract, denoted by  $\text{R}_3\text{N}$  in the organic phase, is allowed to react with

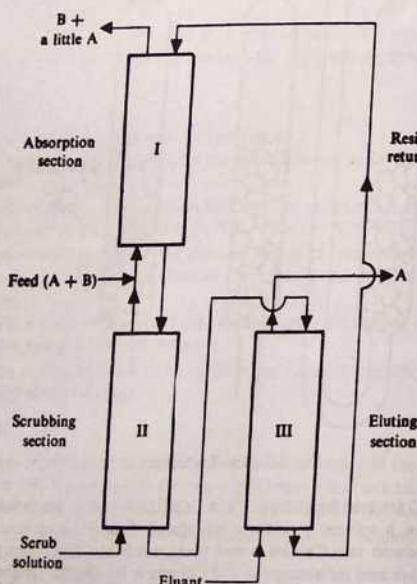


Fig. 5.6 Three-Column Continuous Countercurrent Ion Exchange.

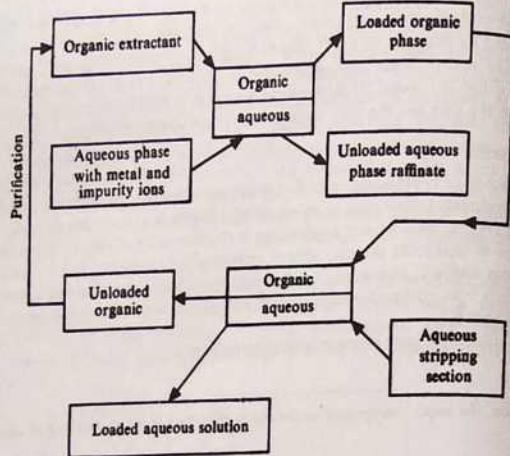
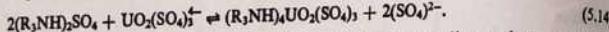
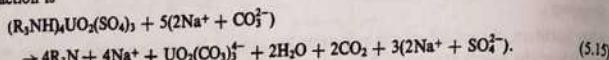


Fig. 5.7 Basic Scheme of Solvent Extraction.

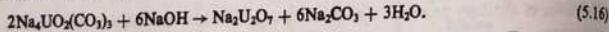
the sulphate ion in the presence of an acid. The reaction is



(3) In the third step, the loaded organic phase is scrubbed by a sodium carbonate solution. The reaction is

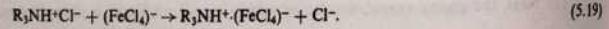


(4) In the fourth step, uranium is precipitated from the aqueous solution by adding sodium hydroxide. The reaction is

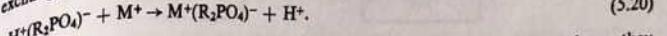


It is necessary to employ an organic phase that is almost immiscible with water. Typical organic phases are diethyl ether, methyl isobutyl ketone, and higher alkyl amines. The metal salt in the aqueous phase is usually a halide, sulphate, or nitrate with an excess of the corresponding acid.

Another example of ion exchange is provided by the extraction of iron by a ternary amine hydrochloride which reacts with the  $(FeCl_4)^-$  complex in an acid solution. The reactions are



Some acidic organic extractants, e.g., dialkyl phosphoric acids and carboxylic acids, function as cation exchangers. A metal ion is extracted according to the reaction



Since all extraction reactions are normally dependent on the pH of the aqueous phase, they can be reversed and the metal values stripped by using a second aqueous phase at a different pH. It should be obvious that stripping is difficult when extraction is easy. When two metal species are extracted simultaneously (e.g., Ta and Nb, Zr and Hf), selective stripping may be possible. If not, the separation of one metal from the other can be carried out by selective precipitation from the strip solution.

#### Extraction coefficient

Solvent extraction involves mass transfer across the interface between two dissimilar liquids. The ratio of the concentrations of a solute in two phases at equilibrium is called the *extraction coefficient* ( $E$ ) and is given by

$$E_{(o/a)} = y/x, \quad (5.21)$$

where  $o$  and  $a$  denote, respectively, the organic and aqueous phases and  $y$  and  $x$  are, respectively, the concentrations in the organic and aqueous phases. If equilibrium is established between the solvent organic phase and the aqueous phase, with respect to the partitioned metal ions, the chemical potential of the metal ions and, hence, the activity will be the same in the two phases. The activity coefficient of the metal ions in the complex dissolved in the organic solvent is much lower than that in the aqueous solution. Hence,  $E_{(o/a)}$  will be high.

The extraction coefficient is sometimes independent of the concentration of the phases. An equation that incorporates the volumes of the two phases and is more meaningful than eq. (5.21) is

$$E_t = \frac{Ly}{Hx} = \frac{L}{H} E_{(o/a)}, \quad (5.22)$$

where  $E_t$  is the extraction factor and is a measure of the distribution of the solute between the phases.  $L$  and  $H$  are, respectively, the volumes of the light organic phase and the heavy aqueous phase. It should be noted that the greater the value of  $E_t$ , the more effective is the separation.  $E_t$  may be made high by increasing the  $L/H$  ratio or by making the value of  $E_{(o/a)}$  high for comparable values of  $L$  and  $H$ . Since organic extractants are usually expensive, their volumes must be kept to the minimum. Small volumes are also preferable because they facilitate handling. Several techniques have been employed to achieve better utilization of solvents, some of which are now considered.

#### Simple extraction: single stage contacting

In the simplest case, a given volume of the solvent is thoroughly mixed with the aqueous feed and then the liquids are separated (see Fig. 5.8). In this figure, let  $L$  be the volume of the light organic phase,  $H$  the volume of the heavy aqueous phase,  $x_1$  the concentration of the solute in the aqueous phase, and  $y_1$  the concentration of the solute in the organic phase. As is evident from Fig. 5.8, the  $Ly_1$ ,  $Hx_0$ , . . . , terms give the total weight of the solute in the organic phase and the aqueous phase, respectively.

If the initial concentration of the solute in the organic phase is zero (i.e.,  $y_0$  is zero), then a

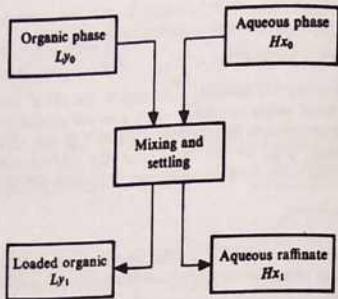


Fig. 5.8 Simple Extraction with Single-Stage Contacting.

material balance across the extraction step gives

$$Hx_0 = Hx_1 + Ly_1. \quad (5.2)$$

Also, we know

$$E_f = \frac{L}{H} E_{(ols)} = \frac{L}{H} \frac{y_1}{x_1}. \quad (5.24)$$

Hence,  $x_0/x_1 = 1 + (L/H)(y_1/x_1) = 1 + E_f$ , i.e.,

$$x_1/x_0 = 1/(1 + E_f). \quad (5.25)$$

In practice, the contacting step is effectively carried out by agitating the two phases together in a vessel so that one phase is finely dispersed in the other. Subsequently, i.e., when agitation has been stopped, one phase is allowed to separate from the other. Single-stage contacting results in a high extraction efficiency (i.e., a low value of  $x_1$ ) only if  $E_f$  is high.

#### Simple multistage cocurrent contacting

The aforementioned single-stage contacting can be repeated several times by contacting the raffinate left over with successive batches of fresh solvent. This leads to an improved recovery of the metallic values. If the quantities of solvent used during each contacting are equal in volume, then the overall change in the concentration of the raffinate after  $n$  contacts is given by

$$\frac{x_n}{x_0} = \frac{1}{(1 + E_f)^n}. \quad (5.26)$$

We now compare the efficiency of multistage contacting with that of single-stage contacting. Suppose the volume of solvent used in single-stage contacting is divided into  $n$  equal parts for contacting in  $n$  number of stages. For each stage in the multistage contacting, the extraction factor is given by  $E_f/n$  because of the reduced volume of the extractant solvent. The fraction of raffinate left over after  $n$  contacts is given by

$$\frac{x_n}{x_0} = \frac{1}{(1 + \frac{E_f}{n})^n} = \frac{1}{1 + E_f + \frac{(n-1)}{2! n} E_f^2 + \frac{(n-1)(n-2)}{3! n^2} E_f^3 + \dots}. \quad (5.27)$$

In the limiting case, i.e., when  $n$  approaches infinity, the limiting loss of the metallic values is given by  $x_\infty$  in the equation

$$\frac{x_\infty}{x_0} = \frac{1}{\exp E_f} = \exp(-E_f). \quad (5.28)$$

It is obvious that the efficiency of the multistage operation is greater than that of the single-stage operation. The recovery is the highest when  $n$  is large and the individual volumes of the solvent in each stage are small, i.e., when small volumes of the solvent are used for extracting a large number of fines. In practice, however, this would be inconvenient.

#### Countercurrent exchange

The countercurrent principle has found application in several processes involving heat and mass transfer. In fact, countercurrent transfer is known to be far more efficient than cocurrent transfer. For example, two possible arrangements for the drying of a wet slurry by hot air in a cylindrical furnace are shown in Fig. 5.9. This figure also indicates the variation of the moisture content in the two phases, namely, slurry and air, over the length of the furnace. It should be obvious from Fig. 5.9 that the cocurrent arrangement effectively removes the moisture from the slurry only in the initial stages where the driving force for mass transfer, i.e., the difference in the moisture contents in the slurry and air, is high. On the other hand, the countercurrent arrangement maintains a more or less uniform driving force for moisture removal over the entire length of the furnace and, therefore, is much more effective than the cocurrent arrangement, provided sufficient contact time is allowed.

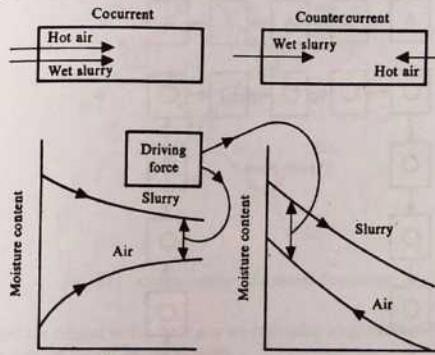


Fig. 5.9 Cocurrent and Countercurrent Flow.

**Countercurrent batch extraction**

In the countercurrent batch extraction process (see Fig. 5.10), those portions of the aqueous phase that contain the solute are extracted with successive portions of the organic phase in a manner such that the fresh organic solvent always comes in contact with the dilutest aqueous feed. On the other hand, the organic solvent that is almost saturated with the solute contacts the fresh aqueous feed that has the maximum concentration of the solute. The solvent and feed having intermediate concentrations contact each other. In countercurrent batch extraction, every contacting involves the operations of mixing, settling, and separation. It is obviously far more convenient to allow the aqueous and organic phases to flow continuously rather than in discrete portions.

Multistage contacting can be depicted as in Fig. 5.11. The circles represent the process of

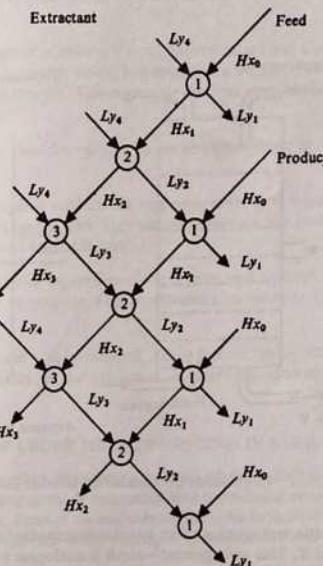
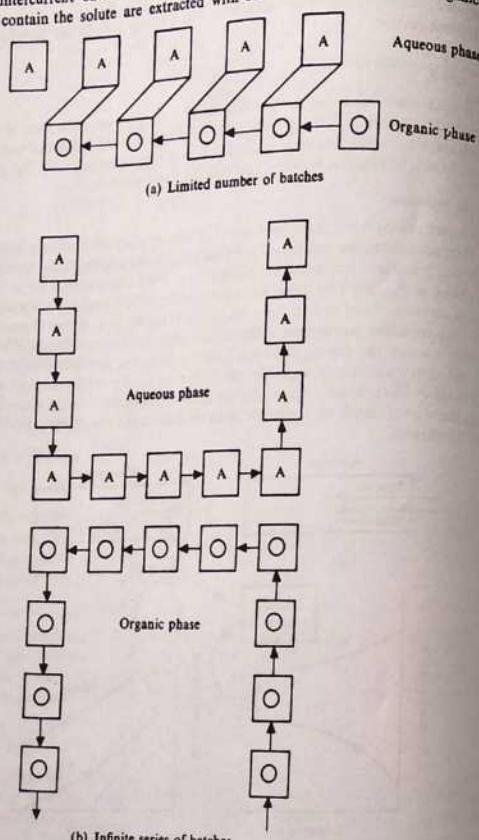


Fig. 5.11 Countercurrent Multistage Contacting.

equilibration and the integers within them give the contacting stage number. We can show that, for the scheme depicted in Fig. 5.4, the equation

$$\frac{x_n}{x_0} = \frac{E_f - 1}{E_f^{n+1} - 1} \quad (5.29)$$

s valid. The loss of solute to the raffinate is minimized by increasing the number of stages (e), provided the extraction factor is greater than unity.

#### Continuous countercurrent extraction

It should be noted that the foregoing multistage contacting scheme is not strictly countercurrent because the countercurrent flow is not continuous. In actual countercurrent schemes, the phases pass against each other in opposite directions in simple packed or unpacked columns. In many of these schemes, one phase remains completely dispersed in the other. In some others, the entire column resembles a continuous series of mixers-settlers. In Fig. 5.12, the left-hand side

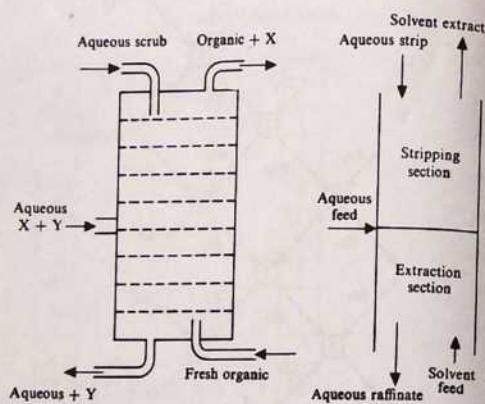


Fig. 5.12 Continuous Countercurrent Solvent Exchange.

diagram shows a schematic arrangement of an actual countercurrent extraction for separating an impurity Y from a metal X. This arrangement—which is analogous to that shown in the right-hand side diagram of Fig. 5.12, i.e., it has distinct sections for extraction and stripping—allows the initial loading of the solvent and then a multistage wash by a suitable aqueous phase which eventually blends with the main aqueous feed. The flow rate of the aqueous stripping solution is adjusted so that it strips the impurities but not the principal solute.

#### Choice of extractant

We now discuss some of the factors that determine the choice of an organic solvent.

**Cost** The cost of the solvent is often the most important factor.

**Selectivity** Analogous to the term used for ion exchange, selectivity here indicates the ability of the organic solvent to dissolve one material in preference to another, i.e., the selectivity K is given by

$$K = \frac{\left(\frac{Y_A}{X_B}\right)}{\left(\frac{X_A}{X_B}\right)}, \quad (5.30)$$

where  $X_A$  and  $X_B$  are the concentrations of A and B, respectively, in the raffinate and  $Y_A$  and  $Y_B$  in the extraction phase.

**Solvent power** For reasons of economy, a small amount of solvent should be able to dissolve a large amount of solute. Generally, strong solvents have a tendency to react with all solutes and, therefore, exhibit a low selectivity. Consequently, the best compromise between solvent power and selectivity is chosen.

**Adaptability** The solvent should be adaptable to variations both in the feed composition and in the desired product.

**Ease of recovery** Since organic solvents are very expensive, it is necessary to recover them as completely as possible. Solvents with high vapour pressures are preferred because they can be easily purified and recovered by distillation.

**Density** For a clear and quick separation of the organic and aqueous phases, the density of the solvent should be as low as possible. Lighter solvents also consume less power during handling and circulation.

**Other factors** Besides those just mentioned, other factors which also have to be considered include the chemical stability of the extractant, its inertness towards plant materials, and its viscosity.

#### 5.3 PURIFICATION OF CRUDE METAL PRODUCED IN BULK

In metal purification, very often, the starting material for the refiner is the crude metal produced in bulk. The various refining methods commonly used for refining crude metals may be classified under the following heads. Some of the methods are the same as those described in Section 5.2, but they are considered with reference to the refining of individual metals.

- (1) Selective distillation.
- (2) Liquation.
- (3) Purification by solvent extraction.
- (4) Chemical methods (including fire refining and precipitation of impurities).
- (5) Electrolytic refining.
- (6) Indirect distillation (purification by forming an intermediate gas phase).
- (7) Zone refining for the production of ultra-pure metals.

Apart from the foregoing methods, special remelting techniques such as vacuum arc remelting, electron beam melting, and electroslag refining are used for metal refining.

#### SELECTIVE DISTILLATION

The principles of separation by distillation have already been described in Section 5.2. In selective distillation, the impurities are separated from the desired metal by distillation at a suitable temperature. It is customary to apply this method when the impurities are more volatile than the metal so that the power required for heating purposes is low. However, in some instances, selective distillation has been used to separate metals from less volatile impurities.

We now list some of the metals that are separated from their impurities by vaporization.

(1) Pure zinc (boiling point 907°C) can be preferentially distilled from brass because copper has a much higher boiling point than zinc, i.e., 2570°C. It is advisable to vaporize zinc from brass (say, 30 per cent zinc) at about 800°C when the brass is still a solid because at temperatures higher than 800°C, and with liquid alloys, the boiling may be violent.

(2) Lead (boiling point 1740°C) can be refined by removing zinc from it by vacuum distillation at around 600°C. The zinc content may be reduced from 2-3 per cent to a few hundredths of a per cent. However, the zinc vapours liberated would be impure and may contain up to 20 per cent lead.

(3) Magnesium and aluminium can be separated from each other by virtue of the substantial differences in their vapour pressures and boiling points. Magnesium (boiling point 1107°C) is more volatile than aluminium (boiling point 2450°C), as shown in Fig. 5.13. The actual vapour pressures over the magnesium-aluminium alloy, however, would depend on the activities

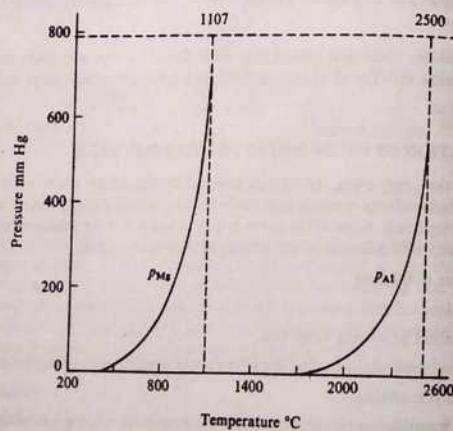


Fig. 5.13 Vapour Pressures of Aluminium and Magnesium.

as described in Chapter 2. It is necessary to apply a vacuum to attain a high rate of vaporization.

It is obvious that magnesium containing, say, 10 per cent aluminium can be more easily refined than aluminium containing, say, 10-15 per cent magnesium. The former can be refined by vaporization at high rates at 600°C and under a vacuum pressure 0.1-0.2 mm Hg. At this temperature, the vapour pressures of magnesium and aluminium are, respectively, around 0.65 mm and 10<sup>-6</sup> mm Hg. As magnesium vaporizes, the bath becomes richer in aluminium and, therefore, the temperature of the bath gradually increases.

It is necessary to refine aluminium at higher temperatures because the magnesium activity in the alloy is low. Refining aluminium to few tenths of a per cent of magnesium (0.1-0.2 per cent) is possible by single-stage distillation at 900°C.

It should be noted that during distillation different depths of liquid metal remain under different pressures due to variations in the hydrostatic head. The upper layers always boil first. It is, therefore, advantageous to have thin layers of liquid metal with a large surface area.

The basic principles of selective distillation of metals are identical to those discussed for the purification of compounds and are, therefore, not repeated. The relative volatilities of various metals are available in standard publications in the form of graphical plots of vapour pressures (as log p) versus temperature. These curves indicate, at a glance, the possibilities of separation by distillation.

#### Rectification

Single-stage distillation yields good results when the difference in the vapour pressures of the two metals to be separated from each other is sufficiently high. When this difference is small, special distribution techniques such as rectification may be resorted to. For example, crude zinc that is obtained by reducing a zinc concentrate may contain 2-3 per cent lead and about 0.4 per cent cadmium (boiling point 767°C as compared with zinc 907°C and lead 1740°C). The impurities in the crude zinc can be removed using fractionating columns containing 35 to 40 trays with a temperature distribution ranging from 800°C to 1200°C.

#### Rate of Distillation

Let us consider a pure metal surface under absolute vacuum. If we assume the distance between the evaporating and condensing surfaces to be less than the mean free path of the distilling molecules, collisions among them in the vapour phase are eliminated. The rate of molecular distillation under this idealized condition is given by the Langmuir equation

$$E = 44.32 \alpha p \sqrt{\frac{M}{T}} \quad (5.31)$$

where E is the rate of evaporation, gm cm<sup>-2</sup> sec<sup>-1</sup>,  $\alpha$  the accommodation coefficient (usually unity for metals with clean surfaces), p the vapour pressure of the metal in atm, M the molecular weight of the metal in gm, and T the temperature in K. Equation (5.31) gives surprisingly high values of distillation rates. For example, at 600°C the vapour pressure of zinc is 11.53 torr and the rate of vaporization, according to eq. (5.31), works out to be 0.184 gm cm<sup>-2</sup> sec<sup>-1</sup>. In reality, however, the observed rates are lower than this figure because of the collisions of gas molecules with other molecules in the system.

When a metal A is in solution of a mole fraction  $X_A$ , the rate of evaporation depends on the rate at which the vaporizing A is replenished by diffusion from the bulk of the solution. If this transport step is fast, then local equilibrium exists between the surface layer and the bulk. In that case, the equation for  $\dot{E}$  is given by

$$\dot{E} = 44.32aX_A p_A^2 \sqrt{\frac{M_A}{T}} \text{ gm cm}^{-2} \text{ sec}^{-1}. \quad (5.12)$$

where  $y_A$  is the activity coefficient of A in the solution,  $p_A^2$  the vapour pressure of pure A in atm, and  $M_A$  the molecular weight of A in gm. If the transport step is slow, i.e., it becomes rate-determining, then a general mass transfer equation becomes applicable. In terms of the mass transfer coefficient  $K_M$  and concentrations of A  $C_{A,B}$  and  $C_{A,S}$  in the bulk and the surface, respectively, the mass transfer rate of A ( $J_A$ ) is written as

$$J_A = K_M(C_{A,B} - C_{A,S}) \text{ gm cm}^{-2} \text{ sec}^{-1}. \quad (5.13)$$

#### Liquation

Liquation implies the selective melting of a component in an alloy. Liquation refining is a technique for removing impurities from metals based on factors such as the difference in the melting points of the alloy components, the immiscibility of phases, and the difference in densities of the alloy components which causes the alloy to separate into two or more layers. The phenomena of immiscibility is governed by the phase diagram of the alloy system. Some phase diagrams which readily allow separation by liquation are shown in Figs. 5.14 (a-c).

Crude zinc containing about 5 per cent lead can be refined in a reverberatory furnace by slowly cooling the molten metal, i.e., over a period of two to three days. Eventually, lead separates out and accumulates at the bottom of the furnace. Solid lead dissolves about 0.05 per cent zinc at 318°C, whereas the solubility of lead in solid zinc is very small, i.e., about 0.001 per cent or less. From Fig. 5.14d, which shows the zino-rich portion of the Pb-Zn system, it is evident that on cooling the molten metal below a certain temperature, it separates into two layers, one rich in zinc and the other rich in lead. Below 417.8°C, almost pure solid zinc separates out, leaving behind a lead-rich liquid. At 418°C, the zinc phase contains about 0.5 per cent lead and the lead phase about 2 per cent zinc.

Although the foregoing process seems theoretically easy, there are some practical limitations. For example, it is desirable to have zinc in the liquid form. This would necessitate temperatures of at least 420°C. At this temperature, however, there would be three phases in the system. Because of this problem and other problems, liquation of lead finds little industrial application.

Liquation refining of crude lead containing copper is conducted either as an independent or a complementary process. The process can be understood with the help of Fig. 5.14b. As lead is cooled down to 320-380°C, a copper-rich scum crystallizes out and floats to the surface. This scum is usually a mixture of oxides of copper and lead. Theoretically, liquation allows the refining of lead up to 0.06 per cent copper but, in practice, it is difficult to proceed beyond 0.1 per cent.

It is also possible to remove iron by liquation from crude tin containing about 10 per cent iron and from crude zinc containing 3 per cent iron. As Fig. 5.14c shows the Fe-Sn phase diagram is a complex one. On gradual heating to 240-325°C, pure tin melts and can be separated using a furnace with an inclined bottom. The Fe-Zn system also has a complex phase diagram. Theoretically it is possible to eliminate iron almost completely from crude zinc containing about 3 per

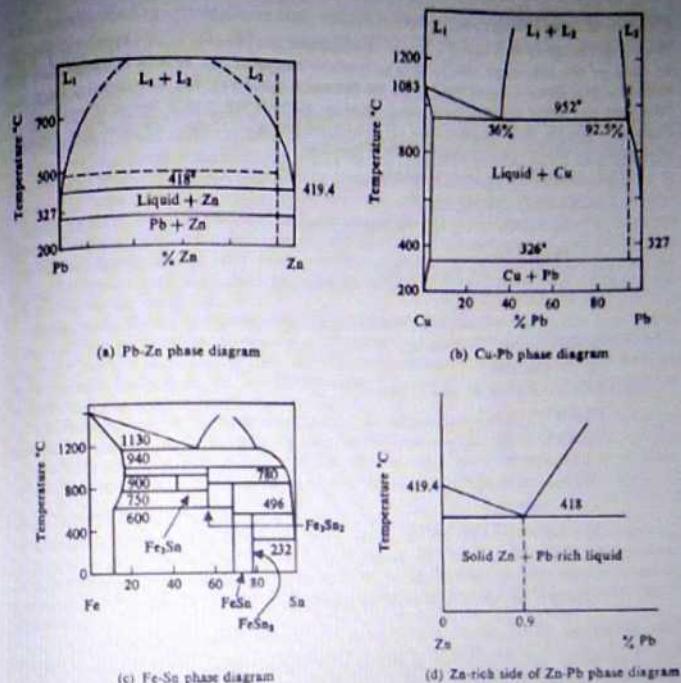


Fig. 5.14 Phase Diagrams Indicating Possibility of Separation by Liquation.

cent Fe. The separation is carried out by slowly cooling the alloy from an initial temperature of about 780°C. During cooling several Fe-Zn compounds and solid solutions separate eliminating iron almost completely.

#### LIQUID-LIQUID EXTRACTION

In principle, liquid-liquid extraction is similar to the solvent extraction method discussed in Section 5.2. Here, the crude liquid metal is brought in contact with another liquid metallic phase which preferentially dissolves either the impurities or the desired metal itself. In the well-known Park's process for refining lead, molten zinc is added to crude lead to preferentially dissolve gold and silver contained in lead.

**CHEMICAL METHODS**

In chemical methods of refining, a reagent is introduced into the basis metal to combine with one or more of the impurities and to form an insoluble compound or a mixture of compounds. The impurity often forms a liquid phase with the flux and is called slag. For the removal of impurities which are less noble than the basic metal, chemical methods are usually the most preferred. In these methods, the chief reagents used are oxygen, sulphur and chlorine. We now give examples of chemical precipitation processes and their functions:

## (1) Oxidation can be used to remove

- (a) C, Si, P, and Mn from Fe.
- (b) Pb, As, Sb, Se, S, Mg, Al, and Fe from Cu.
- (c) Na from Zn.
- (d) Sb, As, Sn, and Zn from Pb.
- (e) Fe, Al, and Zn from Sn.
- (f) Pb, Sb, As, Sn, and Zn from Bi.
- (g) Pb, Zn, and Cu from Ag.
- (h) Zn from Au.

## (2) Sulphidation can be used to remove

- (a) Cu from Pb.
- (b) Cu from Bi.
- (c) Cu from Sn.

## (3) Chlorination can be used to remove

- (a) Zn from Pb.
- (b) Zn, Cu, and Pb from Bi.
- (c) Pb from Sn.
- (d) Ag, Cu, and Zn from Au.
- (e) Alkali and alkaline earth metals from Mg.

**Fire Refining**

The fire refining technique is used to remove more reactive elements from a molten metal by preferential oxidation. This technique is suitable for refining iron, lead, tin, and copper. The cheapest reagent available for oxidation is atmospheric oxygen, which is blown through the metal or drawn over the surface. Frequently, a flux is added so that the impurity oxide is removed as a solid, but dissolved in a mixture of liquid oxides, as is done during open hearth steel-making. The oxygen may be supplied through a gas-metal transfer (as in the Bessemer converter), through a slag layer (as in the open hearth), or through a combination of both (as in the LD process for steel-making). Oxidizable impurities are removed from copper by fire refining in a reverberatory furnace. The softening of lead is also accomplished in a reverberatory furnace.

In some cases, oxygen is provided not from the atmosphere, but in the form of a salt such as  $\text{NaNO}_3$  which is added to the melt. The nitrate decomposes to give nascent oxygen. The removal of impurities is further aided by fluxing the slag formed with  $\text{NaOH}$  and  $\text{NaCl}$ .

The removal of copper from lead by the addition of sulphur is a widely used process. Notable examples of chlorination refining are the removal of alkali and alkaline earth metals from

magnesium by reacting with  $\text{MgCl}_2$  or  $\text{MgF}_2$  and the removal of magnesium from aluminium by  $\text{AlF}_3$ . In the Betterton process, direct chlorination reduces the zinc content in lead from 0.55 per cent to 0.005 per cent.

**Precipitation Method**

In the so-called precipitation method, the impurity phase is separated from the metal by lowering the temperature, which causes the solubility of the impurity to decrease. It should be noted that the extent of separation of the impurities is governed by the impurity-metal phase diagrams. The impurity may precipitate as pure solid crystals of the element itself (e.g., copper from lead) or as a compound with the basis metal (e.g.,  $\text{FeZn}_3$  from zinc or  $\text{FeSn}_3$  from tin). Sometimes, a reagent is added to form either a compound with the impurity or a triple compound with both the impurity and the basis metal. For example, the solubility of bismuth in lead near the freezing point of lead is reduced from 100 per cent (complete miscibility) to 0.04 per cent by the presence of only 0.07 per cent calcium in lead. The solubility can be further reduced by using Ca-Mg alloys, which form ternary compounds.

Besides those already mentioned, other examples of the precipitation method are now listed. Copper is removed from lead as metal or as crystals of  $\text{Cu}_3\text{S}$ ,  $\text{Cu}_3\text{As}$ ,  $\text{Cu}_2\text{Sb}$ , and  $\text{Cu}_3\text{Sn}$ . Lead is removed from zinc in the form of metal droplets. Iron, arsenic, and copper are removed from tin as intermetallic compounds. Zinc is used to precipitate As and Sb from tin and sodium is used to precipitate Bi from lead.

The simplest and the cheapest of all refining techniques is the elimination of a sufficient quantity of impurity from a metal in one stage itself without the addition of a reagent. All that is required is the controlled cooling of the metal produced at a high temperature. In practice, however, a clear separation of metal from impurity in a single stage is seldom possible.

**ELECTROLYTIC REFINING**

In electrolytic refining, the crude metal to be refined is made the anode and the pure metal is deposited on the cathode. The cathode may be a pure strip of the metal itself or some other metal and the electrolyte should contain an ionizable salt of the metal. A large number of metals including Cu, Ag, Au, Ni, Co, Pb, Sn, and Bi can be electrorefined using aqueous electrolytic solutions.

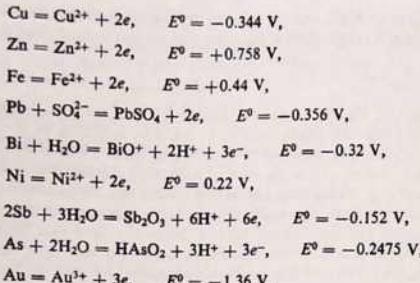
During the passage of current through a cell, the impurities associated with the parent metal dissolve in the electrolyte if they are more reactive than the primary metal. If the impurities are more noble, then they either remain in the anode or, as the anode is consumed, accumulate at the bottom of the cell below the anode. This is called *anode slime*. It should be noted that the baser metals which dissolve in the electrolyte and form ions are likely to contaminate the cathode on prolonged electrolysis.

The basic concepts of electrorefining are best understood by considering a few examples.

**Electrorefining of Copper**

In the electrorefining of copper, impure copper anodes are placed in a tank filled with a solution of  $\text{CuSO}_4$  to which  $\text{H}_2\text{SO}_4$  is added as an electrolyte. The cathodes are either pure copper sheets which eventually become part of the pure copper produced or stainless steel blanks.

The metal-ion equilibria for copper and for some of the common impurities such as Zn, Fe, and Pb and their electrode potentials with respect to the standard hydrogen electrode are as follows:



It should be noted that these electrode potentials are valid only for certain standard conditions, namely, at 25°C and when the concentrations of the ionic species containing the metal are unity. Although these potentials are not valid in a real situation when a finite current flows through the cell and when the ionic concentrations vary, they serve as a useful guide in understanding the electrorefining process. For example, metals such as Zn, Fe, Ni, As, and Sb, which are more reactive, are likely to dissolve in the electrolyte, remain in solution and are not likely to be deposited on the cathode. Antimony and arsenic are oxidized by water and atmospheric oxygen; the oxides forming a sludge of insoluble compounds. Noble metals such as gold do not dissolve in the electrolyte because the potential requirement is not met. Sulphur, selenium, and tellurium present in copper as compounds also pass into the anode slime.

The minimum theoretical voltage necessary for electrorefining is the sum of the potentials at the electrodes and the polarization or counter-emf's. In the absence of polarization, the voltage should be zero when the electrodes are both copper. In practice, however, there is a definite counter-emf. Some additional voltage is also necessary for overcoming the resistances in the circuit including the ohmic resistance of the electrolyte and the ohmic resistances of the electrodes themselves. For copper electrorefining, the approximate voltages are as follows:

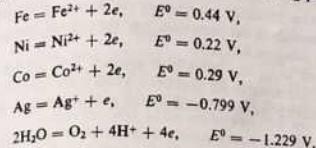
Resistance of electrolyte	0.239 V (80 per cent)
Counter-emf	0.016 V (5.3 per cent)
Anode slime	0.020 V (6.7 per cent)
Cathodes and anodes	0.003 V (1 per cent)
Contacts	0.018 V (6.5 per cent)
Total	0.296 V (100 per cent)

#### Electrorefining of Nickel

Electrorefining yields nickel with a purity of 99.95 per cent. This process also allows the recovery of precious metals, selenium, tellurium, and cobalt as byproducts.

In the electrorefining of nickel, the electrolytic bath consists of a solution of nickel sulphate

of a mixture of nickel sulphate and nickel chloride along with some current-conducting agents. The electrochemical reactions assumed to be taking place at the nickel anode are:



A comparison of the  $E^{\circ}$  values indicates that iron and cobalt would tend to enter the solution, but silver and the noble metals would pass into the anode slime after the anode has been fully dissolved. Here, the anode slime contains sulphur, carbon, selenium, tellurium, slag inclusions and platinum group metals, and undissolved broken anodes. Theoretically, oxygen should not be evolved at the anode at the low potentials usually applied during nickel refining. In practice, however, some oxygen is evolved, which passivates the anode. This passivation can be prevented by the addition of sodium chloride.

#### Electrorefining of Lead

Lead is commercially electrorefined using a fluorosilicate electrolyte, which is a colourless liquid composed of about 9 per cent Pb as  $\text{PbSiF}_6$  and 8 per cent free fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ). This electrolyte has certain advantages, i.e., it is very stable and is hardly contaminated during electrolysis. Further, mechanical losses are said to amount to only 3–4 kg of acid per ton of lead refined. Although electrolytic refining of lead produces a purer lead than that obtained by furnace refining, it is seldom employed due to the toxicity of the electrolyte.

During the electrorefining of lead as the impure anodes dissolve only lead, zinc and tin pass into solution. The other impurities sink to the bottom of the electrolytic tank. Copper must be removed prior to electrolysis as its presence causes anode polarization and consequent hindrance to normal electrode reactions. The temperature of the electrolyte is maintained at 35–40°C with an initial cell voltage of about 0.5 V.

#### Electrorefining of Tin

Crude tin usually contains, among other impurities, Sb, As, Bi, and Cu. These metallic impurities are, however, more electropositive than tin according to the standard potential series and, therefore, would contaminate the cathode if taken into solution. Common solutions based on sulphuric and hydrochloric acids cannot be used as electrolytes because they dissolve the impurities. These impurities, however, do not dissolve in a hydrofluosilicic electrolyte made up of  $\text{H}_2\text{SiF}_6$ ,  $\text{SnSiF}_6$ , and  $\text{H}_2\text{SO}_4$ . This electrolyte, however, is dangerous because of its toxicity. Presently, electrolytes such as sulphur-organic acids obtained by the action of strong sulphuric acid on organic compounds such as benzene, phenol, and cresol are used as they are safer. Another electrolyte used is a solution of  $\text{Na}_2\text{SnS}_4$  and  $\text{Na}_2\text{S}$ . In this electrolyte, the tin anodes dissolve according to the reaction



This reaction is reversed at the cathode. The impurities Fe, Cu, Pb, and Bi collect in the anode slime as insoluble sulphides.

#### Electrolytic Refining Using Molten Salts

Electrolytic refining using molten salts involves the same principles as refining in aqueous solutions. In this case, the purity of the cathode deposit is primarily governed by the decomposition potentials of the electrolyte and the discharge potentials of the impurities, and the current density.

We now give examples of electrorefining using molten salts.

Aluminium is commercially electrorefined using the three-layer process. This process (see Fig. 5.15) uses heavy Al-Cu anodes that are immersed in the electrolyte which is mainly a mixture of  $\text{AlF}_3$  and cryolite. The density of the electrolyte is adjusted so that pure aluminium, which serves as the cathode, floats on the surface.

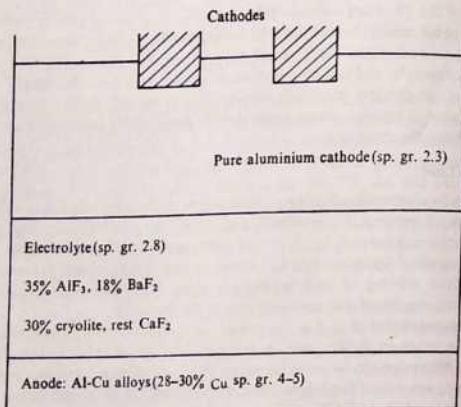


Fig. 5.15 Scheme of Three-Layer Process.

Magnesium is electrorefined by a similar process that uses Mg-Cu, Mg-Zn, or Mg-Zn-Al anodes and an  $\text{MgCl}_2$  electrolyte. This method, however, does not offer any special advantages over other methods of refining.

Titanium, zirconium, and molybdenum are refined on a laboratory scale using molten halides dissolved in alkali metal chlorides. The anode is usually enclosed within a porous graphite cup, and the latter is allowed to absorb some of the impurities. In the titanium-refining cell, a crude titanium anode is located in a porous graphite cup divider which is partially filled with  $\text{TiCl}_3$  and heated to 850°C. The open circuit voltage is 0.5 V and a variable resistance is adjusted so as to keep the voltage of the graphite cup slightly below this value. The melt is electrolyzed at 4.2 V at 250 A. Nickel and iron impurities are deposited on the graphite cup. The cathode deposit of titanium contains 0.005 per cent iron and a much lesser quantity of nickel.

In addition to the foregoing metals, several other metals have also been successfully electrorefined using fused salts. These include manganese (in a  $\text{MnCl}_2\text{-NaCl-KCl}$  bath), vanadium (in a

$\text{VCl}_3\text{-KCl-LiCl}$  bath), tin (in a  $\text{SnCl}_2\text{-NaCl-KCl}$  bath), and zirconium and hafnium [ $\text{K}_2\text{Zr}(\text{Hf})\text{Cl}_6$  in an alkali halide]. However, the commercial application of fused salts in electrorefining is still very limited.

#### Electrorefining Organic Baths

Many workers have reported the use of organic media for electrorefining of metals. It has been shown that all Group III metals of the periodic table (except Al and B) can be deposited from an electrolyte consisting of a complex salt of the type  $(\text{Al}_2\text{R}_4\text{X})\text{M}$  in which R is a hydrocarbon radical, X a halogen, and M an ion of an alkali metal or ammonium. Attempts have been made to refine aluminium using an ether solution of triethyl aluminium fluoride, which is prepared by reacting triethyl aluminium with sodium fluoride. Triethyl aluminium fluoride melts at 72°C and, in the molten state, conducts current readily. The ether solution may be electrolyzed at the room temperature, the bath requiring only about 3 kWh per kg of metal compared with about 20 kWh per kg required for the cryolite bath.

The foregoing organic electrolytes, however, have some inherent disadvantages. They often decompose when exposed to moisture, air, and current. Also, the metal liberated must always be in the solid form because of the low temperatures that have to be employed. Solid particles of metals seldom give good coherent deposits.

Although of much theoretical interest, organic baths are yet to find commercial application in electrorefining.

#### Refining Using Multiple Methods

The nature of the impurities in the crude metal often prevents their removal by a single method. This necessitates the use of two or more methods in conjunction. The sequence of these methods is extremely important, as illustrated by the example that follows.

Let a metal A contain the impurities B, C, D, and E, of which B is nobler than the parent metal A and the other three baser. Let us assume that only impurity C dissolves in the electrolyte, only impurity D has a very high vapour pressure, and impurity E gives a very stable oxide. In such a situation, the recommended sequence of refining methods is as follows:

(1) First, impurity E is removed as a scum by subjecting the impure metal to fire refining.

(2) Next, impurity D is removed by distillation at a suitable temperature.

(3) The resulting crude metal contains impurities B and C. Since impurity B is nobler than metal A, it collects at the bottom of the tank during electrorefining. Impurity C is dissolved by the electrolyte and does not contaminate the cathode.

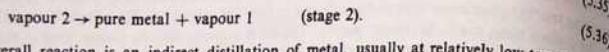
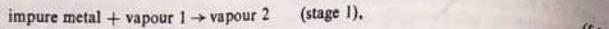
The first two operations are necessary to prevent the deposition of impurities D and E (which are more reactive than impurities B and C and are insoluble in the electrolyte) on the cathode, thus contaminating the metal.

#### INDIRECT DISTILLATION: PURIFICATION BY FORMING INTERMEDIATE GAS PHASE

The refining of a metal using an intermediate gas phase may be viewed as a process of indirect distillation. It is well known that volatile metals such as zinc and mercury can be produced in a state of extreme purity by distillation. The vapour pressures of most metals are, however, too low to allow distillation at ordinary temperatures even under reduced pressures. For example, it is practically impossible to distil refractory metals such as titanium and zirconium because they

have very high melting points and even higher boiling points. Moreover, at high temperatures, the refractory metals may pick up additional impurities from the container materials.

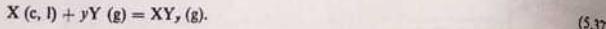
For metals which cannot be distilled at ordinary temperatures, there are indirect methods for producing a vapour species from the impure metal and then reclaiming the metal by heating or cooling this species. The impurities are eliminated during the formation of the vapour species, and the metal liberated subsequently is very pure. These reactions usually also liberate the original vapour-forming reagent which can be recycled. The reaction in the two-stage process may be written as



The overall reaction is an indirect distillation of metal, usually at relatively low temperatures. The deposition of metals from vapours is generally known as *chemical deposition*. The chemical deposition process can have many variations depending on the nature of the vapours.

#### Basic Thermodynamic Considerations

Schafer (1964) has worked out the basic thermodynamics of chemical vapour deposition reactions. Let us consider a reversible reaction



Further, let us assume that the  $XY_y$  formation reaction takes place in one chamber at temperature  $T_1$  and the decomposition reaction (reaction 5.35) takes place in another chamber at temperature  $T_2$ . The total amount of X transported by means of reaction (5.37) from one chamber to the other evidently depends on the difference between the partial pressures of  $XY_y$  in the two chambers. These pressures, and hence the difference between them can be calculated by determining the thermodynamic equilibrium in each chamber. Let  $\Delta G_1^0$  and  $\Delta G_2^0$  be the standard free energy changes of reaction (5.37) at temperatures  $T_1$  and  $T_2$ , respectively. We may therefore write the equations

$$\Delta G_1^0 = -RT_1 \ln \left( \frac{p_{XY_y}}{p_Y} \right)_1 = (\Delta H^0)_1 - T_1(\Delta S^0)_1, \quad (5.38)$$

$$\Delta G_2^0 = -RT_2 \ln \left( \frac{p_{XY_y}}{p_Y} \right)_2 = (\Delta H^0)_2 - T_2(\Delta S^0)_2, \quad (5.39)$$

where  $\Delta H^0$  and  $\Delta S^0$  represent, respectively, the standard enthalpy change and the standard entropy change. Normally, since these values do not change significantly with temperature, we can rewrite eqs. (5.38) and (5.39), respectively, as

$$-RT_1 \ln \left( \frac{p_{XY_y}}{p_Y} \right)_1 = \Delta H^0 - T_1\Delta S^0, \quad (5.40)$$

$$-RT_2 \ln \left( \frac{p_{XY_y}}{p_Y} \right)_2 = \Delta H^0 - T_2\Delta S^0. \quad (5.41)$$

At this stage, it is possible to formulate some simple general rules for vapour transport processes:

(1) Vapour transport would not be possible if  $\Delta H^0$  has an absolute value zero because in

$$\text{that case } \ln \left( \frac{p_{XY_y}}{p_Y} \right)_1 = \ln \left( \frac{p_{XY_y}}{p_Y} \right)_2 = \frac{\Delta S^0}{R}. \quad (5.42)$$

In other words, the equilibrium constant becomes independent of temperature. Since the aforementioned chambers are interconnected, the total pressure in both chambers is constant. Therefore,  $p_{XY_y}$  also remains constant.

(2) If the absolute value of  $\Delta H^0$  is very large, then too, there is no measurable vapour transport. This is so because for a very large value of  $\Delta H^0$ , the equilibrium constant becomes insensitive to temperature changes.

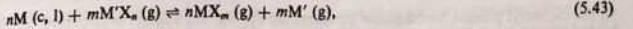
(3) The sign of  $\Delta H^0$  determines the direction of vapour transport. For an endothermic reaction, the vapour is transported from a higher to a lower temperature. This is because  $p_{XY_y}$  decreases with temperature. On the other hand, for an exothermic reaction, the direction of transport is reversed. And, as just mentioned, there is no transport when  $\Delta H^0$  is equal to zero.

(4) It can be shown that for any value of  $\Delta S^0$  other than zero, there is a value of  $\Delta H^0$  which gives the maximum transport effect.

(5) It should also be clear that the maximum transport effect increases as the absolute value of  $\Delta S^0$  increases (when  $\Delta H^0$  changes correspondingly).

It is also possible to formulate several similar rules. If thermodynamic data are available, then it is possible to calculate the most effective conditions for material transport. This shall be done later in this chapter.

Reaction (5.37) applies to the formation of a second vapour from the reacting elements. It should be noted that Vapour 1 (Y gas) need not be an element. Also, vapour transport is possible according to the reaction



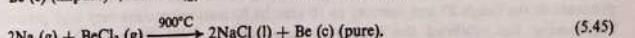
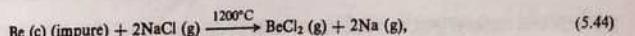
where M is a nonvolatile metal of valency  $m$ ,  $M'$  a volatile metal of valency  $n$ , and X a halogen. It is necessary to ensure that neither the two metals nor their halides react to form stable compounds with each other under the conditions of the reaction.

We now consider examples of vapour transport processes.

#### Examples of Vapour Transport Processes

##### Metals from intermediate halide

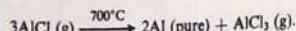
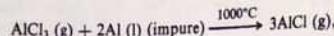
Beryllium can be purified by making it to react with sodium chloride vapour around 1200°C followed by cooling the vapour. The reactions are



Titanium can also be purified by a similar process.

For aluminium, the disproportionation process is employed in which impure aluminium is made to react at approximately 1000°C with its own trichloride vapour ( $\text{AlCl}_3$ ) to form the vapours of the monochloride ( $\text{AlCl}$ ). On cooling to around 700°C, very pure aluminium is liberated and the

trichloride is regenerated according to the reactions



The  $\text{AlCl}_3$  produced from reaction (5.47) is recycled to convert additional impure aluminium to purified metal. To achieve 99.99 per cent pure aluminium, the intermediate halide process should start with a metal that has a low content of metallic impurities, such as, Cu, Ti, Mn, Mg, Zn, and Ca because these impurities cannot be adequately eliminated by this process. The impurities that are effectively removed by the cyclic process from commercial aluminium are Si and Fe.

The best known intermediate halide technique is the *iodide process*, also known as the De Boer or Van Arkel process. In this process, the impure metal is made to react with a halogen gas to form an intermediate halide at low temperatures. The halide is then decomposed at higher temperatures to produce the refined metal. This method is discussed in detail later in this chapter.

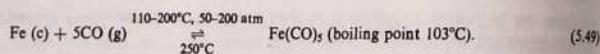
#### Metal from intermediate carbonyl

The *carbonyl process* is commercially used to purify nickel and can also be employed, at least in theory, to purify iron. When dry carbon monoxide is passed over reduced impure nickel in a finely divided form at a temperature of about  $45^\circ\text{C}$ , volatile nickel carbonyl  $[\text{Ni}(\text{CO})_4]$  is formed. When the temperature is increased, i.e., to about  $240^\circ\text{C}$ ,  $\text{Ni}(\text{CO})_4$  (boiling point  $43^\circ\text{C}$ ) decomposes to give pure nickel and carbon monoxide according to the reaction



In the carbonyl process, atmospheric pressures are applied and sulphur is employed as a catalyst for the formation of the carbonyl gas. This process is particularly useful in removing cobalt from nickel. The forward reaction (5.48) leads to a reduction in the volume and is, therefore, aided by increased pressures in the system. On the other hand, the decomposition reaction is aided by a vacuum.  $\text{Ni}(\text{CO})_4$  decomposes into Ni and Co readily in the temperature range  $200$ – $260^\circ\text{C}$  under pressures in the range  $30$ – $760$  mm of mercury. At lower temperatures and pressures, however, there is some codeposition of carbon along with nickel.

Iron exhibits a reaction similar to reaction (5.48), i.e.,



Although iron carbonyl  $[\text{Fe}(\text{CO})_5]$  decomposes easily in the temperature range  $250$ – $300^\circ\text{C}$  under pressures in the range  $20$  mm mercury to  $10$  atm, its formation requires very high pressures. This requirement has inhibited the commercial application of the carbonyl formation method. Table 5.1 lists relevant thermodynamic data for the formation of  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ . From this table, it is evident that the thermodynamics of reactions (5.48) and (5.49) differs significantly. At low temperatures, the vapour pressure of  $\text{Ni}(\text{CO})_4$  is significantly greater than that of  $\text{Fe}(\text{CO})_5$ . This fact may be made use of in the separation of the two carbonyls when they are present together. When nickel is extracted from ores containing high percentage of  $\text{Fe}_2\text{O}_3$ ,  $\text{Ni}(\text{CO})_4$

Table 5.1 Free Energy Changes for Carbonyl Formation ( $\Delta G_f$ )

Temperature ( $^\circ\text{C}$ )	$\Delta G_f$ (cal/mole)		Equilibrium constant	
	$\text{Ni}(\text{CO})_4$	$\text{Fe}(\text{CO})_5$	$\text{Ni}(\text{CO})_4$	$\text{Fe}(\text{CO})_5$
26	-21,081	-8369	$2.87 \times 10^{15}$	$1.37 \times 10^6$
126	-10,975	+10,085	$9.94 \times 10^5$	$3.08 \times 10^{-6}$
226	-1158	+26,057	3.21	$4.06 \times 10^{-12}$

contains significant amount of  $\text{Fe}(\text{CO})_5$ . However, the vapour pressure of  $\text{Ni}(\text{CO})_4$  is about seven times that of  $\text{Fe}(\text{CO})_5$  at  $27^\circ\text{C}$  and ten times at  $43^\circ\text{C}$ , the temperature at which  $\text{Ni}(\text{CO})_4$  boils under 1 atm. The distillation of Ni-Fe mixture and the fractionation of the condensate thus produce a higher concentration of  $\text{Ni}(\text{CO})_4$  in the first fraction. This method is commercially employed for nickel-iron separation and for the production of pure nickel.

#### Iodide process (Van Arkel process)

The *iodide process* was introduced by De Boer and Van Arkel, independently, in 1925. This process has been used in the small-scale purification of a large number of metals including Be, Cr, Cu, Fe, Hf, Ni, Pa, Si, Th, Ti, U, V, and Zr. Occasionally, the iodide process is also called the hot filament or hot wire process because of the universal use of heated filament for the decomposition of vapours.

The iodide process aims at the formation of a volatile halide of a metal at low temperatures by reaction with a halogen and its subsequent decomposition to produce very pure crystalline metal. A thermodynamic analysis shows that this process works better in the case of metal halides having high oxidation states because this ensures the necessary large entropy change for the decomposition reaction. A necessary precondition for this process is that the volatile halide must be capable of decomposing at a temperature lower than the melting point of the metal. Moreover, this halide should be capable of being synthesized from its elements under the prevailing conditions. This precondition becomes imperative because of the nature of the set-up actually used. The halide vapours are decomposed by a hot filament on which crystals of the metal grow. If the filament temperature is higher than the melting point of the metal, then the build-up of crystals would not take place. Moreover, the liquid metal may attack the filament itself.

#### Thermodynamics of the Van Arkel process

The first reaction to be studied was the vapour phase deposition of tungsten from tungsten hexachloride, i.e.,



The thermodynamics of reaction (5.50) is, of course, governed by the entropy and heat content changes. In this reaction, there is a large change in the volume, leading to a large change in the entropy of the system. Since  $\Delta S$  is large, it becomes obvious that  $\Delta G$  and, therefore, the process itself, is sensitive to changes in temperature. Thus, the free energy change, which is positive at

the room temperature, rapidly becomes negative with increasing temperature, and the decomposition of hexachloride results.

The elements immediately preceding tungsten in the periodic table, namely, tantalum and hafnium form chlorides, i.e.,  $TaCl_5$  and  $HfCl_4$ , respectively. For these compounds, the number of chlorine atoms set free is smaller than in the case of tungsten and so is the entropy change. The melting point of Hf is lower than that of Ta and the melting point of Ta is lower than that of W. Therefore, as we move across the transition series in the direction W to Ta to Hf, the melting point and covalency with respect to chlorine decrease, and the probability of achieving decomposition at a temperature below the melting point of the metal under consideration also decreases (Shelton, 1968a).

Table 5.2a Standard Heats and Entropies of Formation of Some Chlorides and Iodides (crystals)\* (Shelton, 1968a)

Compound	$\Delta H_{298}^0$ (kcal/mole)	$\Delta S_{298}^0$ (cal/degree mole)	Melting point of metal (°C)
$TiCl_4$	-191.6	-54.3	1668
$ZrCl_4$	-234.7	-71.5	1852
$HfCl_4$	-236.7	-71.4	2150
$TaCl_5$	-205.5	-87.1	2996
$WCl_6$	-97.0	-93.0	3410
$TiI$	-122.0	-70.0	1668
$ZrI_4$	-145.7	-73.0	1852
$HfI_4$	-149.8	-75.0	21.50

\*To obtain the data for the formation of vapour, we must take into account the vaporization reaction, for example, for the  $ZrI_4(g)$  reaction, the data are given in Table 5.2b.

Table 5.2b Thermodynamic Data for Formation of  $ZrI_4(g)$ \*\*

Reaction	$\Delta H_{298}^0$ (kcal)	$\Delta S_{298}^0$ (cal/deg <sup>-1</sup> )
$Zr(c) + 2I_2(g) = ZrI_4(c)$	-145.7	-73.0
$2I_2(c) = 4I(g)$	72.2	48.3
$ZrI_4(c) = ZrI_4(g)$	29.2	42.0
$Zr(c) + 4I(g) = ZrI_4(g)$	-188.7	-79.3

\*\*For rough calculations, we may assume  $\Delta H^\circ$  and  $\Delta S^\circ$  values to be independent of temperature (i.e.,  $\partial C_p = 0$ ).

The variation of  $\Delta G$  for the Van Arkel process would also depend on the enthalpy change ( $\Delta H$ ). The exothermic heat of formation of these halide compounds increases as  $\Delta S$  decreases. This again operates against decomposition below the melting point of the metal. In the case of hafnium, this becomes decisive. The thermodynamic data given in Table 5.2 can be used to calculate the temperatures for the reversal reactions if the conditions of pressure and temperature are known. The literature on the Van Arkel process indicates that under optimum conditions the vapour pressures of the volatile compounds are of the order of  $10^{-3}$  atm. It can be assumed that during reaction, the vapour pressure of both the halide and the halogen set free (perhaps in the atomic state because of the high temperatures involved) is equal to  $10^{-3}$  atm.

Consider the general reaction



for which,

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln p_{MCl_n} - nRT \ln p_{Cl} \\ &= \Delta G^\circ + 4.575T \log 10^{-3} (1-n) \\ &= \Delta G^\circ + 13.73(n-1)T. \end{aligned} \quad (5.52)$$

From eq. (5.52), it is possible to calculate  $\Delta G$  as a function of both  $T$  and  $n$ . From this equation, it should be evident that for the formation of the chloride,  $\Delta G$  must initially be negative at lower temperatures. As the temperature increases, the second term on the right-hand side of eq. (5.52) must become sufficiently positive so as to make  $\Delta G$  itself positive so that reaction (5.51) is reversed. Other factors being equal, the reversal is brought about more easily when  $n$  is higher. As already mentioned, the higher oxidation states bring about a greater change in the entropy of the reaction favouring the decomposition reaction.

Figure 5.16 illustrates the variations in  $\Delta G$  for reactions at different pressures. The slopes of the lines given in this figure change with a change in  $n$ , for the reasons already discussed. The relative positions of the pairs of lines representing the free energy changes for the chloride compounds indicate that  $WCl_6$  can be decomposed over a range of temperature and pressure as experimentally substantiated. It will be seen that such a range of conditions does not exist for  $TaCl_5$ . Tantalum is obtained in the solid state only when reduced pressures are used. Even then, the decomposition temperature of  $TaCl_5$  would be rather high. Hafnium, obviously, cannot be deposited below its melting point under the conditions shown in Fig. 5.16. It may be possible to do so using pressures as low as  $10^{-6}$  atm or lower, but in such a situation, the metal yield would be extremely small.

The entropy change of the decomposition reaction becomes a decisive factor in the decomposition of a halide under optimum conditions.

The entropies of reactions involving tetraiodides, such as those used for the deposition of Ti, Zr, or Hf, are smaller than those of reactions involving pentachlorides and hexachlorides. As indicated in Table 5.2a, the heats of formation of iodides are, however, much less negative than those of the corresponding chlorides. This leads to a situation where this relatively smaller change in entropy can promote the deposition of the metal. The dissociation temperatures of the iodides of some metals are as follows: Be, 800°C; Cr, 1100°C; Cu, 900°C; Fe, 1100°C; Hf, 1600°C; Ni, 1030°C; Si, 1000°C; Th, 1700°C; Ti, 1400°C; U, 1200°C; Zr, 1400°C.

From the foregoing discussion, we may be tempted to conclude that all decomposition reac-

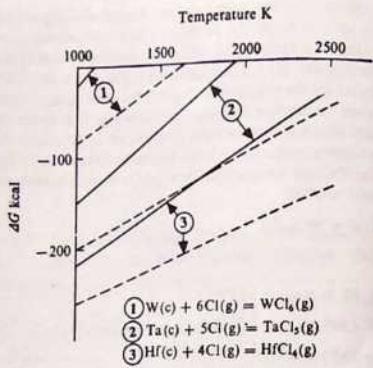


Fig. 5.16 Variation of Free Energy of Formation of Chlorides with Temperature (solid lines for 1 atm, dashed lines for  $10^{-3}$  atm) (after Shelton, 1968a).

tions are aided by applying reduced pressures. Although this conclusion is thermodynamically true, practical limitations set a lower limit for the pressure reduction. This limit corresponds to the pressure at which the rate of deposition just equals the rate of evaporation of the deposited element due to its own vapour pressure at the given temperature.

#### Kinetics of iodide process

The kinetics of the deposition of a metal on a hot filament depends on a large number of factors (see Shelton, 1968b). These factors can be better understood with reference to a typical set-up (see Fig. 5.17) for the iodide process that allows the formation and decomposition of vapours. It should be emphasized that Fig. 5.17 depicts only one of the several arrangements possible.

Some general observations on reaction kinetics are as follows:

(1) The deposition of the metal involves several steps, namely, the diffusion of the compound (say, iodide vapours) to the filament, the chemical decomposition reaction at the filament, and the outward diffusion of the gaseous decomposition product (iodine in this case). In addition, the reaction of the crude feed with iodine should also be considered. If it is assumed that the rate of combination of iodine with the impure metal is as rapid as the rate of decomposition of the iodide on the filament, then the rate of deposition in the case of small filaments, would increase proportionately with the surface area. However, a point is soon reached at which the gases are not supplied to or removed from the filament rapidly enough for the rate to be determined by the surface area alone. In other words, the rate initially depends on the reaction at the filament surface, but, with the passage of time, the diffusion phenomena become important. In fact, unless the filament is very small, the diffusion of the gaseous species becomes independent of the available surface area.

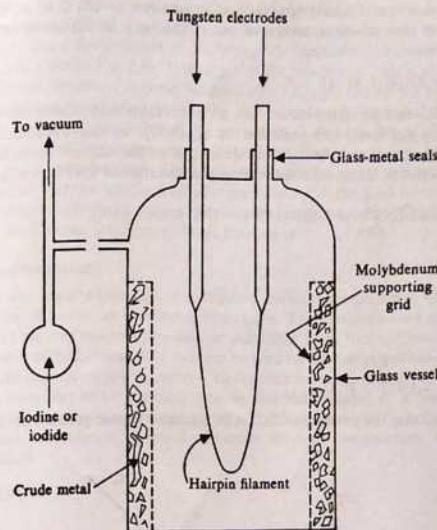


Fig. 5.17 Set-Up for Van Arkel Process.

(2) The rate of deposition is very sensitive to the geometry of the arrangement of the filaments with respect to the crude feed.

(3) The nature of the feed material also influences the process. For example,  $ZrI_4$  when reduced with sodium in a bomb, produces a metal feed material which is superior to the feed prepared by some other methods.

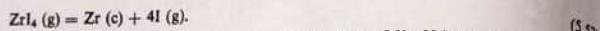
(4) Theoretically, the deposition reaction is not influenced by the lower iodides which may be formed at the surface of the crude metal. However, the subhalide formation has an indirect effect. At low rates of metal deposition, the subhalide formation causes the solid tetraiodide to disappear, thus altering its vapour pressure in the system. A change in the vapour pressure changes the rate of deposition.

(5) The temperature of the vessel and that of the filament seem to be the most important parameters.

#### Effect of ambient or vessel temperature

The rate of metal deposition usually increases with the ambient temperature up to a certain limit and then decreases. For example, the rate of deposition of zirconium from zirconium

tetraiodide, at a constant filament temperature, is very low at 150°C or at 350°C. However, around 260°C, this rate attains a maximum value. This may be explained as follows. Let us consider the reaction



The thermodynamic data for this reaction are given in Table 5.2b. Using the known value of  $\Delta G^\circ$  and following the procedure indicated in eq. (5.52), we can calculate the equilibrium pressure of both the iodine and the iodide in the system at the ambient temperature as well as the filament temperature. At an arbitrary filament temperature of 1377°C, we have

$$\Delta G_T^\circ = -RT \ln \frac{p_1^4}{p_{\text{ZrI}_4}} = (188.7 \times 10^3) - (79.3 \times 1.65 \times 10^3).$$

This gives

$$\log \frac{p_{\text{ZrI}_4}}{p_1} = 7.7,$$

i.e.,

$$\log p_{\text{ZrI}_4} - 4 \log p_1 = 7.7,$$

$$\log p_1 = -1.925 + \frac{1}{4} \log p_{\text{ZrI}_4}. \quad (5.54)$$

It should be noted that the pressure of  $\text{ZrI}_4$  is its saturated vapour pressure at the ambient tem-

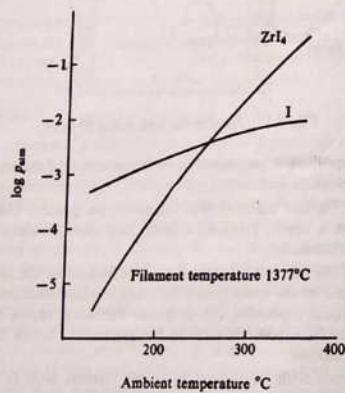


Fig. 5.18 Variation of Pressure of Iodine at an Arbitrary Filament Temperature of 1377°C and of Zirconium Tetraiodide, as a Function of Ambient Temperature (after Shelton, 1968a, 1968b).

perature, as given by the data for vaporization of  $\text{ZrI}_4$  (see Table 5.2b). From eq. (5.54), we can calculate, for the same filament temperature, the vapour pressure of iodine for different ambient temperatures (i.e., for different values of  $\text{ZrI}_4$  pressure). Some of the values calculated by Shelton (1968a, 1968b) are given in Fig. 5.18. It is seen that the pressure of  $\text{ZrI}_4$  is more sensitive to the ambient temperature. However, at lower temperatures, i.e., up to about the temperature at which the rate of deposition is maximum, the kinetics is predominantly governed by the diffusion of iodine. In fact, the tetraiodide vapours do not influence the kinetics at all. Beyond a certain temperature, the tetraiodide pressure rapidly exceeds the iodine pressure. Moreover, the total pressure in the system also increases. These factors alter the transport process drastically. At this stage, iodine, which makes a smaller fractional contribution to the total pressure, must diffuse in an increasingly dense medium. In a sense, this may be construed as interfering with the removal of iodine from the filament, implying a slower reaction rate.

#### Effect of filament temperature

As the filament temperature increases, at a constant ambient temperature, the equilibrium dissociation pressure of iodine at the filament increases. The pressure values at different filament temperatures and ambient temperatures can be calculated from thermodynamic data using the procedure already outlined. These data can also be used for an analysis of the transport process.

In general, the deposition rate increases with the filament temperature. At very high temperatures, however, there may be an apparent drop in this rate because of a loss of metal due to evaporation. This is specially true if the melting point of the metal is not very much higher than the filament temperature. Below a minimum filament temperature, the rate becomes immeasurably small.

#### ZONE REFINING

##### Basic Principles

In zone refining, the principles of fractional crystallization are made use of in a more efficient way. Since this refining technique is employed for producing ultra-pure materials, the starting material has only a low concentration of the impurity.

Let us consider the phase diagram of metals A and B shown in Fig. 5.19. The addition of B lowers the melting point of A and the addition of A raises the melting point of B. When a melt of composition P solidifies, the first solid to separate has a composition Q and contains less of B, provided equilibrium conditions prevail. However, under normal conditions, solidification takes place so quickly that no equilibrium is established at the liquid-solid phase boundary. If equilibrium is reached, an equilibrium distribution coefficient or segregation coefficient  $K_0$  may be defined for each component of the solution. For solvent A which has B as an impurity, at equilibrium, we have

$$\Delta G_{B(1)} = \Delta G_{B(0)}.$$

Therefore,

$$\Delta G_{B(1)}^{XS} - \Delta G_{B(0)}^{XS} = \Delta G_{B(1)}^{id} - \Delta G_{B(0)}^{id} = RT \ln \frac{a}{b},$$

where  $a$  is the concentration of the impurity in the solid and  $b$  its concentration in the liquid.

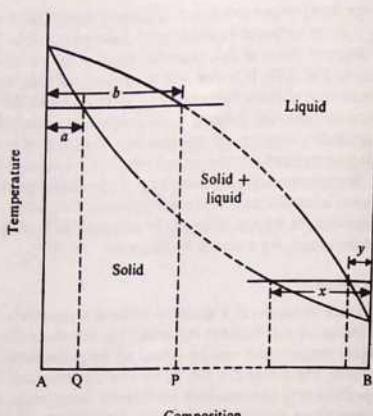


Fig. 5.19 Segregation Coefficients.

Now, we know

$$K_0 = \frac{a}{b} \quad (5.55)$$

i.e.,

$$[\Delta \bar{H}_{B(t)} - \Delta \bar{H}_{B(0)}] - T[\Delta S_{B(t)}^{XS} - \Delta S_{B(0)}^{XS}] = RT \ln \frac{a}{b}$$

If the excess partial molar entropies of a solution of B are the same in both the solid and the liquid, then

$$K_0 = \frac{a}{b} = \exp \left[ -\left( \frac{\Delta \bar{H}_{B(t)} - \Delta \bar{H}_{B(0)}}{RT} \right) \right]. \quad (5.56)$$

At very low concentrations of the impurity, the solidus and liquidus lines are almost straight, and  $K_0$  can be assumed to be a constant which is independent of temperature in this narrow concentration range. It is evident that when the solidus and liquidus are close to each other, the segregation coefficient is close to unity, and the possibility of refining by this technique is very small. The greater the difference between the solubility values of the impurity in the liquid and solid phases, the greater the deviation of the segregation coefficient from unity and the greater the chances of zone purification. This difference is due to the fact that the strain energy arising from the different sizes of atoms present in the solid is absent in the liquid. Consequently, the partial molar heat of solution of the solute B, i.e.,  $\Delta \bar{H}_B$ , in solvent A at a high dilution is normally more positive in the solid than in the liquid, i.e.,  $\Delta \bar{H}_{B(t)} - \Delta \bar{H}_{B(0)}$  may be large and positive, resulting

in a greater deviation of the segregation coefficient from unity. When  $K_0$  is less than unity, as at the A-rich end, the first solid to separate is purer than the liquid and when  $K_0$  is greater than unity, as at the B-rich, the impurity collects in that part which solidifies first.

It is necessary to ensure that the impurities rejected by the freezing metal are able to move away from the advancing solid. In practice,  $K_0$  depends on the diffusivities near the phase boundary in the melt, particularly if the solidification rate is greater than the diffusion rate. In such a situation, a concentration gradient exists from the solid-liquid interface to the bulk of the melt. Consequently, an effective distribution coefficient  $K_{eff}$  becomes more meaningful than  $K_0$ .  $K_0$  and  $K_{eff}$  are related by the equation (see Pfann, 1966)

$$K_{eff} = \frac{K_0}{K_0 + (1 - K_0) \exp \left( \frac{-f\delta}{D} \right)},$$

where  $f$  is the rate of crystallization,  $\delta$  the effective boundary layer thickness at the interface, and  $D$  the diffusion coefficient. The diffusion coefficient can be assumed to be a constant in the temperature range just above the melting point. Therefore,  $K_{eff}$  is mainly influenced by the crystallization rate  $f$  and the effective boundary layer thickness  $\delta$ .  $K_{eff}$  has the highest possible value when the values of  $f$  and  $\delta$  are small. The value of  $\delta$  can be made small by agitating the melt vigorously. To ensure efficient purification, provision should be made for a very low solidification rate and for the melt to be vigorously agitated. In zone refining, the impure material is taken in the form of a rod, and a travelling melting zone is set up in the rod. A narrow zone near one end of the rod is first melted and then moved slowly to the other end of the rod. This is achieved by the slow movement of the rod or of the heating unit. The zone passage is repeated several times in the same direction. The principle of the zone refining process is illustrated in Figs. 5.20a and 5.20b (Pfann, 1952).

Let us consider the zone refining of a rod of element A which contains element B as an impurity having a composition P (as shown in Fig. 5.19). Let us take the length of the rod as  $L$  and the width of the zone as  $l$ , as shown in Figs. 5.20a and 5.20b. The distribution of B along the length of the rod after one zone passage is shown in Fig. 5.20b. Before the zone passage, the concentration of B throughout the material is  $C_0$ . Assuming that the diffusion in the solid is slow, the first liquid is formed at temperature  $T$  with composition P (see Fig. 5.19). In the zone at the left extremity, which solidifies first, the concentration of B changes to  $K_0 C_0$ , corresponding to Q (see Fig. 5.19). This concentration increases as the distance from the end increases because the concentration of B in the molten zone gradually increases due to rejection from the solid. After a certain distance from the end, a point is reached where the concentration  $C_0$  remains unchanged, showing that the solidified material and the freshly melting material have the same concentration of B. At the other end, the concentration of B is increased. After each zone passage, the left extremity of the rod becomes purer, and the impurity accumulates at the right extremity. After repeated passes, the impure end is removed, leaving behind a zone-refined pure material. Maximum segregation is obtained under freezing conditions, which prevent any significant diffusion in the solidifying metal and, at the same time, permit the liquid to maintain as uniform a composition as possible. At the solid-liquid interface, when a layer enriched in impurities builds up in the liquid phase, the crystallization of the less pure solid results. Therefore, as already mentioned, agitation helps in maintaining uniformity in composition in the liquid phase. If agitation is not possible, then such uniformity depends on convection and diffusion. When the

zone is heated by induction, the characteristic induction stirring of the melting process is helpful. A reciprocal turning of the two solid parts of the rod around their mutual axis may also contribute to mixing.

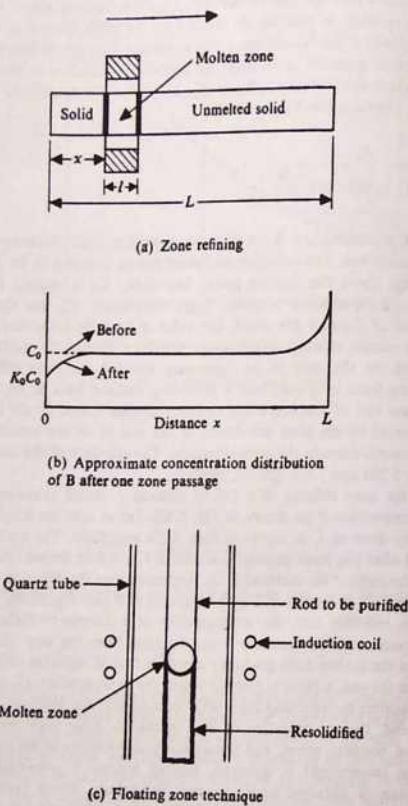


Fig. 5.20 Illustration of the Principle of Zone Refining.

Zone refining is particularly useful for preparing high-purity metals for a variety of applications. One of the earliest applications was in the purification of germanium, which is used in

transistors. By this technique, the level of each impurity can be reduced to one part per million or less. The rod to be purified can be maintained either in a vertical or horizontal position.

#### Floating Zone Technique

If it is desired to avoid contamination by contact with the crucible material, the *floating zone technique* can be resorted to. The rod to be purified is kept in a vertical position without any side support in a quartz tube having a provision for controlling the atmosphere. This arrangement is shown in Fig. 5.20c. The heating is by induction or, alternatively, by electron bombardment. The collapse of the molten zone is prevented by (1) surface tension effects, (2) the presence of surface films on the metal, and (3) the application of an electromagnetic field. The dissolved gases are also removed by the continuous evacuation of the tube.

#### VACUUM ARC REMELTING

*Vacuum arc remelting* has been primarily developed for consolidating and refining reactive and refractory metals, for example, titanium, zirconium, and tungsten, which are initially produced in the form of powder, sponge, or granules. At present, vacuum arc remelting is also employed for producing quality steels and alloys.

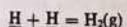
Figure 5.21 serves to illustrate the principle of a consumable vacuum arc remelting furnace. A d.c. power supply is used during consumable arc melting. The metal to be refined is first cast or forged in the form of an electrode. If the metal is in the form of a powder, it is die-pressed into compacts of suitable size which are then welded together to form a long electrode. Alternatively, isostatic pressing can also be used to prepare the electrode.

After the furnace chamber has been evacuated, an electric arc is struck between the metal electrode (negative) and a metal pad kept on the base of the water-cooled copper crucible (positive). The electrode is gradually lowered with the help of the sliding vacuum seal as its tip melts due to the arc power. A constant spacing is maintained between the electrode tip and the surface of the metal pool formed. A refined ingot builds up progressively inside the crucible. A pressure of the order of  $10^{-3}$  mm Hg is normally maintained during arc melting. Arc control during melting is essential because the uniformity of arc conditions has a profound influence on the homogeneity of the resulting ingot. During melting, the following metallurgical effects are observed which contribute to the purification of the metal:

(1) There is considerable degassing in the arc zone, mainly from the electrode surface and the bath surface and volatile impurities are removed depending on the pressure and temperature prevailing in the arc.

(2) The deoxidation of the metal may be brought about if an element with a stronger affinity for oxygen is present in the metal, provided the metal oxide is volatile enough. For example, if carbon is present in a tungsten electrode, both carbon and the dissolved oxygen are removed in the form of gaseous carbon monoxide because of the high temperature and vacuum conditions prevailing. Deoxidation of the metal by vaporization of the metal oxide is also possible.

(3) Dissolved gases in the metal, i.e., atomically dissolved, are also removed by diffusion to the liquid metal-gas interface where a reaction of the type



can occur. In this reaction,  $\underline{H}$  denotes dissolved hydrogen. The gaseous product is continuously pumped out.

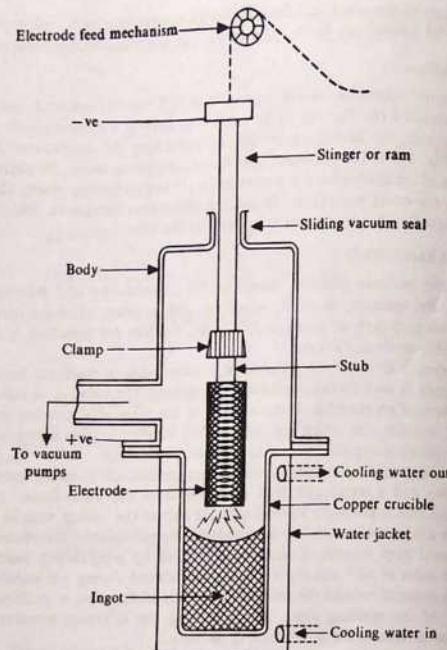


Fig. 5.21 Consumable Vacuum Arc Remelting Furnace.

(4) The cleanliness of an ingot depends on the size, distribution, and concentration of the nonmetallic inclusions. As the metal falls from the electrode surface to the metal pool in the form of droplets, the large inclusions present in the metal are dispersed by the arc, and this dispersion brings about a uniform distribution of small inclusions throughout the melt.

(5) The vacuum remelting process produces an ingot which is free from axial unsoundness with the minimum amount of macro-segregation (in the case of alloys). This improvement in quality is characteristic of all ingot solidification processes, where continuous freezing out of the material from a small molten pool occurs. When a large volume of a liquid alloy solidifies, the first solid that freezes may have a different composition from the last drop that freezes. This effect is minimized in processes such as vacuum arc remelting and electroslag refining.

(6) The vacuum arc remelting process does not remove the sulphur and phosphorus dis-

solved in the electrode material.

(7) The water-cooled, noncontaminating copper mould prevents the pick-up of impurities from the container material.

#### ELECTRON BEAM MELTING

The development of electron beam melting as a remelting technique has taken place through the processing of reactive and refractory metals. When a highly accelerated beam of electrons impinges on any material, the kinetic energy of the electrons is transferred to the lattice and its temperature rises gradually due to the thermal energy generated in the material. In due course, the material melts. Any material known to undergo solid-liquid transition can be melted by this technique. A vacuum is needed for the production and operation of the electron beam. Therefore, the melting unit requires a pumping system with a high capacity in addition to a high-power electron gun. A schematic drawing of the melting system is shown in Fig. 5.22. Droplets of the

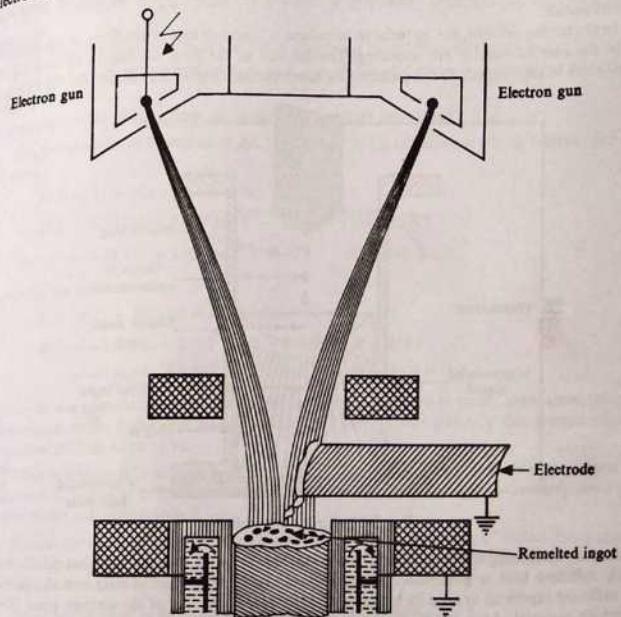


Fig. 5.22 Electron Beam Melting.

molten metal collect and solidify in the water-cooled mould. Unlike in vacuum arc melting, in this melting process, the material can be maintained in the molten state for long periods, and, as a result, the volatile impurities can be eliminated to a greater extent. A vacuum better than  $10^{-3}$  mm Hg is applied, which leads to the selective distillation of the volatile impurities. These factors help in obtaining a purer ingot than in the case of vacuum arc melting, although the metallurgical effects brought about by both the processes are the same. Tantalum and niobium are two of the metals exclusively processed by electron beam melting and zirconium and hafnium are two of the reactive metals which are customarily processed by electron beam melting. In addition, the purity of metals such as molybdenum, tungsten, and titanium can be considerably improved by electron beam melting.

#### ELECTROSLAG REFINING

In contrast to the vacuum arc remelting process, electroslag refining has been primarily developed for refining steels, but is also finding application in the consolidation and refining of some non-ferrous metals.

In electroslag refining, the material to be refined is forged or cast in the form of an electrode, as in the case of vacuum arc remelting. The droplets of the metal are refined under a reactive slag, which is kept molten by the passage of a heavy current. Figure 5.23 illustrates the principles

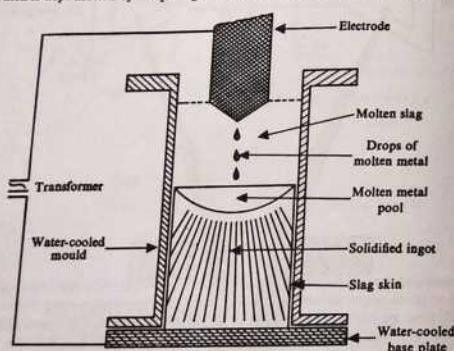


Fig. 5.23 Electroslag Refining.

underlying electroslag refining. When a heavy current is passed through the electrode and the melt, sufficient heat is generated in the slag to maintain it in the molten state and also to build up sufficient superheat to raise its temperature to a value above that of the melting point of the electrode material. As a result, the submerged electrode tip melts and droplets of molten metal fall through the reactive slag and solidify in the water-cooled mould. The electrode is continuously

lowered as its tip gets consumed. The refining reactions take place at the interfaces between the electrode tip and the slag, the droplet and slag, and the metal pool and the slag.

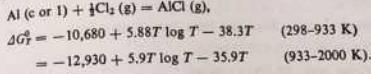
Calcium fluoride-base slags are commonly used in the electroslag refining of steels and nickel-base alloys. Calcium oxide and alumina are the other constituents of the refining slag. Some other halide slag compositions are being tried for the refining of nonferrous metals. The basic slag considerably reduces the sulphur content of the electrode material. It has been found that large-sized nonmetallic inclusions present in the electrode material are eliminated and the finer inclusions are uniformly distributed in the ingot. As in the case of vacuum arc remelting, the solidified ingot obtained by solidification in a shallow liquid metal pool is comparatively free from segregation. It is evident from the very nature of the electroslag refining process that dissolved gases are not removed.

#### PROBLEMS

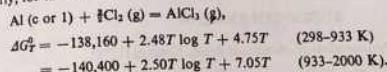
1. In the production of pure metals, the majority of existing processes fall into two broad categories:
  - (a) Refining after reduction, i.e., the conventional pyrometallurgical process.
  - (b) Reduction after refining, i.e., a pure compound of the metal is prepared before the metal is produced.

Discuss the factors which govern the choice between these two routes.

2. The free energies of formation of  $\text{AlCl}_3(\text{g})$  and  $\text{AlCl}_2(\text{g})$  in cal/mole are as follows. For the reaction



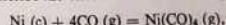
Similarly, for the reaction



Discuss how a monohalide disproportionation process can be used to purify aluminium. Give the approximate values of the operating temperatures of the different stages in this process when it is used for plating Al on to Fe.

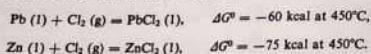
3. What is a chemical transport reaction? Describe how the suitable operating parameters for the chemical transport of a metal in the vapour phase can be related to the thermodynamic properties of the reactions involved.
4. Discuss the electrochemical principles involved in the electrorefining of metals using molten salts. Illustrate your answer with reference to the refining of (a) titanium, (b) lead, and (c) aluminium.

5. Describe the effect of an increase of pressure on the reaction



which is used for the purification of nickel. Calculate the volume fraction of  $\text{Ni}(\text{CO})_4$  in a  $\text{CO}_2$ - $\text{Ni}(\text{CO})_4$  gas mixture that is in equilibrium with pure nickel at a temperature of  $180^\circ\text{C}$  and a total pressure of 70 atm. Also calculate the temperature at which we can obtain the same volume fraction of  $\text{Ni}(\text{CO})_4$  at a total pressure of 1 atm. Assume that for the aforesaid reaction,  $\Delta H^\circ = -35,000 \text{ cal}$  and  $\Delta S^\circ = -100 \text{ cal}/\text{degree mole}$ .

6. In Parke's process for the desilverization of lead, lead is contaminated with a small percentage of zinc. This zinc may be removed by the chlorination of the melt at  $450^\circ\text{C}$ , when zinc chloride and lead chloride form a solution immiscible with the metal phase. Assuming equilibrium conditions to prevail and that the chloride solution is ideal, determine the wt % zinc in the refined lead when the chloride solution contains 0.12 mole fraction lead chloride. The activity coefficient of zinc at  $450^\circ\text{C}$  may be taken as 14. The reactions are



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## 6 Extraction of Metals from Oxides

### 6.0 INTRODUCTION

Since oxygen is abundant both in the earth's crust and in the atmosphere, and also since oxides are comparatively stable, numerous metals exist in nature as compounds of oxygen. These compounds include simple oxides, carbonates, double oxides, complex silicates, and phosphates. The concentration of such compounds in ore deposits may sometimes be sufficiently high to approach the theoretical obtained composition, for example, iron in deposits rich in hematite and aluminium in deposits rich in bauxite. In other ore deposits, the mineral values may be very dilute due to the presence of excessive amounts of gangue materials such as silica and clay; for example, oxide ores of tin such as cassiterite are invariably of a very low grade.

We now discuss some of the important criteria used for the extraction of metals from oxide ores.

(1) The ore must be rich in mineral. A low-grade ore must be beneficiated prior to reduction in order to (a) minimize the use of the reductant, (b) maximize metal recovery, (c) minimize the energy requirements, and (d) obtain a metal of the desired purity. In general, oxide ore is upgraded by magnetic separation, electrostatic separation, or gravity separation. Flotation is employed only in exceptional cases, for example, in the enrichment of a copper oxide ore.

(2) The thermodynamic stability of an oxide dictates the choice of reductant. From the free energy diagram for oxides (Fig. 2.1), we observe that the oxides of most common metals can be reduced by carbon at temperatures below 1600°C. Wherever feasible, the reduction of a metal oxide to metal is carried out by a carbonaceous reductant because of the low cost involved. On the other hand, carbon is not suitable for reducing the oxides of alkali and alkaline earth metals because of their high thermodynamic stability. Also, in the case of metals such as titanium and uranium, which form stable carbides, carbonaceous reductants are not preferred because the further process of separating the metal from the carbon in the carbide is uneconomical. For such metals and also for alkali and alkaline earth metals, the oxide is first converted to the chloride and the metal is subsequently produced by reducing the chloride either by another metal that forms a more stable chloride or by the electrolysis of the fused chloride. (This chapter deals with the direct extraction of the metal from the oxide mineral; processes where the oxide ores are first converted to halides before reduction are discussed in Chapter 8.)

(3) A metal which forms an oxide more stable than that of the desired metal can be used instead of carbon for reduction. However, in most instances, this method is not economically attractive except when carbon cannot be used or where carbon cannot be tolerated in the product metal as in the case of many ferroalloys.

(4) Generally, at the temperature needed for oxide reduction, the metal is in a molten form, and the gangue softens or melts. In general, fluxes such as lime and silica are used to react with the gangue to produce a fluid slag to enable a good separation of the metal from the

slag. In order to recover the metal to the maximum extent possible, it is essential that the metal loss in slag be minimized.

### ENERGY-SAVING AND ENVIRONMENTAL FACTORS

The reduction of a metal oxide to metal by carbon is an endothermic process, i.e., it requires a large amount of energy. As is evident from Table 4.9, the extraction of magnesium from seawater and that of aluminium by the Bayer process are the most energy-intensive, after titanium extraction. Some new extraction processes such as the ALCOA (Aluminium Company of America) process for aluminium are being developed mainly to save energy.

In the extraction of metal from oxide ores, carbonaceous reductants are used for reduction and fossil fuels are used for supplying heat. Alternatively, electrical reduction is employed when carbon reduction is not feasible. The main gaseous discharge from these unit operations consists of CO<sub>2</sub> and water vapour which are relatively harmless to the environment. The slags produced during pyrometallurgical operations also have little harmful effect on the environment. However, when hydrometallurgical process is used in the refining of oxide ores, care has to be exercised while disposing of the residues.

### 6.1 MAGNESIUM

#### USES

Magnesium is the only metal in group IIA of the periodic table which finds extensive application. The general uses of the metal fall under two main heads, namely, nonstructural and structural.

#### Nonstructural Uses

Nonstructural uses include application in alloying, deoxidation and desulphurization of molten metals, modifying the structure of graphite in cast irons, pyrotechnics, photography, and cathodic protection.

#### Alloying

Magnesium is widely used in alloying, especially in aluminium-base alloys, to which it imparts hardness, strength, and corrosion resistance. It is also used to improve the mechanical properties of lead-base alloys containing Ca, Sn, and In.

#### Deoxidation and desulphurization

Magnesium is used to deoxidize and desulphurize molten metals. Since magnesium has a strong affinity for oxygen, it effectively deoxidizes many molten metals.

At present, in the production of iron and steel, the sulphur content in the blast furnace coke is rather high, and the product, namely, pig iron, contains a large quantity of sulphur. To reduce the sulphur level to less than 0.01 per cent, magnesium, in the form of Mag-Coke or as magnesium wire, is injected into the hot metal.

#### Modifying structure of graphite in cast irons

Magnesium can effectively nodulize graphite particles in cast iron producing spheroidal graphite (S.G. iron) which is stronger, tougher, and more ductile than ordinary cast iron. S.G. iron is widely used in the automotive industry.

**Pyrotechnics and photography**

When ignited, magnesium emits a brilliant light. This property is extensively applied in pyrotechnics and photography. Flashlight powder consists of magnesium powder mixed with chemicals which readily give off oxygen when heated, for example, potassium chlorate, potassium permanganate, and manganese dioxide. It may be noted that the intensity of light emitted by the ignition of magnesium is exceeded only by the combustion of zirconium or tantalum.

**Cathodic protection**

To provide cathodic protection to pipelines, storage tank bases, and lead-sheathed cables, 'sacrificial' magnesium anodes are placed in the soil and connected by means of an insulated wire to the material that is to be protected against corrosion. In such an arrangement, the corrosion attack is directed preferentially against the magnesium, and the material is spared.

**Structural Uses**

Alloys of magnesium and aluminium are noteworthy for properties such as light weight, machinability, damping capacity, rigidity (without excessive weight), and resistance to corrosion by chemicals. Consequently, magnesium alloys find structural use mainly in the aircraft industry. Of late, their application has been extended to land transportation and material handling.

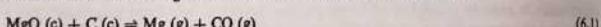
**6.2 MAGNESIUM ORES**

The most important minerals of magnesium are dolomite ( $MgCO_3 \cdot CaCO_3$ ); magnesite ( $MgCO_3$ );  $MgCl_2$  and  $MgSO_4$ , present in sea-water; brucite [ $Mg(OH)_2$ ]; carnallite ( $MgCl_2 \cdot KCl \cdot 6H_2O$ ), present in exposed sea beds; olivine ( $Mg_2SiO_4$ ); serpentine ( $Mg_3Si_2O_5$ ); asbestos ( $CaSiO_3 \cdot 3MgSiO_3$ ); and kainite ( $MgSO_4 \cdot KCl \cdot 3H_2O$ ). As mentioned in Chapter 3, India has abundant reserves of the first three minerals. At present, a major portion of the world's magnesium is produced from these three minerals.

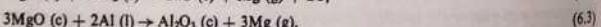
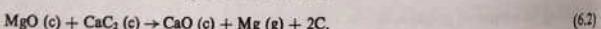
The commercial minerals, namely, dolomite and magnesite, and the magnesium hydroxide derived from sea-water have a sufficiently high magnesium content and do not require upgrading before being subjected to subsequent metal extraction processes.

**6.3 METHODS OF MAGNESIUM EXTRACTION**

As is evident from Fig. 2.1,  $MgO$  is one of the most stable oxides, and a temperature higher than  $1800^\circ C$  is required to reduce it with carbon. The reduction temperature can be lowered by applying a vacuum to distil off the magnesium and to drive the reduction reaction



to the right. It is, however, very difficult to prevent the backward reaction of the  $Mg$  vapour with  $CO$ , and hence, carbon reduction has not found commercial acceptance. Consequently, other reductants such as  $CaC_2$  (which provides  $Ca$ ) and  $Al$  have been successfully employed at  $1200^\circ C$  under vacuum in order to reduce  $MgO$ . The reactions are



Although reduction by  $CaC_2$  and  $Al$  is feasible, it is not commercially attractive. Pidgeon

(Pidgeon and Alexander, 1944) developed a process that is both economic and commercially acceptable to reduce  $MgO$ . It is based on the reduction of  $MgO$  by ferrosilicon in the presence of  $CaO$ , under vacuum.

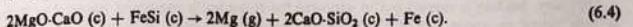
Magnesium cannot be readily electrolyzed from aqueous media because hydrogen is evolved before magnesium can be deposited. This is because  $Mg$  requires  $2.3\text{ V}$  more than  $H_2$  for deposition and the hydrogen overvoltage is not sufficiently high to overcome this voltage (for details, see Chapter 2). To generate a sufficiently high hydrogen overvoltage, the use of an amalgam cathode has been suggested. An amalgam cathode serves two purposes. First, because of its extremely smooth surface, the evolution of hydrogen is rendered difficult. Second, the low magnesium activity in the amalgam cathode lowers the magnesium deposition potential. An amalgam cathode has, however, not been found commercially acceptable.

**MAGNESIUM FROM SEA-WATER**

Most of the magnesium presently produced is by the electrolysis of fused salts that contain magnesium chloride. Magnesium chloride is mainly obtained from sea-water by the Dow process (for details, see Chapter 8).

**6.4 PIDGEON PROCESS**

As Fig. 2.1 shows, on thermodynamic grounds, pure silicon cannot reduce  $MgO$  when both the reactants and the products are in their standard states. To overcome this difficulty, Pidgeon applied a reduced pressure in order to remove the  $Mg$  vapour and to drive the reduction reaction. In the Pidgeon process, calcined dolomite is briquetted with powdered ferrosilicon (75 per cent Si), and the reduction is carried out under a vacuum of  $0.1\text{ mm}$  of mercury at  $1100-1200^\circ C$  in an externally heated retort (see Fig. 6.1). The overall reaction is



In reaction (6.4), magnesium is the only gaseous product and is removed from the retort to

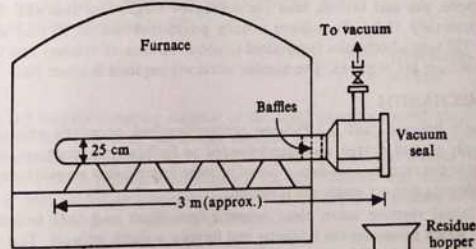
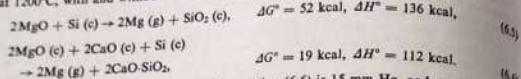


Fig. 6.1 Retort for Pidgeon Process.

avoid the possibility of back reaction during cooling and condensation.

To appreciate the advantages of the presence of  $CaO$ , we consider the free energies of reac-

$$2\text{MgO} + \text{Si}(\text{s}) \rightleftharpoons 2\text{Mg}(\text{g}) + \text{Si}$$



At 1200°C, the equilibrium pressure of Mg for reaction (6.6) is 15 mm Hg, and to attain 1 atm of Mg, a temperature of about 1700°C is required. Since such a high temperature is not practicable, especially when indirect heating is desired, Pidgeon resorted to the use of vacuum to drive reaction (6.6) to the right (see Pidgeon and King, 1948).

Reaction (6.6) is highly endothermic, and hence, a large heat input is required. It has been found that a small addition of  $\text{CaF}_2$  or  $\text{MgF}_2$  to the reactants speeds up the evolution of the Mg vapour. Since the vapour pressure of Mg is not altered, the effect of the fluoride addition is considered catalytic.

## EQUIPMENT AND OPERATION

In the Pidgeon process, the retorts, each of which is nearly 25 cm in diameter and 3 m in length, are inserted horizontally in a single furnace (about 20 per furnace), as shown in Fig. 6.1. These retorts are usually made of NiChrome steel (Ni 15 per cent, Cr 28 per cent, Mn 1.25 per cent, Si 1.5 per cent, C 0.3 per cent, and Fe balance) and last for about a year when continuously employed for batch operation. There is no special cooling arrangement for the exposed ends, which are merely air-cooled. The furnace is heated either by gas or electricity. The furnace feed material consists of briquettes made out of powdered calcined dolomite and ferrosilicon in the proportion one silicon to six calcine. The total weight of the charge is approximately 100 kg.

Initially, heating is carried out to vaporize the structurally combined water. The temperature is then raised to about 1150°C, and the application of vacuum is commenced. At this stage, magnesium vaporizes and condenses at the cool end. In some cases, baffles may also be provided for the condensation of the Mg vapour at the cool end. After 8-10 hours, the application of vacuum is stopped, the seal broken, and the condensed magnesium removed. The yield per retort is approximately 15 kg. To achieve a daily production rate of 10 tons of magnesium, approximately 12 tons of dolomite (equivalent to about 60 tons of calcine) and approximately 12 tons of ferrosilicon are required. The number of retorts required is about 300.

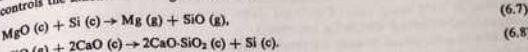
## REACTION MECHANISM

It was originally believed that the Pidgeon process involved essentially solid-state reactions. Therefore, a finely ground charge was recommended to facilitate the reactions. However, it is now accepted that the reactions produce a liquid at some intermediate stage. During the Pidgeon process, the following distinct stages are observed:

(1) The initial reaction takes place between ferrosilicon and CaO to produce a liquid Ca-Si-Fe alloy, which permeates the briquette and forms a metallic network. This reaction takes place rapidly at around 1000°C and is mildly exothermic. The ternary alloy serves as the main reducing agent.

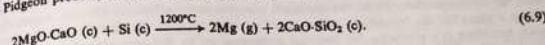
(2) Magnesium vapours are produced by the reduction of MgO by the Ca-Si-Fe alloy. At this stage, the pressure builds up rapidly, slowing down the rate of reaction. The subsequent reaction rate is governed by the rate at which magnesium can escape from the briquettes.

$$Toguri \text{ and Pidgeon (1962) have proposed that the presence of the SiO vapour in the Pidgeon process controls the kinetics according to the reactions}$$



REQUISITES REQUIRED FOR THE PIGEON PROCESS

Ridgway process, the overall reaction taking place is



reaction (6.9), we can calculate the energy required as follows:

	kcal/kg Mg
Heat necessary to heat reactants to 1200°C	920
Heat required for reaction (6.9) at 1200°C	2330
Total	3250
If the heat is supplied by fuel combustion, the estimated heat efficiency for indirect heating at 1200°C is 40 per cent.	
Therefore, heat to be supplied by fuel	8125
Assume auxiliaries and heat losses consume equal amount of energy, i.e.,	8125
Total heat required per kg of Mg according to reaction (6.9)	16,250
Next, the energy for silicon production has to be considered:	
Energy needed for Si production (at 15 kWh/kg Si and 2650 kcal of fuel generates 1 kWh)	23,180
Total energy required	39,430

Despite the fact that the foregoing estimate of the total energy required assumes high heat losses for a small-scale operation, the energy required is only  $39.43 \times 10^6$  kcal/ton, which is only 46 per cent of the energy required by the Dow chemical sea-water process (see Table 4.9). This is because the Pidgeon process uses a higher grade raw material and does not require the large amount of heat needed to evaporate solutions as in the Dow process and the electrical energy needed in the subsequent fused chloride electrolysis.

#### MAGNOTHERM PROCESS

A magnetherm process is essentially a ferrosilicon reduction process similar to the Pidgeon process, except that it is carried out at a temperature of 1500°C and the bath is maintained in a molten state by the addition of alumina to form a molten slag. This process has been in operation since 1964 in France (see Campbell, 1971).

### 6.5 MAGNESIUM PRODUCTION IN INDIA

At present, India's requirement of magnesium is met exclusively by imports, the total quantity imported in 1978 being around 257 tons. (This figure does not include the finished magnesium components, which are also being imported.)

There is a persistent demand for magnesium; for example, from aluminium companies which produce various alloys, from mints for coinage applications, from the uranium plant of the Department of Atomic Energy, and from the defence establishments.

We now discuss two schemes that have been initiated in India for the limited indigenous production of magnesium. First, the National Metallurgical Laboratory (NML), Jamshedpur, has set up a plant for the ferrosilicon reduction of calcined dolomite. The present capacity is 250 tons/year, but there is a provision for eventual expansion up to 500 tons/year. Second, the Central Electrochemical Research Institute (CECRI), Karaikudi (Tamil Nadu), has successfully tested a pilot plant based on the electrolytic reduction of  $MgCl_2$  produced from magnesite.

#### NML PROCESS

In the NML process, the basic raw materials employed are dolomite, ferrosilicon (75–80 per cent silicon), and fluorspar. Dolomite is calcined in the temperature range 950–1100°C. The calcined dolomite and the ferrosilicon are first ground and then mixed with 1 per cent fluorspar. The mixture is then briquetted, and the briquettes are charged into tubular retorts made of high-resistant alloys with a high content of chromium and nickel. These retorts are set horizontally in an oil-fired furnace with the open ends projecting out of the end walls. The retorts are shut in an airtight manner and vacuum is applied. Magnesium is distilled from the charge [according to reaction (6.9)] and then condensed on a removable sleeve at the cold end of the retorts. Sodium and potassium, if present in dolomite, are also liberated, distilled, and condensed on the removable sleeve. Once the distillation of magnesium is complete, the retorts are opened, their contents discharged, and the cyclic operation continued. As pointed out in Section 6.4, the fluorspar essentially acts as a catalyst.

#### CECRI PROCESS

In the CECRI process, magnesite is initially converted to anhydrous magnesium chloride by chlorination. This chloride is then melted and electrolyzed in a fused salt medium, as in the Dow process and shall be discussed in Chapter 8.

### 6.6 ALUMINIUM

#### USES

Next to copper, aluminium is considered the most important nonferrous metal. Aluminium is remarkable in many ways. For example, it can be rolled, extruded, cast, formed, and machined as readily as, if not more readily than, competing metals such as iron and titanium. Its high strength-to-weight ratio is a distinct advantage in many structural applications. Further, the metal exhibits excellent corrosion resistance, electrical conductivity, and thermal conductivity. Some of the applications of aluminium and its alloys are mentioned in Table 6.1 along with the properties exploited in these applications.

The fact that aluminium is a good conductor of heat and electricity and is less expensive than copper, aids in rendering Al as a replacement for Cu.

Table 6.1 Applications of Aluminium

Application	Properties exploited
In impact extrusion of vessels and containers of various shapes	Ductility and flow properties
In kitchenware, chemical and brewing industries, and milk processing	Corrosion resistance and nontoxic properties
In packaging industry and decorative and protective surfaces	Rolling properties and ability to acquire brilliant surface finish
In roofing systems and thermal insulation either as metal foil or aluminium paint	High reflectivity and low emissivity
In aluminium alloys in transport industries and structural applications	Attractive mechanical properties in general and high strength-to-weight ratio
In electrical conductors	Excellent electrical conductivity
Deoxidizing	Strong affinity for oxygen

The thermal conductivities and electrical resistivities of Ag, Cu, Au, and Al (given in Table 6.2) are outstanding when compared with those of other metals. Since silver and gold are

Table 6.2 Thermal Conductivity and Electrical Resistivity of Some Metals

Metal	Thermal conductivity near 20°C (cal cm <sup>-1</sup> sec <sup>-1</sup> °C <sup>-1</sup> )	Electrical resistivity near 20°C (10 <sup>-6</sup> ohm cm)
Ag	1.00	1.59
Cu	0.94	1.67
Au	0.71	2.19
Al	0.53	2.66

highly expensive, they cannot be used on a commercial scale for electrical applications. In this area, copper has been found ideal. Although aluminium has a lower strength and a lower conductivity than copper, the factors that make it a competitor, especially when the copper price is high, are its widespread availability and its high strength-to-weight ratio.

We now give examples of the electrical application of aluminium.

A composite conductor made of aluminium wires that surround a core of steel wires with a high tensile strength is being extensively used as an overhead conductor. The core compensates

## ALUMINIUM ORES

The nature of the common minerals of aluminium has been discussed in Chapter 3. The more common minerals are gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) and diaspore ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). The theoretical percentage of  $\text{Al}_2\text{O}_3$  in gibbsite is 65.4 and that in diaspore 85.4. Bauxite is a mixture of these two oxides and contains varying amounts of impurities such as  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$ . The bauxite ores found in India normally contain between 58 and 67 per cent alumina. These ores have a high content of  $\text{TiO}_2$  (5–10 per cent) and a low content of silica, i.e., 0.5–2.0 per cent. The ore found in Kashmir are, however, strikingly different from the other ores in that they chiefly belong to the diaspore variety and contain around 75 per cent  $\text{Al}_2\text{O}_3$ , essentially no  $\text{TiO}_2$  and a high amount of silica as an impurity, i.e., above 5 per cent. The high silica content of these ores renders the Kashmir deposits unsuitable for purification by the Bayer process. In this process, during the leaching stage, silica forms a compound  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , which, in turn, forms an insoluble residue called red mud by reacting with other impurities in bauxite such as  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ . This causes a serious loss of alumina. For this reason, ores with a silica content above 5 per cent are considered unsuitable.

## 6.7 EXTRACTION OF ALUMINIUM

Like Magnesium oxide, aluminum oxide, too, is very stable (see Fig. 2.1). The carbothermic reduction of aluminum oxide has not been commercially adopted for the reasons now listed: (1) It requires a high temperature, i.e., almost 2000°C. (2) At this temperature, undesirable aluminum carbide is formed. (3) The refractories required for operation at such a high temperature are not only expensive but are also not readily available.

The extraction of aluminium by the electrolysis of aluminium salts in an aqueous medium is not feasible. This is because the decomposition of the aqueous solution, which results in the evolution of hydrogen, occurs at a much lower voltage than that needed for the electrodeposition of aluminium ions. Moreover, the hydrogen overvoltage is insufficient to overcome the 1.67-volt difference in potential between aluminium deposition and hydrogen evolution (for details, see Section 2.24).

The universally adopted process for the extraction of aluminium is the Hall-Héroult process in which alumina ( $\text{Al}_2\text{O}_3$ ) dissolved in cryolite ( $3\text{NaF}\cdot\text{AlF}_3$ ) is electrolyzed. Here, alumina (obtained from the Bayer process) in a pure form is employed as the electrolyte in the electrolytic cell. It may be noted that the Hall-Héroult process consumes a large amount of energy, i.e.,  $6.51 \times 10^6 \text{ kJ/mol}$  (see Table 4.10). A recent innovation seeks to convert the alumina obtained from the Bayer process into aluminium chloride, which is then electrolyzed in a fused salt medium containing  $\text{NaCl}$  and  $\text{LiCl}$ . In this innovation, the energy consumption is decreased by 30 per cent, which is a significant saving of energy especially with respect to the energy-intensive aluminium extraction process. Also, nonelectrolytic processes for the reduction of  $\text{AlCl}_3$  are being studied.

As the high-grade aluminium resources are getting rapidly depleted, low-grade aluminium minerals such as clay are becoming increasingly important in the extraction of alumina and aluminium.

A NEW PROCESS FOR ALUMINA PRODUCTION

In the Bayer process, high-purity alumina (required for subsequent electrolysis) is extracted from bauxite. In this process, bauxite is initially leached by NaOH under conditions of high pressure ( $25\text{ atm}$ ) and high temperature ( $220^\circ\text{C}$ ), to form soluble sodium aluminate, from which  $\text{Al}(\text{OH})_4^-$  is subsequently precipitated. When  $\text{Al}(\text{OH})_4^-$  is calcined,  $\text{Al}_2\text{O}_3$  is obtained. Figure 6.2 presents a

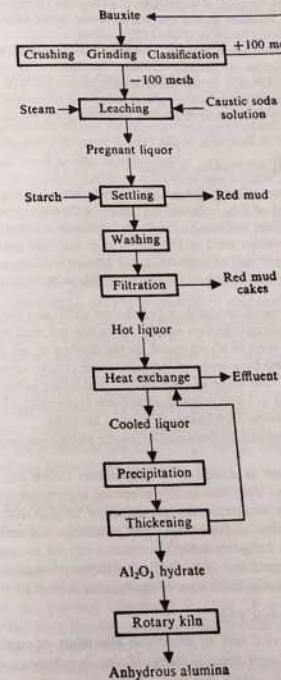
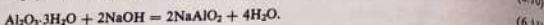
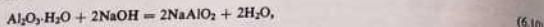


Fig. 6.2 Flowsheet for Bayer Process.

simplified flowsheet for the Bayer process.

At the outset, the bauxite obtained from the mines is crushed and ground to a very fine size in jaw crushers and hammer mills. As a result, the silica present in the bauxite tends to get concentrated in the finer fractions. This characteristic renders the bauxite amenable at least to partial beneficiation by screening. A bauxite with an average composition of 1.5 per cent silica may have, in the -100 mesh fraction, a silica content as high as 10 per cent. Commination thus leads to the enrichment of alumina in the coarser fractions. Some attempts at beneficiation by grinding and screening are being made at INDALCO Limited.

The crushed-bauxite is once again ground along with caustic soda in a ball mill to yield a slurry, which is fed into a digester (or autoclave). Here, the alumina in the bauxite is dissolved in caustic soda (150–350 gm/l Na<sub>2</sub>O) in the temperature range 150–220°C under a pressure of 5–25 atm. This treatment dissolves the alumina and leaves the impurities as suspended solids in the solution. The reactions for the monohydrate and the trihydrate, respectively, are



It should be noted that the dissolution of the monohydrate [reaction (6.10)] requires a temperature of 230°C and a time period of 3 hr, whereas that of the trihydrate [reaction (6.11)] requires a temperature of 180°C and a time period of 1 hr. Since bauxite is a mixture of the monohydrate and the trihydrate, the temperature used is 180–220°C and the time period allowed is 2.5 hr. Under these conditions, 86–88 per cent of alumina in the bauxite is taken into solution. At such high temperatures, a sufficiently high pressure (5–25 atm) must necessarily be applied in order to retain water in the liquid state.

The liquor from the Bayer process cooled to a little below 100°C and completely depressurized is next taken to the settling and clarification section where the red mud is deposited in settling tanks and is removed. Additives such as starch speed up the settling of red mud. Any remaining red mud in the liquor is eliminated by a series of washers where it is confronted with a counter-current flow of hot water. In the final stage of clarification, the liquor is filtered through a series of filters. The filtrate obtained is a clear solution of sodium aluminate. The residue left behind after filtration consists mainly of ferric hydroxide, silica, and alumina.

The heat in the hot liquor is tapped by heat exchanges for energy conservation and for cooling the liquor.

During precipitation, the filtrate is cooled to a temperature below the critical temperature required for alumina precipitation. Very fine freshly prepared aluminium hydroxide is added to make available nuclei in order to accelerate the precipitation of Al(OH)<sub>3</sub>. The precipitate is separated from the liquor in a series of thickeners. The product, a coarse hydroxide, is finally calcined in a rotary kiln to produce anhydrous Al<sub>2</sub>O<sub>3</sub>.

It may be noted that, to produce 1 ton of Al<sub>2</sub>O<sub>3</sub> by the Bayer process, we need 2.2–2.4 tons of bauxite, 0.08–0.12 ton of caustic soda, 8–10 tons of steam, and 0.18–0.20 ton of fuel oil.

#### FACTORS AFFECTING BAYER PROCESS

Several investigations have been carried out to determine the effect of various factors on the efficiency of the Bayer process. We now discuss some of the conclusions drawn from these investigations.

(1) The finer the bauxite, the better the digestion of alumina in the leach liquor.

(2) In general, wet grinding is more efficient than dry grinding. Wet grinding also cuts down the time required for subsequent digestion.

(3) Digestion is accelerated at higher temperatures. However, at a temperature above 100°C water would evaporate. Hence, to attain a temperature up to 220°C, high pressures up to 25 atm are applied.

We now consider an example. Glastonbury (1968) has expressed the kinetics of gibbsite dissolution as

$$r = 4.60 \times 10^5 A(C_{\text{NaOH}})^{1.71} e^{-23,850/(RT)}, \quad (6.12)$$

where  $r$  is the initial extraction rate (gm atom Al/sec),  $A$  the surface area of gibbsite (cm<sup>2</sup>),  $C_{\text{NaOH}}$  the sodium hydroxide concentration (moles/litre),  $R$  the gas constant, and  $T$  the absolute temperature. The relatively large activation energy, i.e., 23,850 cal/mole, required for reaction (6.11) indicates that temperature affects the kinetics to a great extent. For instance, the reaction rate at 100°C is approximately 150 times faster than that at 50°C.

(4) There is a lower limit to the temperature at which the digestion and its subsequent processing can be carried out. At a temperature below this limit, aluminium hydroxide may precipitate, during clarification, leading to a loss of alumina. Further, if it precipitates during the final filtration, not only is the filter cloth ruined due to clogging, but also alumina is lost. For efficient operation, the water is maintained at a temperature as close to the boiling point as possible.

(5) The sensible heat of the hot pregnant liquor after filtration is recovered by heat exchangers. This heat is used for producing steam for the digesters.

(6) In the precipitation stage, the entire quantity of alumina in solution is not allowed to precipitate because this may lead to the simultaneous precipitation of a large amount of dissolved silica, resulting in a product unsuitable for electrolysis. The precipitation is, therefore, deliberately kept incomplete, the residual solution being recirculated to the digestion stage.

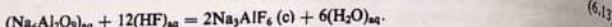
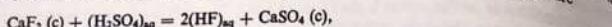
(7) For the efficient calcination of alumina, the rotary kiln should be able to attain a temperature as high as 1400°C. However, if the alumina is only to be dried, a temperature of 200°C is sufficient. The decomposition of Al(OH)<sub>3</sub> produces Al<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> · 3H<sub>2</sub>O (in both cases, water is chemically bound). The minimum temperatures required for the dehydration of the monohydrate and the trihydrate are 1200°C and 800°C, respectively. The addition of a small amount of CaF<sub>2</sub> sometimes helps in dehydration.

#### 6.9 HALL-HEROULT PROCESS

In 1886, Héroult in France and Hall in the U.S.A. independently patented a process which ousted all other existing processes for the commercial production of aluminium. At present, the Hall-Héroult process, which is based on the electrolytic decomposition of alumina dissolved in a liquid bath of cryolite, is the only widely practised commercial method. The modern versions are basically identical to the process introduced in 1886. A source of cheap electric power is the primary requisite for the Hall-Héroult process. This process also requires high-purity alumina, cryolite, and ashless carbon electrodes.

Since alumina is not an ionic compound, very few ionic melts are capable of dissolving it to any appreciable extent. However, cryolite (3NaF · AlF<sub>3</sub>)—a naturally occurring mineral—can dissolve up to 15 per cent alumina at 1000°C.

Of late, cryolite has been successfully synthesized by passing HF through sodium aluminum solutions, the HF being produced from naturally occurring  $\text{CaF}_2$ . The main reactions are



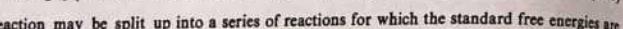
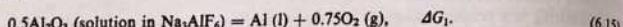
A flowsheet for the production of synthetic cryolite is shown in Fig. 6.3. Aluminium industries in India usually employ a mixture of natural and synthesized cryolite, both of which are imported. It may be noted that cryolite is yet to be synthesized in India on a commercial scale.

Small amounts of  $\text{CaF}_2$  and  $\text{NaF}$  are added to the cryolite bath to enhance its conductivity and to improve the metal recovery. At 1000°C, the density of the molten cryolite is approximately  $2.1 \text{ gm/cm}^3$  and that of  $\text{Al}_2\text{O}_3$  is  $3.96 \text{ gm/cm}^3$ . When a bath containing about 10 per cent  $\text{CaF}_2$ , 80 per cent cryolite, 5 per cent  $\text{Al}_2\text{O}_3$ , and a small amount of  $\text{NaF}$  is electrolyzed, the aluminium liberated (density  $2.3 \text{ gm/cm}^3$ ) is heavier than the bath and sinks to the bottom. (The metal is thus protected against atmospheric oxidation.) It is evident that density is one of the factors which limits the concentration of  $\text{Al}_2\text{O}_3$  in the bath. In other words, the higher the amount of  $\text{Al}_2\text{O}_3$  in the bath, the higher its density and consequently the sinking of aluminium is rendered more difficult.

DECOMPOSITION POTENTIAL OF  $\text{Al}_2\text{O}_3$  DISSOLVED IN CRYOLITE

Before discussing the technical aspects of the Hall-Héroult process, it would be appropriate to first estimate the voltage required for the process. The theoretical computations given here are according to Lancker (1967).

For a cathode of aluminium and an anode of oxygen, the decomposition reaction may be written as



At 1000°C for the reaction



the free energy change is - 306 kcal. Hence,  $4G_F$  is - 154,500 cal/mole.

We can calculate  $\Delta G_3$  from the heat of fusion of  $\text{Al}_2\text{O}_3$ . Here,  $\Delta G_3$  is equivalent to converting  $0.5\text{Al}_2\text{O}_3$ , at  $1000^\circ\text{C}$ , to the molten state. From standard tables,  $\Delta G_3$  is obtained as 3800 cal.  $\Delta G_4$  corresponds to the dissolution of  $\text{Al}_2\text{O}_3$ , molten at  $1000^\circ\text{C}$ , into cryolite. For 1 mole of  $\text{Al}_2\text{O}_3$ , we have

$$\Delta G_f = RT \ln \sigma_{\text{m,f}}$$

where  $a_{\text{Al}_2\text{O}_3}$  is the activity of alumina in cryolite,  $T = 1273 \text{ K}$ , and  $R = 1.987 \text{ cal}/^\circ\text{C}$ . If it is

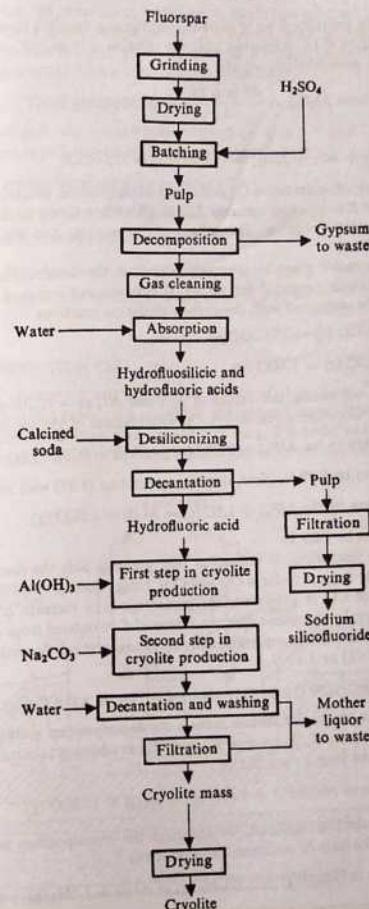


Fig. 6.3 Synthesis of Cryolite.

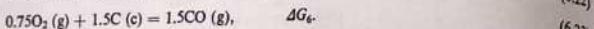
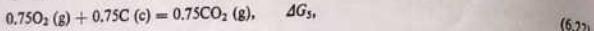
assumed that the bath contains 8 wt % alumina and the rest cryolite, then the mole fraction of alumina works out to be 0.15. Assuming that the solution is ideal and also that the activity of alumina is equal to its mole fraction, we get

$$\Delta G_4 \text{ (for 0.15 mole } Al_2O_3) = \frac{RT \ln 0.15}{2} = -4750 \text{ cal.} \quad (6.20)$$

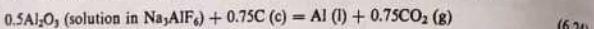
Now,  $\Delta G_1 = [-(\Delta G_2 + \Delta G_3 + \Delta G_4)] = 153,500 \text{ cal} = 23,066ZE,$  (6.21)

where  $Z$  is the valency of aluminium (3) and  $E$  the decomposition potential for reaction (6.15). From eq. (6.21), we get  $E$  to be approximately 2.22 V. This theoretically calculated value compares well with the experimentally obtained values between aluminium and  $Pt(O_2)$  electrodes, which lie in the range 2.1–2.15 V.

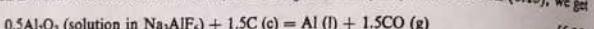
In practice, a *consumable* graphite electrode serves as the anode. Therefore, we have to calculate the decomposition potential for an Al (l) cathode and a carbon (c) anode. To do so, reaction (6.15) has to be combined with the carbon oxidation reactions



From standard tables, we obtain the values of  $\Delta G_5$  and  $\Delta G_6$  as  $-71,200 \text{ cal}$  and  $-81,000 \text{ cal}$ , respectively, at 1000°C. Combining reaction (6.22) with reaction (6.15), we obtain



for which  $E$  works out to be 1.19 V. Next, combining reaction (6.23) with reaction (6.15), we get



for which  $E$  works out to be 1.05 V.

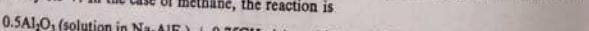
From the foregoing discussion, it is evident that graphite aids the decomposition of  $Al_2O_3$  because it reacts with the oxygen to form CO and  $CO_2$ . Under normal operating conditions, about 50 per cent by volume of CO is produced; the percentage may increase considerably at a low current density. In general, we assume that the values of  $E$  calculated from reactions (6.24) and (6.25) are of equal importance. Consequently, the average theoretical decomposition potential is taken, i.e.,  $[(1.19 + 1.05)/2]$  or 1.12 V.

#### INFLUENCE OF HYDROGEN OR METHANE INJECTION AT ANODE

We have just stated that the use of carbon reduces the decomposition voltage of alumina in the cryolite bath from 2.2 V to 1.2 V. The use of  $H_2$  and  $CH_4$  in addition to carbon has been studied. The reaction with hydrogen may be written as



By following the procedure just outlined, we calculate the decomposition potential value to be approximately 1.3 V. In the case of methane, the reaction is



For reaction (6.27), the decomposition potential works out to be approximately 1.06 V.

Thus, we observe that the injection of hydrogen or methane would not be effective in appreciably reducing the decomposition potential of  $Al_2O_3$ . However, such an injection may effectively cut down graphite consumption and prove economical if hydrogen or methane is available at cheap rates. Natural gas would have a similar effect as methane.

#### ACTUAL DECOMPOSITION POTENTIAL

In an actual plant operation, the voltage is maintained between 5 V and 7 V. The breakdown of the voltage requirement is as follows (the values are approximate):

Voltage needed for electrolytic reduction	1.7 V
Voltage drop across carbon lining	0.6 V
Voltage drop due to anode resistance	0.5 V
Voltage drop due to resistance of electrolyte	1.8 V
Voltage drop due to contact resistance, leads, and joints	0.5 V
Total	5.1 V

#### ELECTROLYTIC REDUCTION CELL

Figure 6.4 shows an electrolytic cell for the electrolysis of aluminium. The cell is sunk into the floor with the top portion (about 0.3 m) above the ground level. It essentially contains rectangular refractory-lined steel boxes, each around 5 m long, 2 m wide, and 1 m deep. The cathode lining which consists of refractory bricks is faced with carbon mixed with a tar binder. An iron

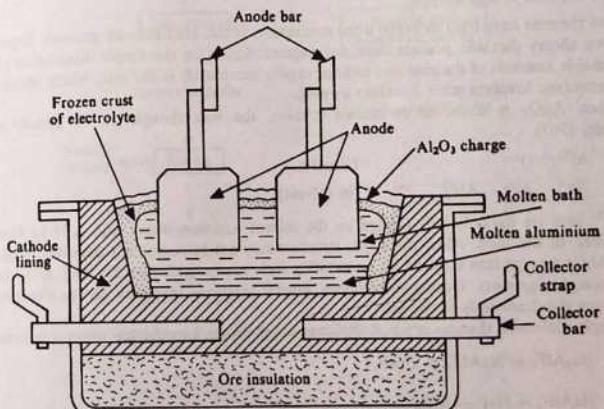


Fig. 6.4 Electrolytic Cell for Aluminium Electrolysis.

plate and an iron bar which form the cathode are embedded in the carbon mixture. A tap hole through which the metal is collected is located at the bottom of the cell. The anode may be either prebaked carbon electrodes that are replaced from time to time or continuous electrodes, in which case a carbonaceous paste is continuously fed into steel moulds. The carbon gets baked in the cell itself and forms the anode. Iron pins are inserted for electrical contact. The baked carbon products for the electrodes and the cathode lining must be sufficiently strong (with a compressive strength of 250–300 kg/sq. cm) and dense (not over 25 per cent of porosity). Figure 6.5 gives a flowsheet for the manufacture of two types of carbon electrodes, namely, prebaked and continuous.

#### Cell Operation

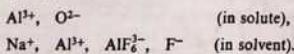
During operation, the cell bath is filled with cryolite and the anode is lowered into it. A current is passed through the cell circuit until the cryolite melts (melting point 990°C). Only when the bath attains a molten state is the addition of alumina commenced. The alumina decomposes to yield aluminium and oxygen, the necessary heat being supplied by the resistance offered by both the electrodes and the electrolyte. If the alumina content of the bath (normally 5–10 per cent) falls below 2 per cent, then normal contact between the anode and the bath is interrupted by a gas film which abruptly increases the resistance. As a consequence, the normal operation ceases. This effect is called the anode effect.

The agitation of the bath caused by the evolution of gas (CO and CO<sub>2</sub>) and the magnetic stirring effect produced by the current flowing through the bath from the anode to the cathode lining of the cell, help maintain fresh additions of Al<sub>2</sub>O<sub>3</sub> in suspension long enough for dissolution in the electrolyte. The depth of the electrolyte is maintained at about 25 cm. Relevant operational data on current, consumption of power and raw materials, are given later in this section.

#### Role of Cryolite in Electrolysis

Various theories have tried to explain the mechanism of the Hall-Héroult process. Experimental evidence shows that the process does not depend merely on the simple dissociation of Al<sub>2</sub>O<sub>3</sub>. Measurable amounts of fluorine and sodium vapour accumulate in the cell, which indicates that the electrolysis involves other reactions as well.

When Al<sub>2</sub>O<sub>3</sub> is dissolved in molten cryolite, the ions thought to be present are (see Lancker, 1967)



The O<sup>2-</sup> ions are the only ions foreign to the solvent and may react with Al<sup>3+</sup> to form AlO<sup>+</sup> and AlO<sub>2</sub><sup>-</sup> in the melt. Also, the Al<sub>2</sub>O<sub>3</sub> structure may not be completely depolymerized. Moreover, Al<sub>2</sub>O<sub>3</sub> may go into solution by assimilating ionic groups such as AlO<sup>+</sup> and AlO<sub>2</sub><sup>-</sup> (or even more complex groups). During electrolysis, several reactions involving all the aforementioned ions take place simultaneously in the melt.

Simple molecular theories of electrolysis are based on the hypothetical dissociation reactions



We assume that the NaF thus produced initiates a number of reactions as indicated by the following two theories.

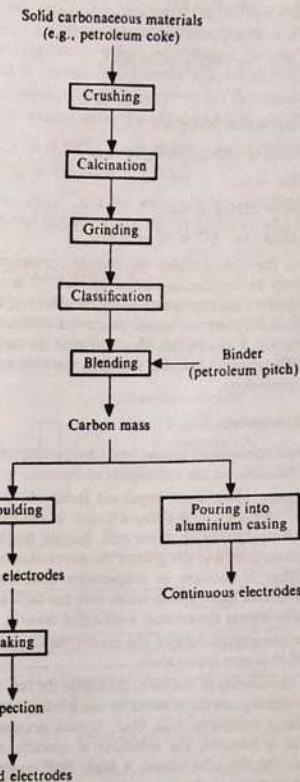
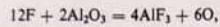
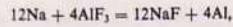


Fig. 6.5 Manufacturing Process for Carbon Electrodes.

#### Theory 1

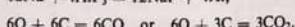
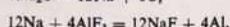
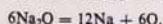
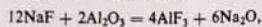
The reactions according to this theory are





#### Theory 2

The reactions according to this theory are



The foregoing two theories attribute the constant presence of sodium vapour and fluorine above the cryolite bath to the decomposition of NaF. It is also obvious that the depletion of Al<sub>2</sub>O<sub>3</sub> or the lowering of its activity enhances the formation of fluorine [reaction (6.30)] or NaF [reactions (6.31) and (6.36)]. An increased generation of fluorine causes the anode effect, which prevents normal operation. Further, it is also clear that the current efficiency of the Hall-Héroult process cannot be 100 per cent. The side reactions show that only a limited quantity of cryolite is consumed during electrolysis.

#### Factors Influencing Electrolysis

We now discuss certain operational factors (see Chakravarty and Monga, 1968; Sevryukov, 1975) that have a marked influence on the electrolysis of alumina:

(1) The bath temperature is an important factor. As a rule, an increase in temperature decreases the current efficiency. For every 4°C rise in the bath temperature (above the normal 970°C), the current efficiency falls by 1 per cent because the higher the temperature, the more the number of side reactions and the greater the dissolution of the metal in the bath. It should, however, be noted that a decrease in temperature does not improve the current efficiency indefinitely. Below a certain limit, which varies with the bath composition, a solid phase appears in the cell. This residue upsets the normal working of the cell.

(2) The higher the current density, the greater the current efficiency. Therefore, the current density is maintained at a very high value.

(3) The lower the density of the bath, the higher the rate of separation of the metal liberated from the bath. The density can be lowered by using a high AlF<sub>3</sub>/NaF ratio. However, when the quantity of AlF<sub>3</sub> is large compared with NaF, certain drawbacks arise. For instance, the conductivity of the bath is lowered, the solubility of alumina is reduced, and a large volume of fluorine is produced. On the other hand, a high NaF content reduces the current efficiency apparently due to an increase in the concentration of sodium ions and the deposition of sodium on the cathode. The sodium deposition directly lowers the current efficiency. An NaF/AlF<sub>3</sub> ratio that is slightly less than three is considered optimum.

(4) The current efficiency is also affected by the interpolar distance, which is the distance from the bottom of the anode to the top of the molten metal bath (see Fig. 6.4). The current efficiency increases along with the interpolar distance, reaching a maximum (about 90 per cent) when the distance is approximately 65 cm.

(5) The cell efficiency can be improved by strictly controlling the addition of alumina. The current efficiency is a minimum when the Al<sub>2</sub>O<sub>3</sub> content in the bath is 4 per cent. At values lower and higher than 4 per cent, the current efficiency increases. However, to maintain a high current efficiency, the cell should be operated consistently with a high Al<sub>2</sub>O<sub>3</sub> content. Welch (1967) has derived the empirical relationship for the dependence of the current efficiency (CE) in per cent on various normal operating variables as

$$\text{CE} = 254.92 - 1.70C_{\text{Al}_2\text{O}_3} + 0.39C_{\text{CaF}_2}^2 + 0.45\text{AlF}_3 + 0.055X_{\text{AlF}_3}^2 + 0.3C_{\text{CaF}_2} - 0.23T + 129(D + 1) + 25i,$$

where  $T$  is the temperature of the cell (°C),  $i$  the anode current density (A/cm<sup>2</sup>),  $D$  the inter-electrode distance (cm),  $C_{\text{CaF}_2}$ , the wt % CaF<sub>2</sub>,  $C_{\text{Al}_2\text{O}_3}$ , the wt % Al<sub>2</sub>O<sub>3</sub>, and  $X_{\text{AlF}_3}$  the wt % AlF<sub>3</sub> in excess of the cryolite ratio of 3.

#### ELECTROLYTIC REFINING OF ALUMINIUM

The purity of metal produced by the Hall-Héroult process seldom exceeds 99.5 per cent. This degree of purity is sufficient for most alloying purposes. However, for electrical applications and for canning, a higher degree of purity is required. To achieve this higher degree of purity, an electrolytic method known as the *three-layer process* (see Fig. 6.6) is employed. In this process, a

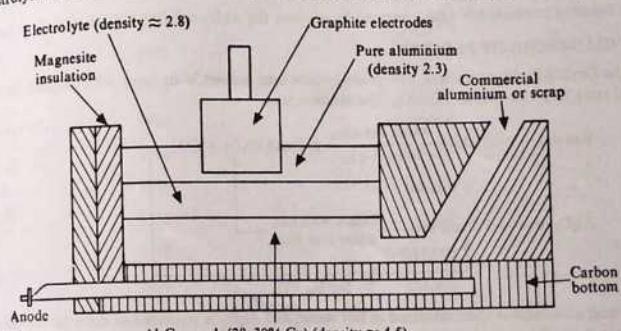


Fig. 6.6 Three-Layer Process.

dense electrolyte forms the middle layer. The approximate composition of the electrolyte is as follows: aluminium fluoride 36 per cent, cryolite 30 per cent, barium fluoride 18 per cent, and calcium fluoride 16 per cent. The density of the electrolyte enables the aluminium purified during electrolysis to float upward (to form the top layer). The impure metal is alloyed with copper, and this heavy alloy forms the bottom layer. The temperature of operation is maintained at about 950°C.

The average output of metal (99.9 per cent purity) is about 100 kg per cell per day. The consumption of the electrolyte and that of the graphite electrodes is each equivalent to about

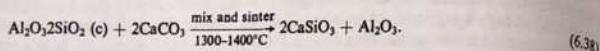
6 per cent of the metal produced. The three-layer process proves ineffective if the impure aluminium contains magnesium, for example, Al-Mg alloy scrap, because magnesium reacts with the electrolyte and renders it unsuitable.

#### 6.10 METHODS OF TREATING LOW-GRADE ORES

The Bayer process has remained unchallenged as far as the extraction of alumina from rich aluminium ores with a low silica content (for example, bauxite) is concerned. This process, however, needs to be modified if the ores have a high silica content. Moreover, the Bayer process proves uneconomical in the case of low-grade ores. Consequently, other processes have been tried out to treat low-grade bauxite and other low-grade minerals of aluminium. We now discuss in brief some of these processes as they are only of minor industrial importance.

##### LIME SINTER PROCESS

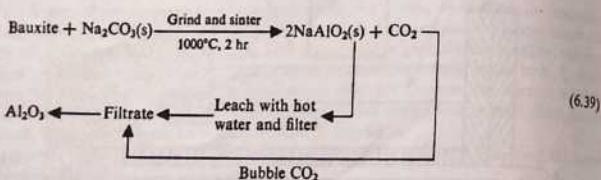
The lime sinter process is suitable for siliceous ores such as clay. Alumina is first liberated by reacting clay ( $\text{Al}_2\text{O}_3\text{SiO}_2$ ) with limestone ( $\text{CaCO}_3$ ):



The reaction products are next separated by leaching the  $\text{Al}_2\text{O}_3$ -rich fractions as now described.

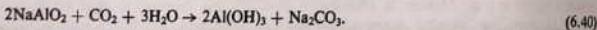
##### DEVILLE-PECHINEY PROCESS

In the Deville-Pechiney process, low-grade bauxite ores are made to react with  $\text{Na}_2\text{CO}_3$  in the solid state to produce solid  $\text{NaAlO}_2$ . The reaction is



The solid aluminate is then dissolved in hot water, and  $\text{Al}_2\text{O}_3$  is recovered as done in the Bayer process. A similar procedure is applicable in the case of the lime sinter process.

The final reaction may be written as



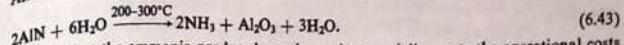
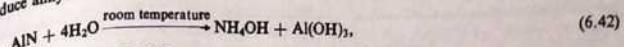
##### SERPECK PROCESS

In the Serpeck process, atmospheric nitrogen is passed through  $\text{Al}_2\text{O}_3$  in presence of carbon to produce a nitride. The reaction is



This nitride is hydrolyzed at room temperature to produce  $\text{Al}(\text{OH})_3$ , or at elevated temperatures,

to produce anhydrous  $\text{Al}_2\text{O}_3$  directly. The relevant reactions are



It may be noted that the ammonia produced as a byproduct partially meets the operational costs of the process.

#### 6.11 PRODUCTION OF ALUMINIUM IN INDIA

The development of the aluminium industry in India was very slow during the first decade after independence, but, subsequently, the growth has been rapid, as shown by the data in Table 6.3.

Table 6.3 Production of Aluminium (tons)  
(after *Minerals and Metals Review*, 1979)

Year	Production
1953	4000
1958	8300
1960	18,000
1965	69,000
1968	120,000
1970	161,000
1975	167,500
1976	211,000
1977	183,900
1978	204,000
1979	208,800

In India at present, four companies, namely, Aluminium India (ALIND), Bharat Aluminium Corporation (BALCO), Hindustan Aluminium Corporation (HINDALCO), and Madras Aluminium Company (MALCO), produce aluminium. Also, two aluminium smelters in the central sector and one aluminium plant in the state sector are envisaged. Table 6.4 gives the details of the aluminium plants in India.

As a typical example of aluminium production in India, we shall consider HINDALCO. The location of this unit enables it to procure bauxite, at economical rates, from several mines situated nearby. The composition of the bauxite obtained from some of these mines is given in

Table 6.4 Aluminium Plants in India (after *Minerals and Metals Review*, 1979)

Name of company	Location of smelter	Location of deposits	Plant capacity (tons/year)
HINDALCO	Renukut (Uttar Pradesh)	Amarkantak (Madhya Pradesh)	95,000
MALCO	Mettur (Tamil Nadu)	Sheavoroy, Kolli Hills (Tamil Nadu)	21,000
INDALCO	Hirakud (Orissa) Alwaye (Kerala) Belgaum (Karnataka)	Ranchi (Bihar) Ranchi (Bihar) Kolhapur (Maharashtra)	103,000
BALCO	Korba (Madhya Pradesh)	Amarkantak, Phutkaphar (Madhya Pradesh)	25,000

Table 6.5 Analysis of Bauxite from Different Mines of HINDALCO (wt %)

Mine	Total Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Loss on ignition (LOI)
Lohardaga	56.50	1.70	9.30	4.30	0.1	27.30
Amarkantak	50.60	4.30	5.30	14.40	0.2	25.20
Katni	55.69	0.99	8.49	7.75		27.01
Richigutta	40.02	2.18	10.73	28.35		19.11
Naini	57.99	1.80	8.07	3.78		28.35
Sindri	49.05	1.74				27.63
Niwar	53.60	2.25	8.67	9.95		25.90

Table 6.5. These bauxite deposits contain considerable amounts of TiO<sub>2</sub> (a valuable constituent) which enters red mud during alkali leaching, but is currently discarded.

#### THE ALUMINA PLANT AT HINDALCO

The rated capacity of the alumina plant is 150,000 tons per year. The flowsheet employed for the

Bayer process at HINDALCO is shown in Fig. 6.7. The ratio by weight of the red mud to the alumina produced is almost 1:1. For producing 1 ton of alumina, the raw material requirement is as follows: bauxite 2.5 tons; caustic soda 0.2 ton; lime 75 kg; starch 4 kg; power 300 kWh; soda ash 40 kg; and coal 1 ton. The consumptions of bauxite and caustic soda are rather high because considerable quantities of Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O are lost in the red mud.

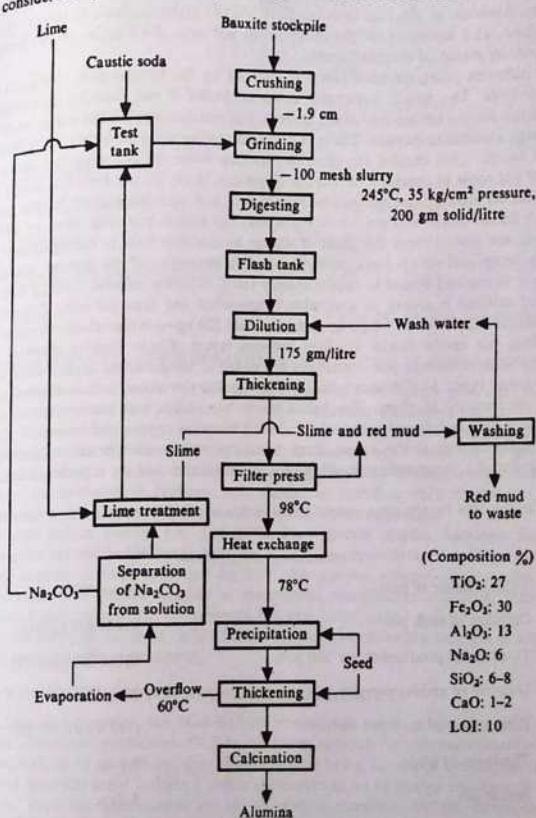


Fig. 6.7 Leaching of Bauxite (HINDALCO).

The percentage composition of the final alumina product is as follows: Loss on ignition 0.8–1.0; moisture 0.7;  $\text{Na}_2\text{O}$  0.5–0.6;  $\text{SiO}_2$  0.2;  $\text{Fe}_2\text{O}_3$ , 0.035; and  $\text{Al}_2\text{O}_3$  balance.

#### THE REDUCTION PLANT AT HINDALCO

The basic raw materials employed during electrolytic reduction are alumina, power, carbon, and fluoride salts. Alumina, as obtained from the HINDALCO alumina plant, is transported to the reduction plant, also known as the pot room. In the pot room, the alumina is distributed to the reduction pots by means of overhead cranes.

For the reduction plant, electrical power is supplied by the Rihand dam through 132,000-V transmission lines. The power is stepped down to 11,000 V and then fed to a mercury arc rectifier station for conversion into direct current. The rectifier supplies the pot room 59.5 kA at 770 V through aluminium busbars. The pots are connected in series such that a pot line consists of two pot rooms. This enables the electricity to flow down one pot room and return through the adjacent pot room to complete the circuit. There are, in all, six pot lines and nearly 500 pots.

The reduction plant utilizes calcined petroleum coke and petroleum pitch for the fabrication of prebaked anode blocks and pot-insulating layers. The carbon materials, most of which come from Assam, are moved from the place of storage by conveyor belts to the equipment used for crushing, grinding, and sizing. Next, carefully weighed quantities of the ground, classified coke and pitch are mixed and heated to approximately 150°C in steam-jacketed 4100-kg batch mixers. The blended mixture is cooled to a suitable temperature and then fed into 1000-ton presses, where the anode blocks—each weighing approximately 120 kg—are manufactured under pressure. After cooling, the anode blocks are kept between layers of coke packing material and then lowered into oil-fired furnace pits. Here, they are baked at temperatures higher than 1150°C in order to harden them, to eliminate volatiles contained in petroleum, and to develop a sufficient degree of conductivity in them. The baked anode blocks are next transported to a rodding room, where a steel stub is cast into each anode block and a copper rod bolted to the stub in order to supply current to the anode. Each block can now be used for about 26 shifts. During the replacement of a consumed electrode, both the carbon stub and the copper rod are reclaimed for reuse.

The relevant data for the main reduction operation in the pot room are now tabulated.

#### Data on pot room operation

Total number of pots	about 500
Capacity of each pot	about 400 kg/day
Total metal production per 500 pots	about 200 tons/day
Number of anodes per pot	24
Dimensions of each pot-shell	(210 × 60 × 90) cm
Thickness of plate	1.6 cm
Anode life	9 days
Current efficiency	86 per cent

#### Material consumption per ton of aluminium produced (in tons)

Alumina	2.0
Cryolite	0.035
$\text{CaCl}_2$	0.0028
$\text{AlF}_3$	0.04
Soda ash	0.7 (for new pots)
Coke	0.5
Hard pitch	0.13
Calcined anthracite	7 (for new pots)
Soft pitch	1 (for new pots)
Fuel oil (for baking furnace)	0.12
Borax	6 tons per pot line per month

#### 6.12 ENVIRONMENTAL CONSIDERATIONS IN ALUMINIUM PRODUCTION

The hydrometallurgical effluents for the Bayer process and the fumes generated by the Hall-Héroult process constitute the major cause of pollution around aluminium plants. For example, during the Bayer process, a large number of sodium ions are introduced during NaOH leaching, and these ions are discharged from the system into the natural water resources. In general, if the effluent is dumped into the sea, which contains large amounts of sodium ions, there is hardly any effect on the environment. However, care should be exercised while discharging them into fresh-water rivers. Also, the disposal of red mud poses a serious problem.

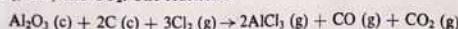
As pointed out in Section 6.9, during the Hall-Héroult process fluorides, fluorine, and sodium vapours are emitted as fumes from the aluminium electrolytic cells. In many instances, due to the absence of fume collection facilities, the gaseous effluent destroys the vegetation around the plant site. The introduction of electrostatic precipitators and other fume-collecting devices cannot only protect the environment but also help recover a large amount of cryolite which can be recycled. In India, BALCO (Korba) claims to have the only gas-cleaning facility capable of protecting the environment.

#### 6.13 NEWER PROCESSES FOR ALUMINIUM PRODUCTION

Since the turn of the century, the Hall-Héroult process has stood out as the only commercial process for aluminium production. Of late, extensive research for alternative methods has been carried out, and, in all probability, the chloride process being developed by ALCOA (Aluminium Company of America) could become a viable alternative as far as energy efficiency is concerned. In addition, work has been carried out on aluminium extraction by the direct carbothermic reduction of alumina and on the monochloride processes.

## ALCOA PROCESS

In the ALCOA process (see Fig. 6.8), the alumina produced by the Bayer process is chlorinated under reducing conditions in the presence of carbon at 700–900°C to produce a mixture containing  $\text{AlCl}_3$ ,  $\text{CO}$ , and  $\text{CO}_2$ . The reaction is



$\text{AlCl}_3$ , which is a vapour at these temperatures, is separated from the reaction products by condensation, at about 70°C, in a fluidized bed containing  $\text{AlCl}_3$  particles. The solid  $\text{AlCl}_3$  particles thus formed are continuously fed into an electrolytic cell containing a fused chloride electrolyte. This electrolyte, which is made up of 5 per cent  $\text{AlCl}_3$ , 50 per cent  $\text{NaCl}$ , and 45 per cent  $\text{LiCl}$ , is maintained at 700°C. Upon electrolysis by a direct current, liquid aluminium is formed at the cathode and gaseous chlorine liberated at the anode. The chlorine produced is recycled in order to chlorinate the fresh alumina.

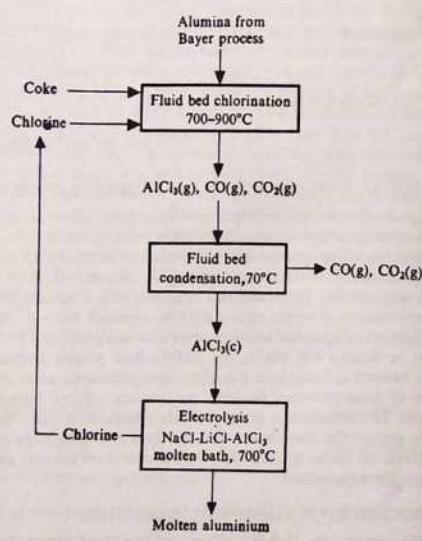


Fig. 6.8 ALCOA Process.

The cell in the ALCOA process has a novel design (see Fig. 6.9), i.e., it is a bipolar cell consisting of several bipolar electrodes. Each bipolar electrode behaves like a cathode at the top surface and like an anode at the bottom surface. A continuous flow of electrolyte must be maintained across the cell in order to prevent the molten aluminium produced upon electrolysis from

forming pools on the electrodes. An arrangement is made to collect this molten aluminium at the bottom. Chlorine rises to the top, where it is collected.

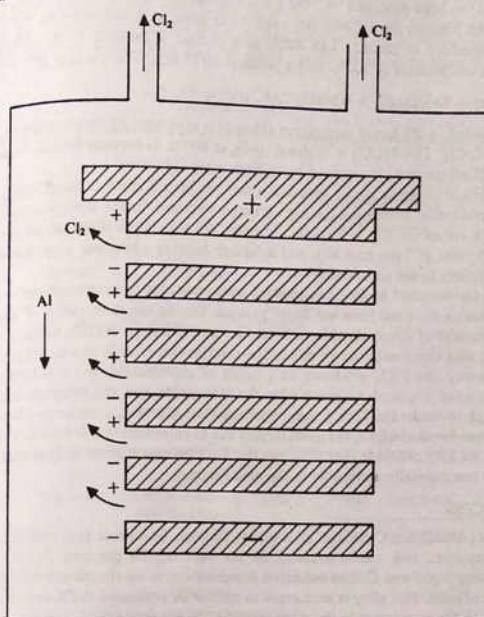


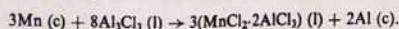
Fig. 6.9 ALCOA Bipolar Cell.

It may be noted that one bipolar cell is equivalent to five conventional monopolar cells in series. Also, the productivity and the cell voltage of a bipolar cell are five times those of the conventional monopolar cell. ALCOA has claimed operation at current densities up to 23,000  $\text{A/m}^2$  with an electrode gap of less than 1.3 cm.

In the ALCOA process, the chloride electrolyte has a much higher conductivity, i.e.,  $4.0 \text{ mho cm}^{-1}$  compared with that of the conventional Hall-Héroult cell, i.e.,  $2.8 \text{ mho cm}^{-1}$ . Also, the distance between electrodes is lower in the ALCOA cell. These two factors appreciably lower the energy wasted in the form of heat that is produced due to the current flowing between the electrodes. Further, the chloride electrolyte leads to a higher current efficiency, and ALCOA hopes to decrease the overall energy consumption by over 30 per cent. If proved successful, this process could revolutionize the aluminium industry which is extremely energy-intensive.

**TOTH PROCESS**

A novel process has been proposed by Toth for the extraction of aluminium. In this process, too, as in the ALCOA process, the alumina from the Bayer process is converted to  $\text{AlCl}_3$  by chlorination in the presence of carbon. The  $\text{AlCl}_3$  thus formed is reduced to Al by treating it with manganese at a temperature of  $300^\circ\text{C}$  and a pressure of 15 atm. The reaction is



The  $\text{AlCl}_3$  dissolved in the liquid manganese chloride is separated by evaporation so as to leave behind solid  $\text{MnCl}_2$ . This  $\text{MnCl}_2$  is oxidized by  $\text{O}_2$  at  $600^\circ\text{C}$  to produce  $\text{Mn}_2\text{O}_3$ , from which Mn, needed for the Toth process, is obtained by carbothermic reduction.

The feasibility of reducing  $\text{AlCl}_3$  with Mn metal has been a much-debated topic. Apparently, the expenses involved in generating the high pressure required for the Toth process and in using manganese as a reductant are prohibitive. Further, the aluminium metal would contain at least the equilibrium value of 1 per cent Mn, and a further refining operation may become necessary to obtain aluminium fit for commercial use.

It has been claimed that in the Toth process, low-grade clay minerals can serve as a substitute for the alumina obtained from the Bayer process. During the chlorination of these minerals, a substantial amount of silicon dioxide, iron oxide, and titanium dioxide present in them will also be chlorinated along with the alumina. The chlorination of  $\text{SiO}_2$  can be suppressed to some extent by recycling the  $\text{SiCl}_4$  produced as a result of chlorination, but it is estimated that the quantity of chlorine required to react with the iron oxide and the titanium dioxide will be excessive enough to render the Toth process uneconomical. Further, in order to obtain  $\text{AlCl}_3$  that is sufficiently pure for electrolysis, the gases formed due to chlorination will have to be fractionated. On the whole, we may conclude that although the Toth process is chemically interesting, it is not expected to be commercially applicable in the near future.

**ALCAN PROCESS**

In the ALCAN (Aluminium Company of Canada) process, bauxite is first reduced to a typical aluminium alloy, i.e., one which contains 50 per cent Al, 30 per cent Fe, 10 per cent Si, 5 per cent Ti, and 5 per cent C. The reduction is carried out in an electric arc furnace, at  $2000^\circ\text{C}$ , in the presence of coke. This alloy is next made to react with preheated  $\text{AlCl}_3$  vapour in a reactor.  $\text{AlCl}_3$  reacts with the aluminium in the alloy according to the reaction



Reaction (6.46) can be reversed by contacting, at  $700^\circ\text{C}$ , the  $\text{AlCl}$  vapour with molten aluminium droplets. The  $\text{AlCl}_3$  thus formed is recycled.

Although the ALCAN process has considerable potential for exploitation, ALCAN has shut down its small-scale plant because of severe stress corrosion problems affecting the  $\text{AlCl}_3$  reactor, and no further work has been reported.

**6.14 TIN****USES**

It is common knowledge that cans made of steel that are used for storing edibles are invariably

coated with tin. This is because tin offers remarkable resistance to both corrosion and toxicity. This particular application is so universal that a can is often called a 'tin'. Although a substantial part of the total tin globally produced is utilized for plating cans, only about 1.4 per cent of the weight of a can is made up of tin, the thickness of the tin layer being 0.00005–0.00025 cm. Apart from plating, tin finds many other applications in modern technology, some of which are listed in Fig. 6.10.

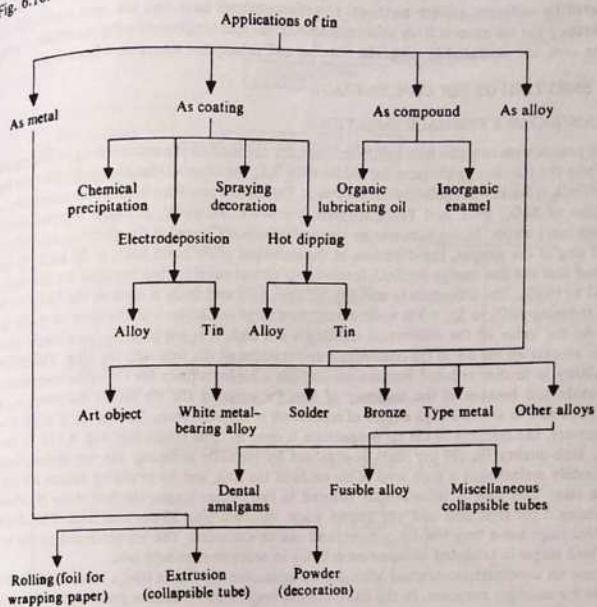


Fig. 6.10 Applications of Tin.

The attractive mechanical properties of tin, mainly ductility and malleability, are exploited in the manufacture of items used on a large scale such as alloys, collapsible tubes, foils, and tin-copper wires. Finally, because tin has a low melting point, it is used for soldering purposes.

**6.15 CONCENTRATION OF TIN ORES**

As mentioned in Chapter 3, cassiterite ( $\text{SnO}_2$ ) is by far the most important mineral of tin. It is found mainly in Bolivia, Malaysia, and Indonesia. In India, no significant tin deposits have yet

been located. Naturally occurring cassiterite is usually associated with the gangue materials and metallic sulphides such as galena, chalcopyrite, iron pyrite, and sphalerite. The theoretical tin content of  $\text{SnO}_2$  is 78.6 per cent. In reality, however, ores may contain as little as 1 per cent tin or even less. To upgrade these ores to about 65 per cent tin, the water gravity concentration methods are employed. During such upgrading the gangue is removed, but since the specific gravities of the other metal sulphides are almost the same as that of cassiterite, they cannot be eliminated by ordinary gravity methods. Flotation methods have also not been successful so far in separating the tin mineral from other minerals. Iron- and tungsten-bearing materials, if present with tin ores, are separated by magnetic roasting and subsequent magnetic separation.

#### 6.16 SMELTING OF TIN CONCENTRATE

##### REVERBERATORY FURNACE SMELTING

If a tin concentrate contains iron sulphides, they are oxidized to the oxide before or during smelting. From the free energy diagram for oxides (Fig. 2.1), we observe that the carbothermic reduction of  $\text{SnO}_2$  is feasible at moderate temperatures. This causes problems because the thermodynamic stabilities of  $\text{SnO}_2$ ,  $\text{FeO}$ , and  $\text{Fe}_2\text{O}_4$  are similar at 600°C. However, at higher temperatures  $\text{FeO}$  becomes more stable. In the temperature range (1200–1300°C) needed for smelting, i.e., obtaining a fluid slag of the gangue, the difference in the stabilities of  $\text{FeO}$  and  $\text{SnO}_2$  is 20 kcal. It should be noted that the free energy for  $\text{SnO}_2$  formation is almost equal to that required for the oxidation of  $\text{FeO}$  to  $\text{Fe}_2\text{O}_4$ . The difference in stability between  $\text{FeO}$  and  $\text{SnO}_2$  is used as the basis for selectively reducing  $\text{SnO}_2$  to Sn, while maintaining, to a large extent, iron in the form of oxide in the slag. As the value of the differential stability is not high, it is not possible, in a single smelting step to recover all the tin in the concentrate and transfer all the iron into the slag. The difference in stability is further reduced because the slag has a higher affinity for tin oxide compared with iron oxide and because of the tendency of iron for entering the tin phase. To overcome these difficulties and to attain a high degree of separation of tin from iron, leading to a high level of tin recovery, the smelting of the tin concentrate is done in three stages (see Fig. 6.11). In the first stage, high-quality tin (99 per cent) is obtained by partially reducing the tin concentrate, by deliberately maintaining a high level of tin oxide in the slag, and by retaining almost all the iron in the slag. This slag is subsequently reduced in two further stages; the first stage produces tin containing 5 per cent iron and the second stage tin containing 20 per cent iron. The slag from the third stage has a very low tin content, and can be discarded. The tin produced in the second and third stages is subjected to liquation refining in order to eliminate iron.

Since tin concentrates obtained after gravity separation are fine in size, a reverberatory furnace is used for smelting purposes. In the conventional reverberatory furnace process, for the primary smelting operation, the quantity of coke and flux materials is carefully adjusted so as to produce an almost neutral slag (acid/base ratio of 1). The normal composition of this slag is  $\text{SiO}_2$  35 wt %,  $\text{CaO}$  30 wt %,  $\text{FeO}$  15 wt %, and  $\text{SnO}_2$  approximately 20 wt %. The tin in this stage is subsequently recovered from the slag.

The tin oxide content in the first slag is deliberately kept high in order to obtain tin with a very high degree of purity (99 per cent). This slag is subsequently smelted, additional flux (limestone), coal, and iron scrap being employed as the ingredients. Iron scrap facilitates the reduction of the tin oxide present in the slag. The second slag, which contains a much smaller amount of tin than the first slag, is also smelted to recover its tin content.

We have already stated in Chapter 5 that the tin-iron alloys such as those produced in the

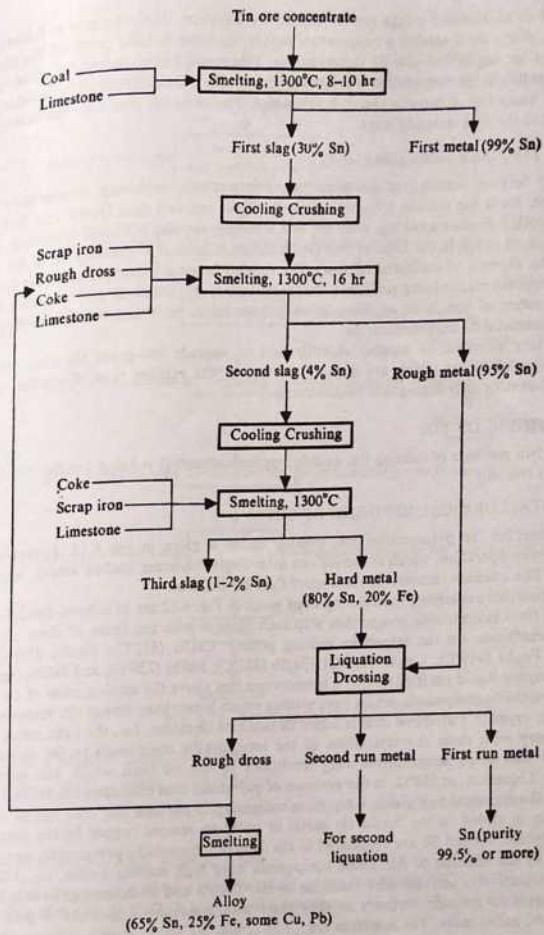


Fig. 6.11 Smelting of Tin Concentrates.

second and third smelting stages can be refined by liquation. The process is as follows. When tin-iron alloys are heated to a temperature higher than the melting point of tin, the liquid tin flows out leaving behind iron-tin intermetallics. This metal, known as first-run metal, contains 99.9 per cent tin. As the temperature is progressively increased, the iron content of the tin increases. This metal, known as second-run metal, is reliquated. The dross left over after the final liquation is returned to the first smelting stage.

#### ROTARY FURNACE SMCETING

The rotary furnace smelting of tin concentrates is gradually replacing reverberatory furnace smelting because it can achieve a higher efficiency of tin recovery (see Davey and Wills, 1977). In rotary furnace smelting, after the first smelting, the slag produced is reduced, and the tin is volatilized either in the form of SnS (when sufficient sulphur is present) or in the form of SnO (in the absence of sufficient sulphur). The tin-rich fumes are transported to the first smelting stage, and the cleaned slag produced after reduction is discarded. It may be noted that the vapour pressure of SnS is of an order of magnitude higher than that of SnO and the presence of  $SO_2$  is beneficial to tin volatilization.

There is a proposal to employ volatilization to upgrade low-grade tin ores. Upgrading produces tin-rich fumes which are used as the feed in the existing type of smelter, which is capable of treating only high-grade concentrates.

#### 6.17 REFINING OF TIN

There are two methods of refining tin, namely, pyrometallurgical refining (or fire refining) and electrolytic refining.

##### PYROMETALLURGICAL REFINING OF TIN

The flowsheet for the pyrometallurgical refining of tin is given in Fig. 6.12. It may be noted that the entire operation, which is carried out in a single container (called kettle), takes about 40 hours. The ultimate recovery of tin is more than 85 per cent.

The principles underlying the refining steps given in Fig. 6.12 are as follows. Several common impurities form intermetallic compounds with each other or with tin. Some of these are (figures in parentheses are the respective melting points):  $Ca_3Sn$  (675°C);  $Sn_3As_2$  (596°C);  $FeAs$  (1030°C);  $Fe_2As$  (919°C);  $Cu_3As$  (825°C);  $Cu_2Sb$  (585°C);  $FeSb_3$  (726°C); and  $FeSN_2$  (very high). Thus, if impure liquid tin is cooled to a temperature just above the melting point of tin (232°C) these intermetallic compounds, which have melting points higher than that of tin, separate out and float as tiny crystals. Pulverized coal is added to facilitate liquation, i.e., the light, rising particles of coal carry with them the crystallites of the intermetallic compounds to the surface. Also, pulverized coal helps maintain reducing conditions in the tin bath which aids intermetallic formation. Liquation, at 550°C, in the presence of pulverized coal eliminates almost 99.8 per cent iron from the tin metal and yields a dry dross containing 25 per cent tin.

Sulphur is added to the liquid tin metal in order to remove copper by the formation of copper sulphide. As and Sb are eliminated in the form of intermetallic compounds, namely,  $AlAs$  and  $AlSb$  by the addition of Al. These compounds have high melting points, i.e., 1720°C and 1070°C, respectively, and are also insoluble in tin. The As and Sb skimmings have to be immediately treated for metallic recovery as they react with atmospheric moisture to produce toxic arsenide and antimonide. The reactions are

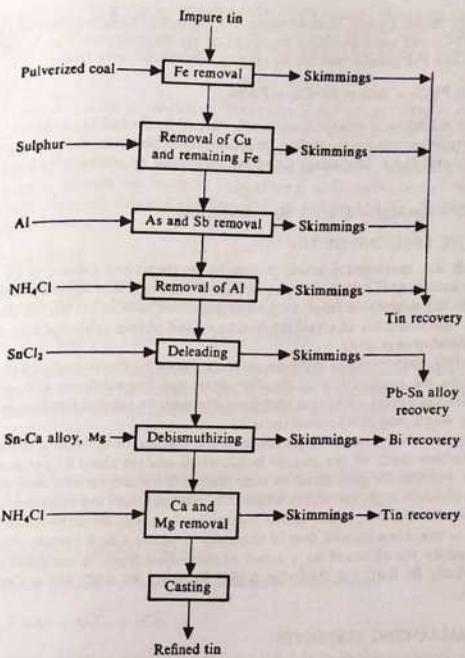
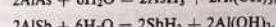
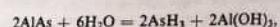


Fig. 6.12 Fire Refining of Tin.

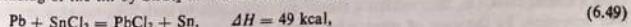


NH<sub>4</sub>Cl is added with tin after Al treatment to remove surplus aluminium according to the reaction

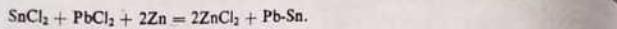


Pulverized coal once again facilitates the separation of the precipitate AlCl<sub>3</sub>.

Deleading of the tin by SnCl<sub>2</sub> is based on the reaction

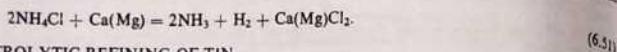


where Pb and Sn denote Pb and Sn in solution. The dross produced as a result of reaction (6.49) contains both  $PbCl_2$  and some unreacted  $SnCl_2$  (which are mutually soluble). A lead-tin alloy is recovered from this  $PbCl_2$ - $SnCl_2$  mixture by melting it in contact with zinc:



Tin metal, after deleading, is treated for bismuth removal by Ca and Mg addition.

Ca and Mg together remove bismuth in the form of insoluble intermetallic compounds, namely,  $Bi_2Mg_3$ ,  $Bi_2Ca_3$ , and  $Bi_2Ca$ . Any excess Ca or Mg is removed by adding  $NH_4Cl$  according to the reaction



#### ELECTROLYTIC REFINING OF TIN

Recent research has developed a viable process for the electrolytic refining of tin. This process, which employs a mixture of sulphuric acid and phenol sulphonate acid as the electrolyte, is feasible especially if the tin contains a large amount of impurities such as Pb, Bi, Sb, and As. Another process, which uses a mixture of cresol sulphonate acid and phenol sulphonate acid as the electrolyte, is in the development stage.

The electrolytic bath contains stannous sulphate, cresol sulphonate acid and phenol sulphonate acid (to improve the conductivity of the electrolyte) and free sulphonate acid with  $\beta$ -naphthol and glue as addition agents. (Addition agents are necessary to prevent tree-like dendritic deposits on the cathode which may short-circuit the cell.)

The cell operates at room temperature at a cell voltage of 0.3 and a current efficiency of 85 per cent. Anodes made of the impure metal, which analyze about 95 per cent Sn dissolve in about 21 days, whereas the pure metal cathode sheets are withdrawn once every week. If the lead content of the anode is high, the slimes which fall from the anode are excessive and have to be removed frequently. Further, other slimes sticking to the anode are scrubbed off with revolving brushes so as to provide a smooth flow of electricity to ensure a high current efficiency.

The high-purity tin obtained as a result of electrolysis typically analyzes (wt %) Sn, 99.95; Sb, 0.02; As, 0.01; Bi, 0.01; Cd, 0.01; Cu, 0.001; Fe, 0.01; Pb, 0.02; (Ni + Co), 0.01; S, 0.01; and Zn, 0.005.

#### 6.18 FERROALLOYING ELEMENTS

A number of nonferrous metals derived from oxide ores are principally used as alloying elements in the steel, stainless steel, and alloy steel industries. In most cases, alloys containing iron (ferroalloys) are produced. This group includes chromium, manganese, silicon, molybdenum, tungsten, vanadium, and niobium. We now describe the methods used in the extraction of these individual metals.

#### 6.19 CHROMIUM

##### USES

Metallic chromium is chiefly used for alloying purposes. The nickel alloys that contain chromium form a special class; i.e., they exhibit a remarkable resistance to both high-temperature oxidation and corrosion. In the case of most other alloys, i.e., those in which chromium is present along

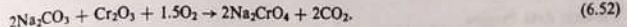
with iron, ferrochromium, which is easier to produce than metallic chromium, is employed as an alloying agent. In austenitic and ferritic stainless steels, which are widely used in chemical processing, oil refining, and food processing, ferrochromium is used as the alloying element.

##### OCCURRENCE

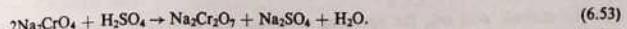
Chromium occurs in nature as chromite ( $FeO \cdot Cr_2O_3$ ). Since either  $Fe_2O_3$  or  $Al_2O_3$  can replace  $Cr_2O_3$  in the chromite grains, the grade of the chromite varies over a wide range. The ore is upgraded by sorting and hand-picking and beneficiated by flotation so as to reject undesirable magnesium silicates and also by magnetic separation. In practice, upgrading is not necessary because high-grade deposits are available to meet the present requirements. The main chromite deposits are found in South Africa, Zimbabwe, Turkey, and the U.S.S.R. India also has sizeable deposits of chromite ores.

##### METAL EXTRACTION

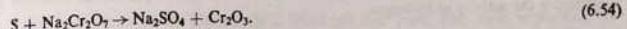
At the beginning, the high-grade chromite ore is finely ground and then roasted with  $Na_2CO_3$  at 800–1000°C in rotary kilns. Roasting converts the  $Cr_2O_3$  in the chromite to  $Na_2CrO_4$ :



To avoid sintering during roasting, limestone is often added. The roasted product is leached with water and filtered to separate the soluble  $Na_2CrO_4$  from the iron oxide and gangue present in the ore. This  $Na_2CrO_4$  is converted to  $Na_2Cr_2O_7$  by treatment with sulphuric acid:



The  $Na_2Cr_2O_7$  in the aqueous solution is selectively crystallized by evaporation, and the crystals are separated by filtration. The dried  $Na_2Cr_2O_7$  crystals are then converted to  $Cr_2O_3$  by sulphur reduction in a furnace:



The  $Cr_2O_3$  is finally reduced by Al metal to yield metallic chromium:



The aluminothermic reduction is described in more detail later in this chapter.

##### ELECTROLYTIC CHROMIUM

###### Chrome Alum Process

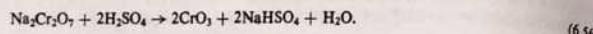
In the chrome alum process, ferrochromium with a high carbon content is converted to  $NH_4Cr(SO_4)_2 \cdot 12H_2O$  by first dissolving it in  $H_2SO_4$  and then adding  $(NH_4)_2SO_4$ . Ammonium chromium sulphate is electrolyzed in a cell with a diaphragm. This diaphragm is used to prevent the sulphuric acid and the chromic acid formed at the anode from mixing with the catholyte and oxidizing the divalent chromium. The breakdown of the composition of the electrolyte in the various compartments of the cell is given in Table 6.6. The cell is operated at 4.2 V at 53°C at a current density of 8 A/mm<sup>2</sup> with a current efficiency of 45 per cent.

Table 6.6 Electrolyte Composition in Chrome Alum Process (gm/litre)

	Chromium				Fe	NH <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	pH
	Total	Cr <sup>6+</sup>	Cr <sup>3+</sup>	Cr <sup>2+</sup>				
Cell feed	130	0	130	0	0.2	43	3	
Circulating mixture	65	0	63	2	0.1	68	1	
Catholyte	24	0	11.5	12.5	0.035	84		2-2.5
Anolyte	15	13	2	0	0.023	24	280	

#### Chromic Acid Process

In the chromic acid process, chromic acid is produced by treating Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with H<sub>2</sub>SO<sub>4</sub>:



For the chromic acid cell, the operating conditions are as follows: concentration of CrO<sub>3</sub> 300 gm/litre, concentration of H<sub>2</sub>SO<sub>4</sub> 4 gm/litre, temperature 85°C, current density 10 A/mm<sup>2</sup>, current efficiency 6-7 per cent, and the chromium deposition time 80-90 hours. The current efficiency is very low due to the evolution of hydrogen (see Chapter 2). This evolution is reduced to a great extent in the chrome alum process by controlling the pH in the catholyte and by suppressing the activity of hydrogen.

#### 6.20 MANGANESE

##### USES

Manganese is primarily used in the manufacture of alloys of iron, nickel, and chromium. Alloying with manganese imparts a higher strength to these alloys. In metallurgy, although a major portion of manganese is consumed as ferromanganese, pure manganese is required in order to produce special alloys and to make finishing additions in the manufacture of high-manganese alloys and for producing copper-base alloys.

##### ELECTROLYTIC MANGANESE

In the aqueous electrolysis of manganese, a diaphragm cell is necessary to control the pH in the anode and the cathode compartments. The pH must be controlled in order to suppress the evolution of hydrogen at the high voltage needed for depositing manganese on the cathode. It should be borne in mind that at such a high voltage, in an acid solution, hydrogen is evolved before manganese can be deposited.

The operating conditions are as follows:

##### Purified solution (feed to electrolysis)

Mn (as MnSO <sub>4</sub> )	30-40 gm/litre
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	125-150 gm/litre
SO <sub>2</sub>	0.01 gm/litre
Glue	0.008-0.016 gm/litre
Anolyte	
Mn (as MnSO <sub>4</sub> )	10-20 gm/litre
H <sub>2</sub> SO <sub>4</sub>	25-40 gm/litre
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	125-150 gm/litre
Current density	4-6 A/mm <sup>2</sup>
Catholyte (pH)	6-7.2
Cell voltage	5.1 V
Current efficiency	60-65 per cent

The manganese produced by electrolysis is 99.94 per cent pure. The main impurities are hydrogen (0.015 per cent) and sulphur (0.04 per cent). Hydrogen is removed by heating the metal to 500°C.

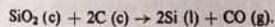
#### 6.21 SILICON

##### USES

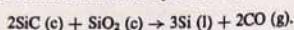
Elemental silicon is used mainly for alloying with copper, aluminium, and magnesium. Silicon, in the form of a ferrosilicon alloy, is employed as a deoxidizer in steel-making. Silicon is also employed as a reductant in metalloceramic reduction. Currently, there is a great demand for extremely pure silicon in the electronic industry for the manufacture of silicon chips.

##### OCCURRENCE AND EXTRACTION

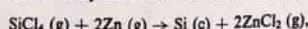
Silicon occurs widely over the earth's surface. Fairly pure quartzite (SiO<sub>2</sub>), i.e., which does not require upgrading, is readily available. This quartzite is reduced by coke and charcoal in an electric furnace to produce silicon:



Any SiC formed is removed by secondary smelting with quartzite:



This silicon is suitable for metallurgical applications. However, silicon of a very high purity is required for semiconductor applications. Such silicon is produced by first obtaining  $\text{SiCl}_4$  gas through the chlorination of metallurgical silicon, then purifying the  $\text{SiCl}_4$  gas by distillation which is followed by reduction with either Zn vapour or hydrogen:



Reduction at about 1000°C gives a crystalline deposit. If the reduction is carried out in the presence of a heated silicon rod, the diameter of this rod gradually increases. This silicon rod can be zone refined and used to grow single crystals. These crystals are widely used in semiconductor applications.

## 6.22 TUNGSTEN

### USES

The most common use of tungsten (as tungsten powder) is in the manufacture of the filament for electric light bulbs. Besides being used as an alloying element in steels, tungsten is widely used for fabricating tungsten carbide tools and dies. Tungsten-molybdenum alloys are employed in thermionic valves and special high-temperature thermocouples. Tungsten-nickel-cobalt-chromium alloys, which offer a high resistance to corrosion and abrasion, are used in hot shears and valve seatings in internal combustion engines.

### OCCURRENCE AND EXTRACTION

The chief ores of tungsten are wolframite  $[(\text{FeMn})\text{WO}_4]$  and scheelite  $(\text{Ca}\text{WO}_4)$ , each containing 0.3–2 per cent tungsten. Since these ores have high densities (wolframite 7.2–7.5 gm/cm³ and scheelite 5.9–6.1 gm/cm³) compared with the density of the gangue (1.8–2.5 gm/cm³), they are concentrated by gravity methods, except when cassiterite (density 6.8–7.1 gm/cm³) is present. Since wolframite is magnetic and scheelite nonmagnetic, only the former can be concentrated by magnetic separation. When cassiterite is present along with scheelite, a multistage procedure involving soda ash roasting, leaching of sodium tungstate, and the precipitation of  $\text{WO}_3$  by HCl is employed to upgrade the ore. The tungsten concentrate, after being subjected to several physical concentration methods, analyzes about 60 per cent  $\text{WO}_3$ .

The flowsheet for the production of  $\text{WO}_3$  from the concentrate is shown in Fig. 6.13. This process consists of soda roasting, leaching, and acidification.

As is evident from the free energy diagram for oxides (Fig. 2.1),  $\text{WO}_3$  can be readily reduced by either carbon or hydrogen. The  $\text{WO}_3$  when mixed with charcoal and heated yields a grey product (tungsten metal), which, after grinding, is suitable for alloying. The  $\text{WO}_3$  is reduced with  $\text{H}_2$  at 700–800°C:



The tungsten powder produced from reaction (6.61) is suitable for the manufacture of the electric bulb filament and tungsten carbide.

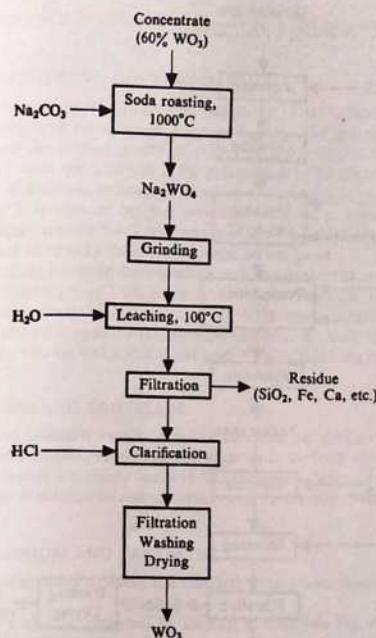


Fig. 6.13 Production of  $\text{WO}_3$ .

## 6.23 VANADIUM

### USES

Vanadium is used primarily as an alloying element in special alloy steels, and is produced mainly as a byproduct during the treatment of the ores of uranium, lead, and zinc. It is also present in the fly ash produced in coal-fired plants, but this source is yet to be tapped.

The flowsheet for the recovery of vanadium pentoxide from carnotite uranium ore is shown in Fig. 6.14. During the initial roasting of the ore, the impure  $\text{V}_2\text{O}_5$  and the lime present in it react to form an insoluble vanadate. The formation of such a vanadate can be partially overcome by adding  $\text{FeS}_2$  to the ore which reacts with the lime to give calcium ferrite. Careful control over roasting is essential to ensure a high percentage of vanadium recovery.

Vanadium metal, in a bright silvery form is ultimately produced by the calciothermic reduc-

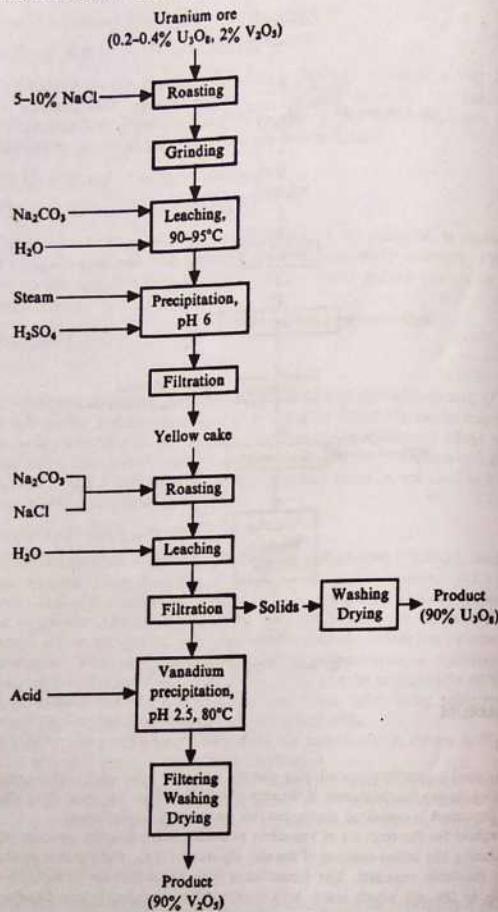


Fig. 6.14 Vanadium Extraction.

tion of the V<sub>2</sub>O<sub>5</sub> concentrate (produced as in Fig. 6.14) in the presence of CaCl<sub>2</sub> in an argon atmosphere.

#### 6.24 NIOBIUM (COLUMBIUM) AND TANTALUM

Both niobium and tantalum have high melting points, i.e., 2415°C and 2996°C, respectively. These two metals along with titanium, zirconium, tungsten, and molybdenum are known as refractory metals. Since the melting points of these metals are high, i.e., they lie in the range 1500-3000°C, some of them are employed in the manufacture of jet engines and guided ballistic missiles. In the case of niobium, because the metal offers an excellent resistance to corrosion at elevated temperatures, it is used as the fuel container material in high-temperature reactors. Niobium alloys (niobium content 0.4-1 per cent) are ideal for high-temperature applications because they are neither affected by creep nor corroded by hot gases.

In the case of tantalum, the metal has certain noteworthy properties, namely, ductility, a high melting point, a high strength at high temperatures, and resistance to corrosion by acids, bromine, and chlorine at normal temperatures. The last property is utilized for manufacturing laboratory apparatus and equipment for the chemical industry. At high temperatures, however, tantalum is corroded by alkalies and hydrofluoric acid. Finally, tantalum has a special but limited use in radio valves.

#### SOURCES OF NIOBIUM AND TANTALUM

In nature, niobium and tantalum usually occur in combination with oxygen and other metals such as iron, manganese, calcium, vanadium, and uranium in the form of niobates and tantalates. The minerals of these metals are chiefly found in Zaire, Nigeria, Norway, Brazil, and Malaysia. In India, small deposits of columbites and tantalites occur in the mica belts of Bihar, Rajasthan, and Madhya Pradesh.

#### EXTRACTION OF NIOBIUM AND TANTALUM

The flowsheet for the extraction of niobium and tantalum from a columbite-tantalite ore is shown in Fig. 6.15.

Tantalum metal can also be produced by heating K<sub>2</sub>TaF<sub>7</sub> (see Fig. 6.15) in the presence of sodium in a steel crucible. The resultant powder is washed free of fluorides and then compacted and sintered to give Ta metal. The reduction of Nb<sub>2</sub>O<sub>5</sub> by calcium metal produces a niobium metal powder useful in metallurgical applications.

#### NIOBIUM AND TANTALUM IN INDIA

India has built up a significant stockpile of columbite-tantalite ores. These ores are obtained mainly as a byproduct from mica mining operations. There are plans to intensify the prospecting for niobium and tantalum in view of the anticipated demand for these metals and their alloys in atomic energy applications.

At present, a major portion of tantalum is utilized in the manufacture of electrolytic tantalum capacitors. The estimated demand for these capacitors is 5 tons per year. To meet this demand, the metal is produced by the sodium reduction of K<sub>2</sub>TaF<sub>7</sub> by the high-temperature sintering of tantalum compacts under high vacuum.

The Bhabha Atomic Research Centre, Bombay, has carried out a development programme for the chemical treatment of the Indian columbite-tantalite ores. This programme entails the

extraction of niobium and tantalum values, the separation of the pure compounds of niobium and tantalum from each other by solvent extraction, the production of the consolidated metals by the metallothermic reduction of the pure metallic oxides, and the preparation of ferroniobium by

the aluminothermic reduction of niobium concentrates. Further, the purification of the metals by electron beam refining and the fabrication of sheets and wire products made of niobium or tantalum have also been examined.

### 6.25 MOLYBDENUM

Although molybdenum is an important ferroalloying element, we discuss its extraction later, i.e., in Section 7.24, because it is extracted mainly from its sulphide ores.

### 6.26 FERROALLOYS

Ferroalloys of vanadium, chromium, silicon, titanium, zirconium, manganese, tungsten, and molybdenum are used mainly to facilitate the addition of alloying elements to molten steel. Ferroalloys ensure that the loss of the alloying elements due to oxidation is kept low because they have fusion points lower than those of the alloying elements and can, therefore, dissolve rapidly in steel or iron.

Ferroalloys help in eliminating oxygen and other dissolved gases from molten steel. (The presence of dissolved gases is usually detrimental to the mechanical properties of steel.) For example, the ferroalloys of silicon, manganese, and titanium remove oxygen by forming stable oxides which do not dissolve in steel and the ferroalloys of titanium and zirconium form stable nitrides and eliminate nitrogen from steel.

Ferroalloys of silicon and nickel control the graphite morphology in cast irons, which improves the mechanical properties of the cast irons.

It should be noted that single ferroalloy may perform more than one function depending on factors such as the composition and the condition of the molten steel, and the amount of ferroalloy used. Some complex ferroalloys have recently brought about improvements in both mechanical properties and chemical refining which are not readily achieved by several alloys used individually.

Table 6.7 summarizes the functions of some important ferroalloys that impart desirable properties to steels and cast irons.

Table 6.7 Ferroalloys and Their Uses

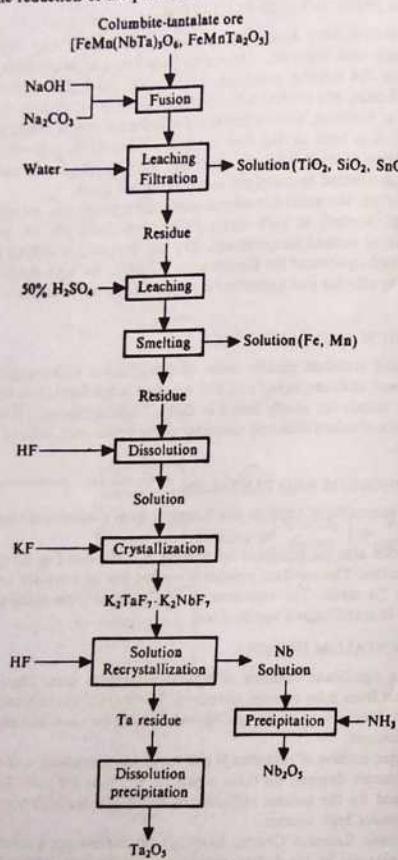


Fig. 6.15 Extraction of Niobium and Tantalum.

Ferroalloy	Use(s)
Fe-Cr [high- and medium-carbon ferrochrome (carbon 2–8% and chromium 68–71%)]	To supply chromium for stainless steel-making and to produce alloy steels for mining and milling applications
Fe-Cr [low-carbon ferrochrome (carbon 0.02–2% and chromium 65–72%)]	For finishing additions in stainless steel-making
Fe-Si	Mainly as a deoxidizer in steel industry Fe-Si (50–75% Si) promotes formation of graphite in cast

Table 6.7 Ferroalloys and Their Uses (cont.)

Ferroalloy	Use(s)
	iron by decomposition of cementite ( $Fe_3C$ ); it is therefore also used to produce malleable iron containing nodular graphite
	Limited addition of Si to low-carbon steel improves tensile strength, yield strength, and impact strength
	$Fe-Si-C$ alloys (Si up to 4.5%) are suitable as magnetic material with high resistivity and permeability with reduced core losses
Fe-W	In manufacturing tungsten steels, e.g., high-speed steel (such steels have ability to retain hardness at high temperatures and are therefore used as machine tools) Typical composition W 18%, Cr 4%, V 1%, Co 65-75% Precipitation-hardening tungsten alloys (carbon-free Fe-W) are suitable as die material
Fe-V	For imparting fine grain size to steels, thereby improving mechanical properties In production of tool steels to reduce grain coarsening during heat treatment and to increase toughness and strength
Fe-Mn	For deoxidation and desulphurization of steel (for every ton of steel, 5-6 kg Mn is required) Alloy steels containing almost 14% Mn are used in manufacturing jaw crushers and railway equipment, e.g., tracks, points, crossings, and switches High-carbon Fe-Mn is generally used for additions to carbon steels, whereas low-carbon variety is used only for alloy steels requiring low-carbon content
Fe-Zr	Sometimes for deoxidizing and scavenging of steel Zirconium treatment improves shock-resisting properties and steels thus treated are used for tools, e.g., rock drills
Fe-Ti	For deoxidation and alloying of steel A strong carbide stabilizer, Ti is used in austenitic stainless steels to prevent intergranular corrosion; its addition also improves hardening characteristic of plain chromium steel

**6.17 GENERAL METHODS OF PRODUCING FERROALLOYS**

The basic steps in the production of ferroalloys are ore beneficiation, reduction, and refining.

**BENEFICIATION**

To produce ferroalloys on a commercially viable basis, it is necessary to ensure that the metal content in an ore is high compared with the iron content. The main purpose of beneficiation is to increase the metal content in lean ores. The principal methods of beneficiation fall into two categories, namely, physical methods such as washing, gravity separation, and magnetic separation and chemical methods such as acid leaching and roasting.

In India, some groundwork has been done with regard to the beneficiation of the indigenous ores of ferroalloying elements. Table 6.8 summarizes some of the typical beneficiation techniques employed in India.

Table 6.8 Mineral Dressing of Indigenous Ores of Ferroalloying Elements (Indian ores)

Deposits	Beneficiation procedure	Remarks
<b>Chromium</b> Total deposits about 3.5 million tons; about 1 million tons with chromium content higher than 48%	Grinding up to -65 mesh to liberate minerals; subsequent tabling and magnetic separation to remove gangue ( $MgO$ , $CaO$ , $Al_2O_3$ , and $SiO_2$ ) Roasting followed by leaching to remove iron oxides Selective chlorination of iron oxides	To obtain high-grade Fe-Cr alloy, ratio of Cr to Fe in the ore should be 3:1 or higher, $Cr_2O_3$ content should be at least 48%, and content of each of $MgO$ and $Al_2O_3$ should be less than 25% To obtain medium-grade Fe-Cr alloy, ratio of Cr to Fe need be only 1:6 Physical methods of separation help in eliminating gangue, but cannot change Cr/Fe ratio as these metals occur in a chemical combination in minerals; on the other hand, chemical methods are effective in preferential removal of iron oxides
<b>Manganese</b> Total deposits about 180 million tons; about 120 million tons with manganese content higher than 46%	Reduction roasting followed by magnetic separation	To obtain high-grade Fe-Mn alloy, ratio of Mn to Fe in nonmagnetic concentrates should be 7:1 In the ore, the manganese content should be about 50% or more and the amount of phosphorus, $Al_2O_3$ , and $SiO_2$ should be low

Deposits	Beneficiation procedure	Remarks
<b>Tungsten</b>		
Limited deposits of wolframite with tungsten content 65–70%	Gravity separation, tabling, magnetic separation, leaching, high-temperature fusion with alkali to produce water-soluble alkali tungstate from which tungsten is recovered	See tungsten extraction (Section 6.22)
<b>Titanium</b>		
Extensive deposits (about 250 million tons) of ilmenite and rutile found in beach sands with $TiO_2$ content 60%	Magnetic separation	See titanium extraction (Section 8.17)
<b>Vanadium</b>		
Total deposits about 22–25 million tons with vanadium content 0.5–2.5%	Soda ash roasting and subsequent leaching to produce liquor containing sodium vanadate from which vanadium pentoxide is precipitated	See vanadium extraction (Section 6.23)

Ferroalloys are generally produced from the beneficiated ore by two processes, namely, carbon reduction and metallothermic reduction.

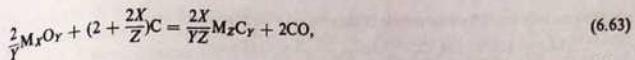
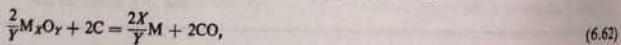
In the first process, suitable minerals mixed with iron ore are reduced by coke to produce high-carbon ferroalloys. The carbon content of these ferroalloys may be lowered by subsequent refining techniques. The carbothermic reduction and the subsequent refining operations, which require high temperatures, are mostly carried out in an electric furnace. Ferromanganese can be produced also in a blast furnace.

In the metallothermic reduction method, commonly referred to as the Goldschmidt process, oxide ores are reduced by aluminium in the presence of scrap iron to yield ferroalloys. This method is suitable for the production of alloys without carbon and for operation on a small scale. Aluminothermic reduction is an exothermic process, and, in most cases, is autogenous and does not require external heating.

We now discuss carbon reduction and aluminothermic reduction in detail.

#### CARBON REDUCTION

The relevant reactions during the carbon reduction of an oxide ore are



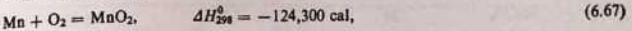
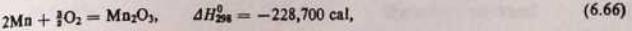
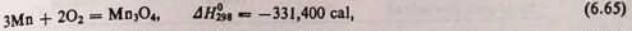
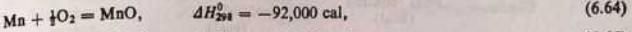
where M is a metal and X, Y, and Z are the valencies of oxygen, the metal and carbon, respectively.

In general, the free energy changes associated with reactions (6.62) and (6.63) indicate that it is impossible to obtain a ferroalloy with a low carbon content by using carbon itself as the reducing agent because stable carbides are formed, as per reaction (6.63). A substantial amount of silicon, produced as a result of the reduction of the silica present in the gangue, may contaminate the alloy unless the composition of the slag produced during reduction smelting is controlled. A basic slag helps in reducing the activity of silica and, therefore, lowers the absorption of silicon by the ferroalloy.

The temperature required for the carbothermic reduction smelting of a ferroalloy lies in the range 1500–1800°C. Such high temperatures are required because a molten ferroalloy is needed and also because oxides such as  $SiO_2$ ,  $TiO_2$ ,  $V_2O_3$ ,  $Cr_2O_3$ , and  $MnO$ , which are desired in the ferroalloy, are highly stable and can be reduced by carbon only at high temperatures (see Fig. 2.1). To attain a temperature in the range just mentioned, an electric furnace is ideally suited.

#### ALUMINOTHERMIC REDUCTION

The aluminothermic reduction of manganese oxides is highly exothermic as is evident from the reactions



where  $\Delta H_{298}^0$ , in each case, is the standard heat of formation of a particular manganese oxide. The standard heat of formation of alumina, at 298°C, according to the reaction



is –400,000 cal.

#### Analysis of Aluminothermic Reduction of Manganese Ores

Let us suppose that, starting with a cold charge, a maximum reaction temperature of 2000°C is needed to effectively separate slag and metal produced during reduction. To analyze the requirement of the net heat, we have to first consider the enthalpy data (given in standard tables) for Mn and  $Al_2O_3$ . For Mn, we have

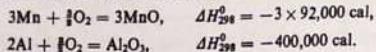
$$H_{2000}^0 - H_{298}^0 = 24,000 \text{ cal/gm atom},$$

and for  $Al_2O_3$ , we have

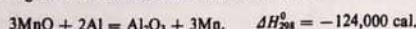
$$H_{2000}^0 - H_{298}^0 = 85,000 \text{ cal/mole}.$$

Let us now consider the reduction of  $MnO$ . We calculate the heat released by the reduction

reaction as follows. The two reactions that have to be considered are



Subtracting the first reaction from the second, we get



Thus, the heat available during reduction is 124,000 cal.

We next take into account the heat required to increase the temperature of the reaction products, namely,  $\text{Al}_2\text{O}_3$  and 3Mn from the room temperature to nearly 2300 K, i.e., heat required =  $85,000 + (3 \times 24,000) = 157,000 \text{ cal}$ .

Thus, the deficiency of heat is  $(157,000 - 124,000) = 33,000 \text{ cal/mole}$ . Extra heat has to be provided to meet this deficiency and also to take care of the heat lost to the surroundings.

The heat balance calculations carried out for other oxides of Mn in a manner similar to the foregoing one, assuming adiabatic conditions, are summarized in Table 6.9. From Table 6.9, we

Table 6.9 Heat Balance for Aluminothermic Reduction of Manganese Oxides

Oxide	Heat required (kcal)	Heat available per mole of $\text{Al}_2\text{O}_3$ (kcal)	Mn/Al ratio in reduction charge
$\text{MnO}$	157	124	1.5
$\text{Mn}_2\text{O}_4$	139	152	1.125
$\text{MnO}_2$	121	214	0.75

observe that the reduction of  $\text{MnO}_2$  generates an excessive quantity of heat. The generation of excess heat is sometimes controlled either by adding cold iron chips or by using coarse particles which lead to a slow reaction rate. On the other hand, when the available heat just falls short of the required heat, including that for heat losses, the process may be made autogenous either by preheating the charge or by adding boosters such as  $\text{NaNO}_3$  and  $\text{KClO}_4$ , which provide a large amount of heat on aluminothermic reduction.

The alloy produced by the aluminothermic reduction of a metal contains a substantial amount of aluminium. Moreover, the formation of aluminates during reduction may lead to the loss of metal oxide. This loss is largely prevented by adding basic oxides such as  $\text{CaO}$ . Further, a suitable flux is necessary to lower the viscosity of an alumina slag, which normally has a high viscosity. For example, a relatively fluid slag can be obtained by using alloys of Al and Ca or Al, Ca, and Si instead of Al as the reductant. The addition of  $\text{CaF}_2$  may also help in lowering the viscosity.

#### Aluminothermic Process Versus Carbothermic Process

Although most ferroalloys are produced by the carbothermic process, the aluminothermic process

is more favourable in cases where ferroalloys without carbon are required or where production is on a small scale. However, apart from these two criteria, other criteria, such as the operating cost (mainly cost of power), the nature of the ore, the cost of charcoal and coke, and the cost of aluminium, determine the choice of process. Table 6.10 compares the scopes of the carbothermic process and the aluminothermic process in the production of ferroalloys.

Table 6.10 Commercial Use of Carbothermic and Aluminothermic Processes

Ferroalloy	Carbothermic process	Aluminothermic process
Fe-Cr	Largely employed	Can be employed
Fe-Mn	Largely employed	Can be employed
Fe-V	Largely employed	Can be employed
Fe-W	Largely employed	Can be employed
Fe-Ti	Largely employed	Can be employed
Fe-Mo	Largely employed	Can be employed
Fe-B		Exclusively employed
Fe-Zr		Exclusively employed
Fe-Cr-Mn		Exclusively employed

#### REFINING OF FERROALLOYS

The main purpose of refining a ferroalloy produced by carbothermic reduction is to lower its carbon content. The methods generally employed are:

- (1) The removal by oxidation. This involves
  - (a) the treatment of alloy by oxidizing slags,
  - (b) the controlled oxidation of carbon by oxygen,
  - (c) the oxidation of carbon under vacuum.

(2) The removal of carbon by the introduction of an element into the molten alloy in order to decrease the solubility of carbon in the alloy.

We now give examples of ferroalloy refining.

In the production of ferromanganese, a high-carbon ferromanganese (7 per cent carbon) is first produced. To obtain a medium-carbon ferromanganese (2 per cent carbon), the high-carbon ferromanganese is initially smelted along with fresh manganese ore and a manganese-rich slag (20-40 per cent manganese). Next, a part of the carbon in the high-carbon ferromanganese is oxidized by the manganese dioxide in the fresh ore to yield medium-carbon ferromanganese. To obtain a low-carbon ferromanganese, the manganese-rich slag is once again smelted along with

carbon to produce silicomanganese and a slag with a low manganese content (2-8 per cent manganese) which can be discarded. (Silicomanganese does not contain any carbon because silicon decreases the solubility of carbon and also because the silicide is more stable than the carbide.) When silicomanganese is smelted with sufficient fresh manganese ore to oxidize only the silicon, low-carbon ferromanganese (0.5 per cent carbon) is produced. We thus conclude that, in ferromanganese production, the principle of oxidation using oxidizing slags and that of decreasing the solubility of carbon by introducing another element form the basis for the production of medium- and low-carbon ferromanganese.

In the case of ferrochromium, a low-carbon ferrochromium is obtained from a high-carbon ferrochromium by applying the principle of the controlled oxidation of carbon with oxygen in the presence of an inert gas or under vacuum. The relevant reactions are



where C and Cr denote, respectively, carbon and chromium dissolved in the ferroalloy. If reaction (6.70b) is made to proceed towards the right, carbon can be removed without oxidizing the chromium from the ferroalloy. The thermodynamics of reaction (6.70b) shows that at high temperatures ( $> 1500^\circ\text{C}$ ), the removal of carbon is favoured. Also, it is clear from reaction (6.70b) that decarburization is favoured when the partial pressure of CO is lowered. This lowering can be achieved either by vacuum or by inert gas (argon) purging. Presently, both techniques, namely, vacuum oxygen decarburization (VOD) and argon oxygen decarburization (AOD), are widely employed in the manufacture of stainless steels, which are mainly Fe-Cr alloys.

## 6.28 PRODUCTION OF INDIVIDUAL FERROALLOYS

### FERROMANGANESE

High-carbon ferromanganese (7.5 per cent C, 74-80 per cent Mn, and balance Fe) is the most important ferroalloy of manganese. It is commonly produced by the carbothermic reduction of high-grade manganese ore (47-50 per cent Mn) with a low iron content (6 per cent Fe), a low silica content (1 per cent  $\text{SiO}_2$ ), and a low phosphorus content (0.14-0.18 per cent). The ore is smelted in an electric furnace with the addition of 15-20 per cent (by weight) of coke. The choice of flux depends on the ore composition. If the ore does not contain the desired lime/silica ratio of about 1, lime is added as flux. This addition is necessary to control the Si content of the ferroalloy. Previously, although manganese recovery was only about 60 per cent, modern techniques, which entail a high degree of feed homogenization, slag control, and scrubbing of the electric furnace gases to recycle the  $\text{MnO}$  dust, have raised the figure to 85-90 per cent.

Medium-carbon ferromanganese (2 per cent C) is produced by smelting high-grade manganese ore with high-carbon ferromanganese. The manganese oxide in the ore oxidizes part of the carbon in the ferromanganese to produce a medium-carbon ferromanganese. The slag produced is rich in manganese (20-40 per cent Mn) and is generally used for silicomanganese production.

The production of low-carbon ferromanganese is accomplished by the silicothermic reduction of the manganese ore in an electric furnace with silicomanganese. As the carbon introduction is kept to a minimum, ferromanganese with 0.5 per cent C can be produced. The slag produced has a high manganese content (40 per cent Mn) and is employed for silicomanganese production.

Silicomanganese (20-25 per cent Si, 60-65 per cent Mn, 1 per cent C, and balance Fe) is

generally produced by the carbothermic reduction of a mixture of a manganese slag and quartzite. The manganese recovery is more than 90 per cent because of the high reduction potential employed. It should be noted that since the stability of  $\text{P}_2\text{O}_5$  is similar to that of  $\text{FeO}$  at high temperatures and since iron is almost completely reduced during ferromanganese production, nearly the entire amount of phosphorus is reduced and enters the ferromanganese. As the maximum desired limit of phosphorus in the ferromanganese is 0.35 per cent, the phosphorus content of the manganese ore and the lime flux, used as raw materials, must be low.

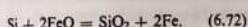
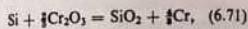
### FERROSILICON

Ferrosilicon is produced by the carbothermic reduction of quartzite (95-97 per cent  $\text{SiO}_2$ ) in an electric furnace. The normal grades of ferrosilicon contain 45 per cent Si or 75 per cent Si, the balance being iron. During ferrosilicon production, since all the phosphorus present in the quartzite would be reduced to the alloy, the raw material employed should have a low phosphorus content in order to restrict contamination of ferrosilicon by phosphorus.

### FERROCHROMIUM (FERROCHROME)

All grades of ferrochromium can be produced in an electric furnace. For example, carbonaceous ferrochrome is obtained by the carbothermic reduction of a chromium ore at high temperatures ( $1600-1700^\circ\text{C}$ ). A basic slag is produced during reduction, which keeps the silica activity in the system at a low level and allows the production of ferrochromium with a low silicon content (about 2.5 per cent).

Low-carbon ferrochrome is obtained by the reduction of a chrome ore by silicon in the form of silicochromium. The reactions are



Silicochromium is produced by melting together high-carbon ferrochrome and ferrosilicon. This melting results in the very rapid elimination of carbon from the high-carbon ferrochrome. The complex process for the production of low-carbon ferrochrome is shown in Fig. 6.16.

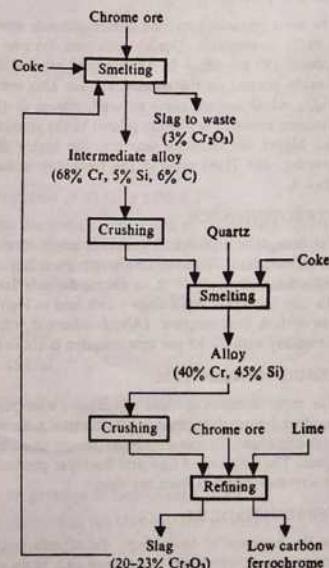


Fig. 6.16 Triplex Process for Production of Low-Carbon Ferrochrome.

Both high-carbon and low-carbon ferrochromium are widely used in the manufacture of stainless steels. However, with the advent of vacuum oxygen decarburization (VOD) and argon oxygen decarburization (AOD), which have modified the electric furnace stainless steel-making process, the demand for low-carbon ferrochromium has rapidly decreased.

#### Charge Chrome

In the past, the minimum limit of the Cr/Fe ratio in ferrochromium had been specified as 3.0, considered unfit for ferrochromium manufacture. Of late, however, the stainless steel industry has rationalized its mix and accepts ferrochromium with a Cr/Fe ratio that lies in the aforementioned range, utilizing the iron present in ferrochromium as a substitute for scrap iron. This grade of ferrochromium (Cr/Fe ratio 1.5–2.0) is referred to as *charge chrome*.

#### FERROTITANIUM

The most important method of ferrotitanium manufacture is by the aluminothermic reduction of a rutile concentrate. During reduction, the iron oxides in the concentrate are almost completely reduced (99 per cent). In addition, 80 per cent of the silica and 70–78 per cent of the titanium dioxide present in the concentrate are also reduced. Lower oxides of titanium such as  $TiO$  and  $Ti_2O_3$ , which are not easily reduced, remain in the slag. It should be noted that the extent of titanium recovery is directly related to the aluminium content of the ferrotitanium produced; i.e., the higher the titanium recovery, the higher the level of aluminium in the ferrotitanium. In practice, the Ti/Al ratio in the ferroalloy is maintained at a value that is equal to or greater than 4.

#### FERROTUNGSTEN

Ferrotungsten is produced by the reduction of tungsten oxides using carbon, silicon, or aluminium as the reductant. To obtain a ferrotungsten that contains less than 1 per cent carbon, carbothermic reduction is carried out in an electric furnace lined with magnesite. The magnesite lining allows the use of highly basic slags which lead to high tungsten recovery and enable the production of low-carbon ferrotungsten. (Aluminothermic reduction can also be employed.) In either case, a ferroalloy with 80–85 per cent tungsten is obtained.

#### FERROMOLYBDENUM

The most common method of reducing a molybdenum concentrate containing  $MoO_3$  in order to produce ferromolybdenum is silico-thermic reduction. In this case, ferrosilicon is employed as the reducing agent. To generate more heat, a small quantity of the ferrosilicon is replaced by aluminium. The addition of lime and fluorspar produces a fluid slag, which facilitates the separation of ferromolybdenum from the slag.

#### FEROVANADIUM

In the presence of basic slags, the silico-thermic reduction of  $V_2O_5$  is rendered possible at high temperatures, which can be attained only in an electric furnace. The formation of lower oxides of vanadium during reduction and the reaction of  $V_2O_5$  and  $VO$  with silica to form vanadium silicates render the reduction reaction even more difficult. Therefore, a two-stage reduction operation becomes necessary. In the first stage,  $V_2O_5$  is reduced under basic conditions to produce silicon-

rich ferrovanadium. In the second stage, silicon is removed using fresh charges of  $V_2O_5$  and lime.

The overall recovery rate of vanadium is 75–80 per cent, the rest being lost in the slag. Ferrovanadium can also be obtained from vanadiferrous iron ores. The procedure is as follows. The ores are first smelted to produce vanadium-rich pig iron which is refined in a steel refining unit to yield a vanadium-rich slag from which  $V_2O_5$  is extracted using hydrometallurgical methods. From this  $V_2O_5$ , ferrovanadium is obtained as in the two-stage reduction process.

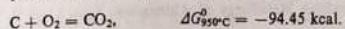
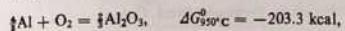
#### PROBLEMS

- Discuss the aluminothermic method used for the production of manganese metal from a pyrolusite concentrate. Using the following data, determine the theoretical optimum Mn/Al ratio of the charge:

	$\Delta H_{298}^0$ (kcal/mole)	$H_{2100} - H_{298}$ (kcal/mole)	
MnO	92.0	Mn	24.0
$Mn_3O_4$	331.4	$Al_2O_3$	85.0
$Mn_2O_3$	228.7		
$MnO_2$	124.3		
$Al_2O_3$	400.0		

The boiling point of Mn is 2368 K and the melting point of  $Al_2O_3$  is 2333 K.

- Discuss the physical chemistry involved in the electrolytic production of aluminium. Using the following data, calculate the power efficiency of the electrolytic process. The voltage of the cell at an operating temperature of 950°C is 5.29 V, the activity of alumina is 0.1, and the anode gas contains 85 per cent  $CO_2$ . (Note: 1 gm equivalent electron volt = 23.01 kcal.) The relevant reactions are



- Is the electrowinning of magnesium and aluminium from aqueous solutions possible?
- Discuss, with reference to decomposition potential, whether chromium and manganese ions can be electrodeposited from aqueous solutions without the evolution of hydrogen. What is the method used to suppress hydrogen evolution?
- Can tin be selectively reduced from  $SnO_2$  in the presence of iron oxides?
- Why does the ALCOA process consume less energy than the Hall-Héroult process?
- What is charge chrome and why has it become popular?
- Will the injection of methane into the Hall-Héroult cell during aluminium extraction decrease its operating voltage?
- Can  $MgO$  be reduced by Si at 1000°C? What are the techniques used to promote  $MgO$  reduction by Si in the Pidgeon process?

10. Discuss the methods used in the production of low-carbon ferrochromium and also explain the principles underlying these methods.

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## 7 Extraction of Metals from Sulphide Ores

## 7.0 INTRODUCTION

A large number of metals are commercially produced from ores that contain sulphide minerals. These include some very common metals such as copper, lead, zinc, and nickel and other metals such as cadmium, cobalt, antimony, bismuth, mercury, and molybdenum. Some of these metals, for example, copper, lead, zinc, and mercury have been produced since ancient times. However, with advances in technology, newer, more energy-efficient processes, which also protect the environment, are replacing the traditional processes.

The metallurgy of some of these common metals is considered complex because, at times, it may involve as many as 25 end products coming from only two or three different metallurgical concentrates which, in turn, may originate from a single mine. Some of the elements involved in the metallurgy of Cu, Zn, and Pb are listed in Table 7.1. The recovery of each of these elements is, in itself, a complex process. Most of the elements must be frequently circulated between two or more extraction circuits before they become sufficiently concentrated to render their recovery feasible and economical.

Table 7.1 Elements Involved in Metallurgy of Cu, Zn, and Pb

Elements recovered	Elements discarded	Elements utilized
Cu, Pb, Zn, S, Ag, Au, Pt, Pd, As, Sb, Bi, Se, Te, Ni, Co, In, Tl, Sn, Cd, Re, Hg	Fe, Ca, Si, Mn, Mg, Al, Cl <sub>2</sub> , S, O <sub>2</sub> , F <sub>2</sub>	C, O <sub>2</sub> , H <sub>2</sub> (in water)

In addition to approximately 20 recoverable elements, there are at least nine other elements which must be separated, usually, in the form of a discard slag or gas, at one stage or the other of the extraction process.

Both hydrogen and carbon are very ineffective reducing agents as far as the direct reduction of a sulphide to a metal is concerned (see Chapter 2). The metallocerhetic reduction of a sulphide, involving direct reduction with a metal, is theoretically possible, but, in practice, it is highly energy-intensive and, in most cases, not commercially attractive.

The sulphide ion S<sup>2-</sup> is more easily polarizable than the oxide ion O<sup>2-</sup>, and, according to Fajan's rules, the M-O bond is more ionic in character than the M-S bond. Therefore, most metallic sulphides tend to be covalent in nature (the notable exceptions being those of alkali and alkaline earth metals). Consequently, in nature, sulphide bonding tends to be metallic, forming

a sequence of phases such as  $\text{Co}_9\text{S}_4$ ,  $\text{Co}_3\text{S}_4$ , and  $\text{CoS}_2$ . Other characteristics of sulphides include stoichiometric variability in composition and a high electrical conductivity, and miscibility with metals, a property which adds to the difficulties encountered in effecting the separation of the metal from the sulphide. Thus, in principle, the extraction of a metal from a sulphide is more difficult than from an oxide. Therefore, a possible method of extraction could be the dead roasting of a sulphide to an oxide followed by the reduction of the oxide by carbon. Although this method has found application in the case of lead and zinc ores, it does not work out satisfactorily in all cases because of the presence of associated sulphides such as those of iron in the ore. Also, the dead roasting of such ores would lead to the formation of iron oxides which are difficult to separate from the desired metal both before and after reduction. Consequently, special methods have to be adopted for the recovery of metals from sulphide ores, some of which are now discussed.

### 7.1 WINNING OF METALS FROM SULPHIDE ORES

A metal can be produced from a sulphide by one or more of the following methods:

- (1) thermal decomposition,
- (2) roasting and subsequent reduction,
- (3) controlled roasting followed by smelting to produce matte and converting the matte to metal,
- (4) flash smelting followed by converting the resultant matte to metal,
- (5) electrolysis of a sulphide matte obtained from smelting or converting operations,
- (6) metallothermic reduction of a sulphide,
- (7) hydrometallurgical processing of a sulphide,
- (8) chlorination of sulphide minerals and subsequent metal recovery.

We now discuss the principles underlying these methods.

#### THERMAL DECOMPOSITION

The thermal decomposition of some sulphides can be carried out according to the reaction



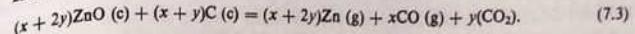
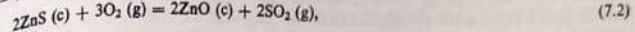
At moderately high temperatures, the sulphides of platinum and iridium decompose to yield platinum and iridium, respectively. Mercury can be obtained by the direct heating of  $\text{HgS}$ . Some other metals, for example, Mo, Cu, and Co can be extracted from their sulphides by applying a vacuum, which shifts the reaction equilibrium to the right. However, in all these cases, practical problems are encountered, such as a slow rate of reaction and the tendency of the metal to form oxides if decomposed in air. Consequently, thermal decomposition does not find application when the metal extraction is on a large scale.

#### ROASTING AND SUBSEQUENT REDUCTION

Roasting of the sulphide mineral and the subsequent reduction of the oxide constitute a conventional pyrometallurgical approach. Traditionally, sulphides are roasted in pots, muffles, travelling grate roasters, or multiple hearth roasters in the presence of air. In recent years, however, flash roasters and fluidized bed roasters, which employ oxygen-enriched air, have been developed in order to accelerate roasting operations and to better utilize the exothermic heat of reaction.

The oxide obtained as a result of roasting is reduced by carbon to yield the metal. (It may be noted that about 40 per cent of the world's zinc is obtained by this method.)

We now consider the roasting and subsequent reduction of some metals. For zinc, the reactions may be written as



In this connection, the Imperial Smelting process, mainly developed for the blast furnace reduction of roasted zinc-containing lead concentrates, is noteworthy because it accounts for well over 10 per cent of the present total world zinc production. (This process is discussed in detail later in this chapter.)

In the case of lead, the metal is produced by first roasting  $\text{PbS}$  to yield  $\text{PbO}$  and then reducing  $\text{PbO}$  by coke in a blast furnace to give  $\text{Pb}$ . The roasting and subsequent reduction technique can also be used for antimony, arsenic, and bismuth.

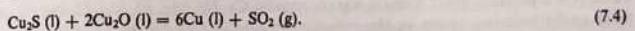
In the case of copper, the metal can be produced by the Brixlegg process (see Kettner *et al.*, 1972), i.e., by the dead roasting of the sulphide to the oxide followed by reduction smelting in an electric furnace to yield black copper which contains about 92 per cent Cu and about 5 per cent Fe. The further hydrometallurgical treatment of black copper produces refined copper. The Brixlegg process is not commonly used because of the high energy requirement compared with the matte smelting process for copper which is described later in this chapter.

Finally, in the case of molybdenum, the metal is generally extracted by roasting molybdenite ( $\text{MoS}_2$ ) to produce  $\text{MoO}_3$  which is reduced by hydrogen.

#### CONTROLLED ROASTING, MATTE SMELTING, AND CONVERSION OF MATTE

Before simple roasting and reduction can be carried out, it is necessary to ensure that the roast is rich in the metallic oxide and has a low content of gangue and other unwanted oxides. Let us first consider the case of copper. Most copper sulphide minerals contain iron sulphide which has to be eliminated before metallic copper can be extracted. Such an elimination is conventionally carried out by subjecting the mineral to roasting, matte smelting, and converting.

The purpose of roasting a copper concentrate is to convert most of the iron sulphide present in it to oxide, leaving behind copper mostly as sulphide. Subsequently, the greater portion of the iron oxide is slagged out. This results in a matte that consists mainly of copper sulphide with residual iron sulphide. This matte is then converted to copper in a side-blown converter in which air is employed to completely oxidize the iron sulphide. The oxidized iron is slagged out by adding silica flux. At this stage, the matte mainly contains  $\text{Cu}_2\text{S}$ , and is further oxidized by air. The reaction is as follows:



In the case of nickel, the processing of the mineral pentlandite [ $\text{FeNi}(\text{S})$ ] is similar to that of copper. When a nickel concentrate containing chalcopyrite (commonly associated with pentlandite) is used for nickel recovery, a copper-nickel matte is obtained after controlled roasting, smelting, and converting. Subsequently, processes such as controlled cooling, grinding, magnetic separation, and selective flotation are employed to obtain three products, namely, copper-nickel alloy,  $\text{Cu}_2\text{S}$  and  $\text{Ni}_3\text{S}_2$ . Nickel can be recovered from  $\text{Ni}_3\text{S}_2$  by dead roasting and subsequent carbon reduction. Nickel can also be recovered by employing a converter that has a top blowing

arrangement. In this case, the reaction is similar to reaction (7.4).

The simultaneous conversion of two sulphides in a mixed matte can produce alloys. This method was employed during the Second World War to produce copper-nickel alloys from copper-nickel mattes.

#### FLASH SMELTING AND CONVERTING

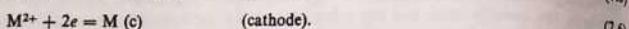
In flash smelting—a recently developed process—flash roasting and matte smelting are carried out simultaneously in a single furnace in which the fine particles of the sulphide concentrate react with a stream of oxygen (or oxygen-enriched air) at high temperatures. The oxidation of the sulphide concentrate itself provides a considerable amount of heat, and, in most instances, smelting can be carried out autogenously without the supply of any external heat. The flash smelting of a copper or nickel concentrate produces a high-grade matte, while in the case of lead, the metal can be obtained directly.

In another recently developed process, namely, *direct smelting*, when the copper concentrate is injected into the molten bath of a converter and blown directly, white metal is obtained.

In recent years, development work has been done on the continuous smelting of copper concentrates in order to combine direct smelting and converting. In Canada, the U.S.A., and Japan, the successful operation of a few continuous smelting plants has been reported.

#### ELECTROLYSIS OF SULPHIDE MATTES

Some sulphide mattes, i.e., those having a sufficient degree of metallic conductivity, can be directly cast into anodes and then electrolytically converted to the pure metal, which is deposited on a pure metal cathode. The reactions are



Not only does the electrolysis of a sulphide matte directly produce the pure metal but it also yields a valuable byproduct, i.e., elemental sulphur. Although this method can be applied to produce refined nickel, copper, and lead, it is employed, on a commercial basis, only in the case of nickel.

#### METALLOHERMIC REDUCTION

The reaction for the metallothermic reduction of a metallic sulphide may be written as



where R is a reducing agent. Certain metals, namely, Ca, Na, Mg, Al, Mn, Si, and Fe are potentially useful reducing agents in the reduction of sulphides of Cd, Mo, Co, Zn, and V under suitable conditions. The recovery of volatile metals, for example, Zn and Cd, can be increased by applying a vacuum or by using an inert gas during reduction. The use of a vacuum or an inert gas, however, makes the process expensive. Also, the batch-type nature of such metallothermic reduction renders it economically unattractive. The only exception could be the reduction of stibnite ( $Sb_2S_3$ ) by iron.

#### HYDROMETALLURGICAL PROCESSING

The hydrometallurgical processing of a sulphide mineral aims at producing a leach liquor that is

suitable for subsequent treatment. Since sulphides do not usually dissolve easily in common inorganic solvents, leaching may be preceded by roasting to convert the sulphides into oxides or sulphates which are easier to leach. Let us consider an example. Zinc ores are carefully roasted in order to minimize the zinc ferrite formation and then leached by sulphuric acid. The ferrite, if formed, is not readily leached, and, therefore, reduces zinc recovery. In recent years, new processes have been developed in order to enhance zinc recovery, in which, the unleached ferrite is leached by concentrated acid solutions. The zinc sulphate solution thus obtained, is purified and then electrolyzed to produce high-grade zinc.

In general, any leach liquor that contains metal ions may be subjected to cementation, hydrogen reduction, or electrolysis in order to extract the metal. For example, since ancient times, copper and silver have been recovered by cementation. Zinc has to be recovered by electrolysis because of its high reactivity. At present, about 60 per cent of the world's zinc, the bulk of the cadmium, and a significant proportion of copper, nickel, and cobalt are produced by hydro-metallurgical processing.

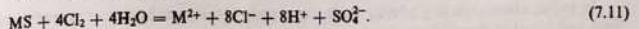
Of late, considerable progress has been made in the leaching of sulphides. Some of the developments have already been discussed in Chapter 4.

#### CHLORINATION OF SULPHIDES

Many metal sulphides may be directly chlorinated at elevated temperatures according to the reactions



The wet chlorination of sulphide pulps at a temperature below 100°C can also be carried out. The reactions, in this case, are



In wet chlorination, the metal chloride is subjected to cementation or electrolysis for metal recovery. The liberated sulphur is recovered by frothing the sulphur with compressed air or by dissolving the residue after filtration in hot kerosene and again filtering and cooling it to precipitate sulphur. On the other hand, in dry chlorination, the sulphur and disulphur dichloride formed as in reactions (7.8) and (7.9) can be recovered by selective distillation.

Dry chlorination is applicable to several sulphides, for example,  $ZnS$ ,  $Cu_2S$ ,  $Sb_2S_3$ ,  $CdS$ ,  $Ag_2S$ , and  $PbS$ , whereas wet chlorination presents problems. For instance, the reaction often ends up with the formation of sulphates, sulphur monochloride, or elemental sulphur.

In general, the chlorination reaction has not been commercially exploited, although the aqueous chlorination of copper concentrates and lead concentrates with ferric chloride is being actively studied.

#### 7.2 COPPER

##### USES

Copper is perhaps the most important nonferrous metal. Not only does it form extremely useful

alloys with metals such as Zn, Sn, Be, and Ni but it also has unique properties in the unalloyed state. At present, the total world production of copper is over 10 million tons per year. In India, however, the per capita consumption of copper remains low, i.e., about 0.15 kg, when compared with the per capita consumptions in the U.S.A., the U.K., and Japan, i.e., approximately 12 kg, 13 kg, and 6 kg, respectively. India produces only about 25,000 tons of copper per year indigenously, which fails to meet the annual demand of 60,000 tons. At present, Hindustan Copper Limited has a capacity of 47,000 tons per year, and plans to increase it to meet the entire domestic requirement.

Copper and its alloys have a unique combination of properties, for example, high electrical and thermal conductivities, adequate mechanical properties, a high resistance to various types of corrosion, a high scrap value, and amenability to fabrication by several techniques. It is often difficult to find a substitute that would have a similar combination of properties for certain specific applications.

Pure copper is unrivalled as a conductor of electricity, and, for this reason, it is extensively used in electrical applications. The relative percentages of the world-wide usage of copper are as follows:

Electrical applications	35%
Telecommunication	5%
Power transmission lines	7%
Automobile industry	10%
Building industry	8%
Railway equipment	3%
Miscellaneous	32%

In India, aluminium is gradually replacing copper in the manufacture of power transmission lines and in other electrical applications.

In nonelectrical applications, copper is used in the form of an alloy. Some of the commonly utilized alloys are Cu-Zn brasses (leaded brasses, Sn and Al brasses), Cu-Sn bronzes (phosphor bronzes) and Cu-Ni-Zn alloys (called nickel silver). Cu-Zn brasses that contain up to 36 per cent zinc are known as  $\alpha$ -brasses and have exceptional cold-working properties. Brasses which contain between 37 and 45 per cent of zinc are known as  $\alpha\beta$ -brasses and those which contain more than 45 per cent Zn are known as  $\beta$ -brasses.  $\alpha\beta$ -brasses are particularly suited for hot working, a property which improves as the zinc content increases, reaching a maximum at about 40 per cent. Cu-Sn bronzes, which are characterized by a higher mechanical strength than Cu, fatigue-resistant properties, and corrosion resistance, are used in engineering. Copper-nickel alloys containing 50–70 per cent copper have excellent ductility and offer a high resistance to corrosion.

#### HARMFUL IMPURITIES IN COPPER

The properties of copper differ depending on the nature of the impurity present in it. For instance, oxygen is present in all varieties of commercial copper except in specially deoxidized grades and adversely affects the electrical properties. In copper, oxygen, which exists either as a Cu-Cu<sub>2</sub>O eutectic or as small globules of Cu<sub>2</sub>O, lowers the electrical conductivity by reducing

the effective cross-section for current transmission. When present in a very small quantity oxygen is not harmful; in fact, it actually increases the electrical conductivity by removing other impurities from the solid solution. The effect of oxygen on the mechanical properties of copper is minimal. However, impurities such as sulphur, selenium, bismuth, antimony, and tellurium have harmful effects on both the mechanical and electrical properties of copper and have to be removed during refining.

#### 7.3 PYROMETALLURGICAL EXTRATION OF COPPER

##### SOURCES OF COPPER

Copper exists in nature mostly in the form of copper sulphide with or without other metallic sulphides. Oxides and oxidized ores are found only in limited quantities. We now list some of the common minerals of copper (the figures within parentheses give the theoretical copper percentage). Chalcopyrite CuFeS<sub>2</sub> (34.5), chalcocite Cu<sub>2</sub>S (79.8), bornite Cu<sub>5</sub>FeS<sub>4</sub> (55.5), covellite CuS (66.5), enargite CuAsS<sub>2</sub> (48.4), malachite, CuCO<sub>3</sub>·Cu(OH)<sub>2</sub> (57.3), azurite, 2CuCO<sub>3</sub>·Cu(OH)<sub>2</sub> (55.1), cuprite Cu<sub>2</sub>O (88.8), and chrysocolla CuSiO<sub>3</sub>·2H<sub>2</sub>O (36.2). Of the aforementioned minerals, chalcopyrite is commercially the most important ore. Although all these minerals theoretically contain a large quantity of copper, the actual ores contain only small amounts of copper because of contamination by other sulphides and the gangue. In fact, a sulphide ore that contains 0.5–2.0 per cent copper is considered satisfactory for copper extraction by concentration followed by pyrometallurgy. In the case of poorer grades, copper is extracted by hydrometallurgical processes.

##### EXTRATION OF COPPER FROM SULPHIDE ORES

We now discuss the steps involved in the extraction of copper by the conventional route (as shown on the left-hand side of Fig. 7.1), namely, concentration, roasting, smelting, converting, and refining. The newer routes, shown in Fig. 7.1, are described later in this chapter.

##### Concentration

A naturally occurring sulphide ore normally contains 0.5–2 per cent copper. Initially, this ore is subjected to crushing and grinding in order to liberate the sulphide grains from the gangue. The average particle size of the ore after grinding should be 40  $\mu$ m. Next, the ground ore is subjected to froth flotation. During froth flotation, the pH is controlled by the addition of CaO and a xanthate reagent is used as a collector. In the case of ores that contain discrete particles of copper sulphide, lead sulphide, and zinc sulphide, a differential flotation procedure is employed to selectively recover the copper sulphide. The copper sulphide concentrate thus produced contains 15–35 per cent Cu, 15–35 per cent Fe, 25–35 per cent S, and 3–15 per cent gangue.

##### Roasting

The purpose of roasting is to partially oxidize the iron sulphide present in the copper sulphide concentrate in order to facilitate its removal in the form of a slag in the next stage, i.e., smelting. The extent of roasting determines the copper grade of the matte (i.e., the percentage copper in the matte) produced in the smelting stage, which, in turn, determines the amount of copper lost to the slag. Therefore, for concentrates with a high iron sulphide content and a low copper sulphide content (< 25 per cent Cu), roasting is resorted to, but for high-grade copper concentrates (> 30 per cent Cu), roasting is often not necessary.

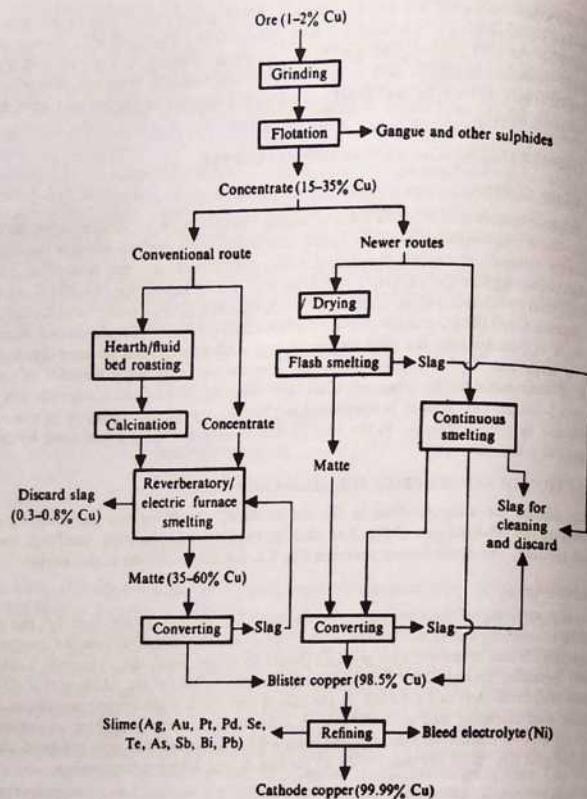
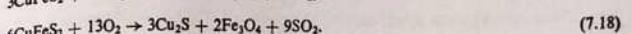
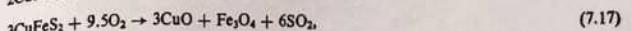
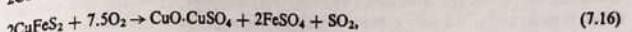
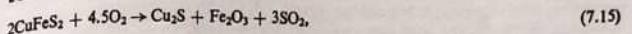
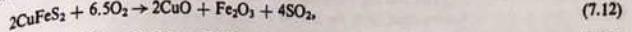


Fig. 7.1 Pyrometallurgical Extraction of Copper from Sulphide Ores.

In conventional plants, roasting is carried out in multiple hearth roasters with the feed travelling from one hearth to the other (see Fig. 4.2). The temperature of each hearth is gradually increased by fuel firing so that the charge gets heated up from the room temperature to about 550°C. In the newer plants, fluidized bed roasters (see Fig. 4.4), operating at about 550°C, are employed. Not only does this provide a more uniform feed for smelting purposes but also

produces a concentrated SO<sub>2</sub> gas stream which can be diverted for the manufacture of sulphuric acid.

During roasting, several reactions take place simultaneously. The roasted calcine consists of sulphides of copper and iron, oxides of iron, and mixed sulphates of copper and iron. Some of the typical reactions are



The roasted calcine is transferred to the smelting furnace in the hot condition itself so as to facilitate the separation and the subsequent recovery of copper.

#### Smelting

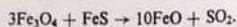
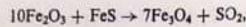
Smelting seeks to separate the metal sulphides in an ore, concentrate or calcine from the gangue. Such a separation can be achieved by smelting the charge with a suitable flux at a temperature of about 1250°C. During smelting, two layers of liquid are formed, namely, an upper slag layer that consists of the gangue and the flux and a lower matte layer that contains metallic sulphides. The specific gravity of the slag layer ranges from 2.8 gm/cm<sup>3</sup> to 3.8 gm/cm<sup>3</sup>, whereas that of the matte layer ranges from 5 gm/cm<sup>3</sup> to 5.5 gm/cm<sup>3</sup>. This difference in specific gravities permits a clear-cut separation of one phase from the other.

The gangue and the iron oxides present in the concentrate/calcine to be smelted combine with each other during smelting to form an iron silicate slag. If the amount of iron oxides is insufficient, lime is added as a flux to form an iron-calcium silicate slag. In most instances, a siliceous flux is needed to provide a low melting slag. The melting points of the slags thus formed are approximately 1150°C, and to obtain a fluid slag with a low copper content, smelting is carried out at a temperature of about 1250°C.

During smelting, both the copper sulphide minerals and the slag melt. In addition, exchange reactions take place between the oxides and sulphates of copper and the iron sulphide present in the furnace charge:



These reactions occur because oxygen has a greater affinity for iron than for copper (see Fig. 2.1). The unoxidized iron sulphide reduces the higher oxides of iron to ferrous oxide as shown by the reactions



The resultant ferrous oxide ( $\text{FeO}$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) react with the flux (silica or lime) to form a slag.

The oxidation taking place during roasting and that resulting from the leakage of air into the furnace during smelting determine the extent of oxidation of the iron sulphide in the charge. Generally, the object is to produce a matte that contains 35–45 per cent Cu, 20–22 per cent S, and 25–35 per cent Fe. This not only minimizes the loss of copper to the slag but also provides a matte with a sufficient quantity of iron sulphide for use in the next stage, i.e., converting, where iron sulphide oxidation provides all the heat required to ensure an autogenous converting operation. The relationship between the percentage Cu in the slag and that in the matte is given in Fig. 7.2 for various reverberatory furnace operations around the world.

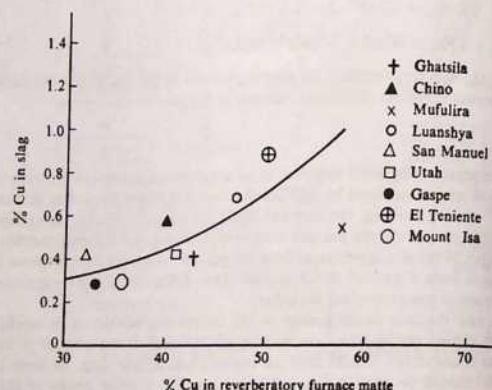


Fig. 7.2 Relationship between Slag Losses and Matte Grades in Copper Smelting Operations.

Conventionally, a smelting operation is carried out in reverberatory furnaces fired with either coal or oil. A typical reverberatory furnace is shown in Fig. 7.3. Smelting has also been carried out in electric furnaces. A typical electric furnace is shown in Fig. 7.4. An electric furnace is more advantageous than a reverberatory furnace if hydroelectric power is available freely and inexpensively because the generation of a large volume of combustion gases is avoided. This facilitates both the recovery of  $\text{SO}_2$  and the cleaning of the furnace gases, which is generally carried out by an electrostatic precipitator in order to recover the copper-bearing dust. However, an electric furnace consumes a large amount of energy, when fossil fuel is burnt especially to generate electricity. It has now given way to more energy-efficient processes, namely, flash smelting and continuous smelting, which are described later in this chapter.

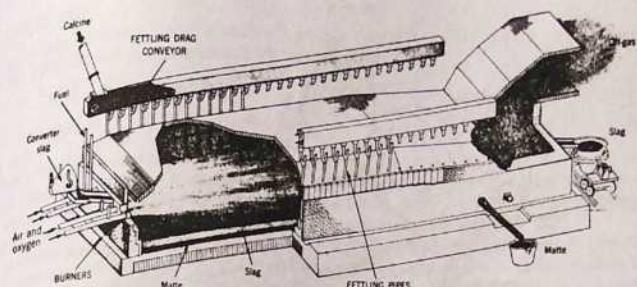


Fig. 7.3 Cutaway View of INCO Reverberatory Furnace (Boldt and Queneau, 1967).

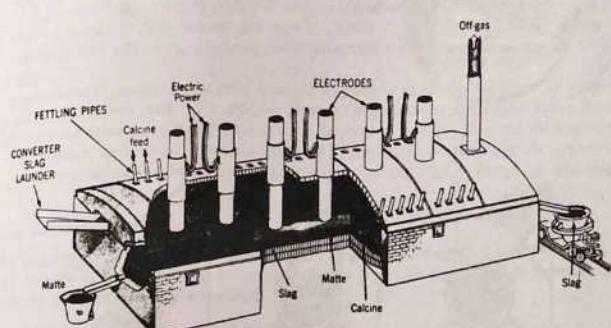


Fig. 7.4 Cutaway View of Submerged Arc Electric Furnace (Boldt and Queneau, 1967).

In the early days of copper concentrate smelting, the average capacity of the reverberatory furnace was 100 tons per day, but, at present, the reverberatory or electric furnace can smelt over 1000 tons a day.

#### Converting

The purpose of converting is to remove iron, sulphur and other impurities from matte. For this, the molten matte produced as a result of smelting is charged into a side-blown converter which is a cylindrical vessel with a capacity of 100–200 tons of matte. A typical vessel is 4 m in diameter and 9 m in length and is lined with a layer of chrome-magnesite refractory (about 40 cm thick). A typical side-blown converter is shown in Fig. 7.5.

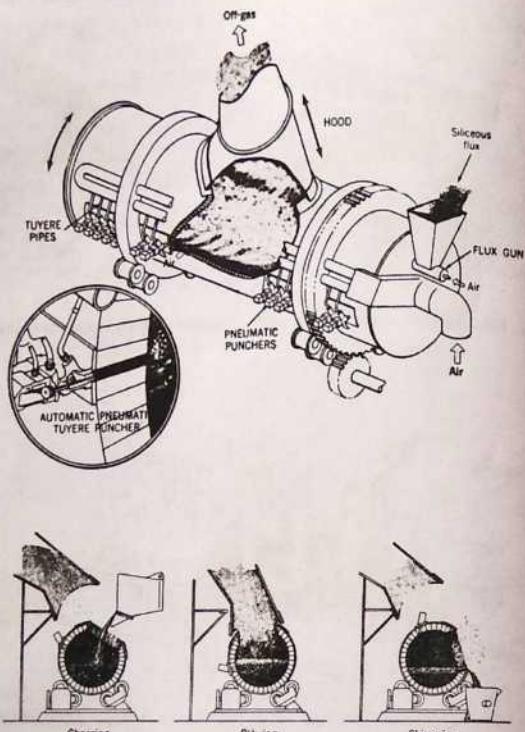


Fig. 7.5 Converter Operation (Boldt and Queneau, 1967)

In the converter, the atmosphere is highly oxidizing compared with the neutral or mildly oxidizing atmosphere during smelting. Air or oxygen-enriched air (up to a maximum limit of 32 vol % oxygen in the blast) is injected into the molten matte through tuyeres. Each tuyere is about 5 cm in diameter, and there are about 40 tuyeres in a converter. The total volume of gas flowing through these tuyeres is about 600 m<sup>3</sup>/min. The products of the converter are slag and blister copper.

We now discuss the two distinct stages in copper converting, namely, the slagging stage and the blister formation stage.

#### Slagging stage

In the slagging stage, the iron sulphide present in the matte is oxidized and the oxide is slagged out by the addition of a siliceous flux. The reactions are



Part of the FeO is also oxidized to magnetite.

Slagging is carried out in stages, i.e., by first adding freshly obtained furnace matte to the converter and then blowing air. Next, the supernatant slag formed is skimmed off by tilting the cylindrical converter. The molten slag and matte phases are immiscible.

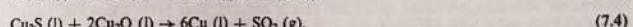
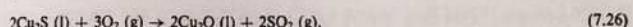
During converting, the oxidation of the iron sulphide generates sufficient heat to overcome the heat lost to the surroundings and to maintain the matte and slag in a molten state in the converter. It may be noted that in a large converter, where the blowing rate is high and, consequently, iron sulphide oxidation rates are also high, extra heat is generated which is utilized for melting scrap copper or cement copper generally produced in the plant.

The slag obtained typically analyzes 2–9 per cent Cu, 40–50 per cent Fe, 20–30 per cent SiO<sub>2</sub>, and 1–5 per cent (CaO + MgO). The iron oxide produced as a result of FeS oxidation is present in the slag mostly as fayalite saturated with magnetite. The magnetite forms a coating on the chrome-magnesite refractory, providing some protection for the refractory against attack by the slag.

Conventionally, copper is recovered from the slag produced in the converter by transferring the slag, in a molten state, to a smelting furnace (reverberatory, electric, or flash). Here, any matte particles present in the slag settle down at the bottom and the slag can be discarded. In modern practice, the metallic values are recovered by employing either an electric furnace with a provision for cleaning the slag or by the slow cooling of the slag followed by grinding and flotation.

#### Blister formation stage

After slagging has been completed, the converter essentially contains Cu<sub>2</sub>S which is called white metal because of its appearance. In the blister copper formation stage, Cu<sub>2</sub>S is oxidized to form copper by a combination of the reactions



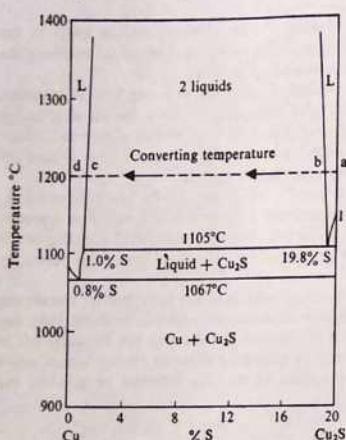
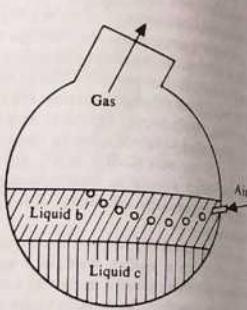
The overall reaction is



From reaction (7.27), we see that cuprous sulphide is reduced without any reducing agent.

The Cu-Cu<sub>2</sub>S phase diagram is shown in Fig. 7.6a. From this figure, we see that when white metal (essentially Cu<sub>2</sub>S) is oxidized and when the quantity of sulphur in the bath decreases to about 19.5 per cent, the bath splits into two layers, i.e., a top sulphide layer (less dense) and a bottom copper layer (more dense) containing about 1.2 per cent sulphur (see Fig. 7.6b). As the oxidation continues, the volume of the sulphide layer (layer b) decreases and the volume of the

copper layer (layer c) increases. The relative volumes of the two layers can be determined by the lever rule. When the sulphur level eventually reaches 1.2 per cent, only the metallic copper phase remains. At this stage, care has to be exercised to ensure that the metal is not overoxidized to Cu<sub>2</sub>O. The completion of blow can be determined by casting a small sample of the copper and examining the fracture of this sample. The blistery appearance of this sample lends the name blister copper to this product. In industrial practice, the blister copper produced contains 0.02–0.05 per cent S along with 0.2–0.5 per cent dissolved oxygen.

(a) Cu-Cu<sub>2</sub>S phase diagram

(b) Converter with immiscible liquids

Fig. 7.6 Illustration of Operating Principles of Side-Blown Converter.

Attempts made in the early days to produce blister copper in the bottom-blown converter used in the steel industry ended in failure. This is because, after point b (see Fig. 7.6a) is reached, a layer of copper rich liquid will be formed at the bottom in contact with the tuyeres. There will be very little heat generation due to Cu<sub>2</sub>S oxidation in this layer, though heat is generated due to oxidation of copper:



Although there is not much difference in the heat generated per mole of oxygen for copper oxidation [reaction (7.28)] and that for Cu<sub>2</sub>S oxidation [reaction (7.27)], the efficiency of copper oxidation is much lower. Consequently, the temperature drops rapidly in the tuyere region of the Bessemer converter. This leads to the clogging of the tuyeres with solid and the stoppage of the conversion of the matte to metal. It was only after the introduction of the side-blown Bessemer converter that the conversion of white metal to blister copper in a converter became possible.

The side-blown converter blows air into the sulphide phase and not into blister copper. The presence of two phases during the conversion of copper can be taken advantage of. Experiments have shown that the precious metals and impurities such as As, Bi, and Sb have an affinity for the metallic copper phase. Consequently, in the subsequent electrolytic refining step, the precious metals and impurity elements can be recovered as valuable byproducts. The value of these byproducts compensates for the high expenses incurred during the refining operation. If the content of precious metals in the blister copper is low, it can be directly fire refined and employed for alloying purposes. However, when the precious metal content is not high enough to justify electrorefining and not low enough to be discarded along with the copper, then the metallic phase can be enriched in precious metals during white metal oxidation as follows. The white metal oxidation can be stopped after about 10 per cent oxidation, the metal enriched in precious metals separated, and the sulphide phase oxidized to blister copper, fire refined, and sold. The metal enriched phase from each such converting operation can be separately collected and electrorefined in order to recover the precious metals. In this manner, only 10 per cent of the metal need be electrorefined to recover over 90 per cent of the precious metals. Also, most of the As and Sb can be recovered as byproducts along with the precious metals during electrorefining.

#### Refining

The purpose of refining—the final step in copper extraction—is twofold. First, to obtain the metal in a purer form (for a higher degree of electrical conductivity) and second, to recover the valuable precious metals contained in the blister copper produced as a result of converting.

#### Fire refining

The main purpose of fire refining is to remove sulphur from liquid blister copper as SO<sub>2</sub> by oxidation with air and to eliminate oxygen by introducing hydrocarbons. Fire refining is the first step in refining and is conducted in a reverberatory furnace with a capacity of up to 400 tons of copper. The fuel used is fuel oil or natural gas or pulverized coal; the oil consumption being 10–11 per cent of the weight of the charge (blister copper). The time taken for the charge to be refined is 12–16 hours. The reverberators from the fire-refining furnace contain an appreciable amount of copper and are re-treated with the matte in a converter for recovering the copper.

In the refining furnace, the surface of the blister copper is oxidized at frequent intervals. The furnace doors are kept open in order to allow a constant mild blast of air. As a result of this slow oxidation process (2–4 hours duration), impurities such as S, Fe, Se, and Zn are oxidized and the solid oxides rise to the top where they are skimmed off. Some copper is also inevitably oxidized during the process; there is, however, a limit to which such oxidation may be permitted. Normally, the process is discontinued when the level of Cu<sub>2</sub>O in the bulk of the metal reaches 6 per cent. At this stage, almost all the sulphur is eliminated from the metal.

Once the oxidation is complete, the oxidized copper is reduced by *poling* with green branches. These branches, on ignition, give off hydrocarbons which not only stir up the entire molten bath but also create a reducing atmosphere which helps reduce the Cu<sub>2</sub>O. Despite its rather crude nature, this operation is highly successful. Recently, some mechanized processes have been developed to bring about the reduction of Cu<sub>2</sub>O using hydrogen or other reducing gases. Poling, however, still remains the most common method. The purity of fire-refined copper is generally around 99.7 per cent.

Fire refining is also carried out in rotary type refining furnaces, where molten blister copper

is treated directly by blowing air through tuyeres.

#### Electrolytic refining

Fire-refined copper can be further refined by electrolysis. An electrolytic refining tank (or cell) is made of either concrete or wood and is well insulated. Each tank is 3-5 m long, 1-1.1 m wide, and 1-1.3 m deep. The design of the cell is based on the utilization of minimum space with maximum cathode and anode areas. During electrolysis, a number of such tanks are arranged in a cascade formation.

Fire-refined copper is cast in the form of an anode that weighs 250-320 kg. The cathode is made of a pure copper sheet that is greased in order to facilitate the subsequent stripping of the metal deposited on it. The electrolyte consists of copper sulphate ( $\text{Cu}$  35 gm/litre),  $\text{H}_2\text{SO}_4$  (200 gm/litre), and some addition agents such as glue and alcohol. Electrolysis is carried out at a temperature of 50-60°C using a current density of about  $200 \text{ A/m}^2$ .

During electrolysis, copper is transferred from the crude anode to the pure cathode. Impurities in the blister copper such as Fe, Co, Ni, Se, and Te go into solution and the precious metals collect below the anode in what is known as the anode slime. As the electrolysis proceeds, some difficulties are likely to be encountered. For example, in the vicinity of the cathode, the concentration of  $\text{Cu}^{2+}$  ions decreases and the water in the electrolyte is electrolyzed, releasing hydrogen which lowers the current efficiency. On the other hand, in the vicinity of the anode, the concentration of  $\text{Cu}^{2+}$  ions increases and  $\text{CuSO}_4$  may tend to crystallize out. These setbacks can be overcome by the proper stirring and circulation of the electrolyte.

It should be noted that if the  $\text{CuSO}_4$  content of the electrolyte increases beyond a certain limit as a result of the dissolution of the residual  $\text{Cu}_2\text{O}$  in blister copper, it may become necessary to electrolyze the electrolyte using an insoluble inert anode made of lead. This procedure would bring down the  $\text{CuSO}_4$  content of the electrolyte. In addition to the removal of copper from the electrolyte, impurities such as As, Sb, Bi, and Ni have to be removed. As, Sb, and Bi are removed during the last stages of copper refining with an insoluble inert lead anode. Nickel is removed together with iron and cobalt as a sulphate from the copper-free bleed-off. The volume of the bleed solution, which has to be purified, varies depending on the impurity content of the anode and lies in the range 0.2-0.6 m<sup>3</sup>/ton of copper produced.

The approximate composition of the anode slime is as follows: Cu = 10-40 per cent, Ag = 8500-14,000 gm/ton, Au = 250-1700 gm/ton, Pb = 2-20 per cent, As = 0.5-5 per cent, Te = 0-4 per cent, Ni = 0-25 per cent, S = 2-10 per cent, Fe = 0.5-2 per cent, and Se = 0-25 per cent. The exact composition depends on the composition of the anode used for electrolysis and the various previous metallurgical operations.

*Recovery of precious metals and chalcogenides from anode slime* The flowsheet that is commonly adopted for the recovery of precious metals and chalcogenides from an anode slime is shown in Fig. 7.7. To remove Cu, the slime is first treated with a dilute acid and sulphated using  $\text{H}_2\text{SO}_4$  at about 200°C followed by leaching. The copper solution contains tellurium which is cemented with active copper and the copper telluride formed is sent for tellurium recovery. The decoppered slime is next roasted at about 700°C by indirect heating. The selenium is volatilized and scrubbed in water to obtain a strong selenic acid solution from which Se is recovered by gaseous reduction with  $\text{SO}_2$ . The decoppered selenium-free slime is then smelted along with soda ash, silica, and return slags as fluxes to produce a silver-rich alloy. This alloy is oxidized to transfer the lead into the slag. During this stage, As, Bi, and Sb are eliminated. If the slag is rich in Pb, then it is sent

to a lead refinery. Otherwise, it is recycled to the smelting stage where the entrained silver-rich alloy is recovered.

The silver-rich alloy, after lead removal, is oxidized in the presence of soda ash to remove

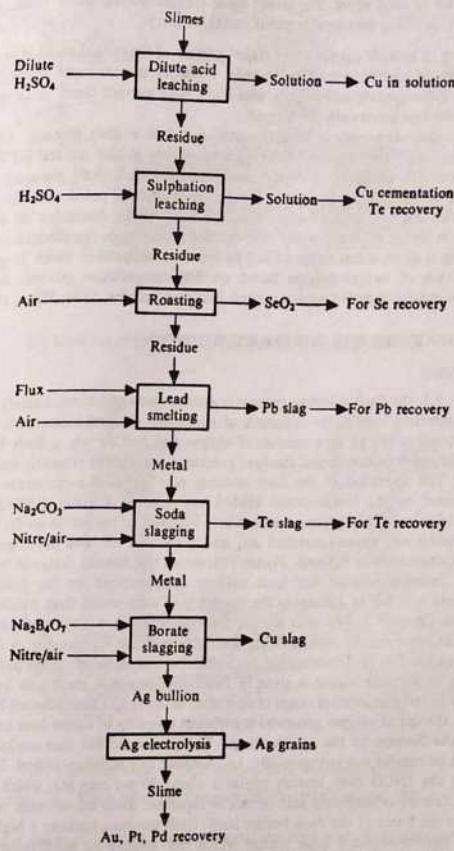


Fig. 7.7 Recovery of Precious Metals and Chalcogenides from Anode Slimes.

any residual tellurium and further oxidized in the presence of borax to remove any residual copper. At this stage, the alloy contains more than 90 per cent silver, the remainder essentially being Au, Pt, and Pd. The alloy is cast in the form of an anode and electrolyzed in the silver nitrate bath in order to yield silver. The anode slime formed during silver refining contains the other precious metals and is sent to a precious metals refinery.

**Melting and casting of cathode copper** The major portion of the refined cathode copper is utilized in the manufacture of electric wire. Customarily, a copper manufacturer supplies copper wire bars that can be subsequently rolled into wire rods. The current trend is to directly cast the wire rods from electrical grade cathode copper.

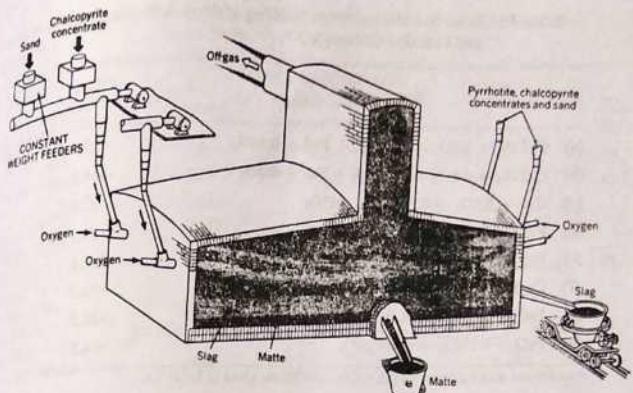
The melting of cathode copper is normally carried out in a shaft furnace. Alternatively, an electric furnace can also be employed. The type of copper mostly needed for electrical applications is the electrolytic tough pitch copper which contains 0.01–0.03 per cent oxygen, 0.001 per cent sulphur, and 0.00005 per cent hydrogen. It should be noted that the molten copper discharged from the shaft or electric furnace must be analyzed to determine its oxygen content prior to casting in order to achieve the desired oxygen level. In the modern refineries, where continuous casting is done, a fast oxygen analysis becomes imperative which is presently being achieved by the use of oxygen probes based on high-temperature galvanic cells with solid electrolytes as the conducting medium for oxygen ions (see Scholes, 1974; Hens, 1975).

#### 7.4 NEWER PROCESSES FOR COPPER EXTRACTION

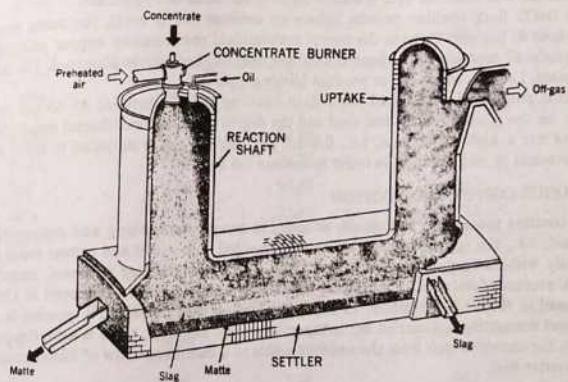
##### FLASH SMELTING

As shown in Fig. 7.1, the flash smelting process combines two operations, namely, roasting and smelting. Flash smelting entails the injection of a mixture of dried concentrate of Cu and flux together with oxygen or hot air or a mixture of oxygen and hot air via a flash burner wherein the iron sulphides are combusted, and the heat generated is sufficient or nearly sufficient to smelt the concentrate. The invention of the flash smelting of a sulphide concentrate using tonnage oxygen is attributed to the International Nickel Company of Canada (INCO). Figure 7.8a shows the INCO furnace. This process was put into commercial operation as far back as 1953. Flash smelting using air, oxygen-enriched air, and preheated air was developed around the same period by Outokumpu in Finland. Figure 7.8b shows the furnace designed by Outokumpu.

A simplified reaction scheme and heat balance computations for the flash smelting of a copper concentrate with air to determine the feasibility of autogenous flash smelting has already been discussed in Chapter 4. We now discuss flash smelting in a little more detail. The main reactions that take place during flash smelting are listed in Table 7.2 along with the corresponding enthalpy changes. The heat balance for flash smelting one mole of chalcopyrite to produce a matte containing 50 per cent copper is given in Table 7.3. This is a mass and heat balance for the final product in the temperature range of operation of the INCO flash smelter. From Table 7.3, it is evident that the use of oxygen generates a sufficient quantity of excess heat to overcome any heat loss from the furnace to the surroundings. Thus, we conclude that smelting in an INCO flash smelter can be carried out autogenously, i.e., without any addition of fuel. In addition, the gas produced in the INCO flash smelter contains about 80 per cent SO<sub>2</sub> which can be directly used in the manufacture of sulphuric acid or can be liquefied. Since all or most of the reactions are completed in the flame of the flash burner itself, flash smelting leads to a high smelting rate. Recently, INCO has developed a flash burner which can achieve an even faster smelting rate.



(a) Cutaway view of INCO oxygen flash smelting furnace



(b) Cutaway view of Outokumpu flash smelting furnace

Fig. 7.8 Flash Smelting Furnace (Boldt and Queneau, 1967).

Table 7.4 compares the smelting rate of conventional smelting with that of newer processes such as flash smelting and continuous smelting. Recent tests at INCO have indicated that in the flash

Table 7.2 Main Reactions in Flash Smelting of Copper Concentrate and Enthalpy Changes\*

Reaction	$\Delta H_{25^\circ\text{C}}$ (kcal/mole)
(a) $\text{CuFeS}_2 + 0.5\text{O}_2 \rightarrow 0.5\text{Cu}_2\text{S} + \text{FeS} + 0.5\text{SO}_2$	-23.5
(b) $\text{CuFeS}_4 + 0.5\text{O}_2 \rightarrow 2.5\text{Cu}_2\text{S} + \text{FeS} + 0.5\text{O}_2$	-16.9
(c) $\text{CuS} + 0.5\text{O}_2 \rightarrow 0.5\text{Cu}_2\text{S} + 0.5\text{SO}_2$	-32.6
(d) $\text{FeS}_2 + \text{O}_2 \rightarrow \text{FeS} + \text{SO}_2$	-54.1
(e) $\text{FeS} + 1.5\text{O}_2 \rightarrow \text{FeO} + \text{SO}_2$	-112.1
(f) $\text{Cu}_2\text{S} + 1.5\text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{SO}_2$	-92.3
(g) $\text{FeO} + 0.165\text{O}_2 \rightarrow 0.33\text{Fe}_2\text{O}_4$	-24.3
(h) $\text{FeO} + 0.5\text{SiO}_2 \rightarrow 0.5\text{Fe}_2\text{SiO}_4$	-4.3

\*Additional data for reactions (a), (e), (g), and (h) are given in Table 7.3.

burner the smelting is completed within approximately 2 seconds and the composition of the smelted particles that reach the bath is almost equal to the value at equilibrium.

In the INCO flash smelting process (where no external fuel is used), the matte produced contains about 45 per cent Cu as in the case of conventional reverberatory copper smelting and the slag produced contains only about 0.5–0.6 per cent Cu, and can be discarded. The matte is further treated, i.e., by converting, to produce blister copper.

The matte produced in the Outokumpu flash smelting process contains 45–65 per cent Cu depending on the quantity of the fuel used and the degree of oxygen enrichment employed. The slag always has a high Cu content, i.e., 0.8–1.5 per cent Cu and is subjected to either electric furnace treatment or slag flotation in order to recover the copper.

#### CONTINUOUS COPPER PRODUCTION

The flash smelting process can be logically extended to encompass smelting and converting in a single vessel, i.e., the copper concentrate can be charged at one end and copper metal can be continuously withdrawn from the other end. Two continuous smelting processes, namely, the WORCRA process (developed in Australia) and the Noranda process (developed in Canada), were patented in 1967. More recently, in Japan, Mitsubishi has developed a process in which smelting and converting are carried out in separate vessels. However, there is a continuous flow of matte to the converter unit from the smelting unit and a continuous flow of blister copper out of the converter unit.

#### WORCRA Process

The name WORCRA is derived by combining the first three alphabets of the inventor's name (H.K. Worner) and CRA (Conzinc Riotinto of Australia Limited).

The WORCRA process seeks to maximize the conservation of energy obtained during smelting and converting of sulphide concentrates by integrating, to a high degree, several efficient

Table 7.3 Heat Balance for Flash Smelting One Mole of Chalcopyrite to Produce 50 Per Cent Copper Matte

Reaction (as given in Table 7.2)	Mole	HEAT GENERATED	
		Number of moles of oxygen needed	$\Delta H_{25}$ (kcal)
(a)	1.0	0.5	-23.5
(e)	0.56	0.84	-62.8
(g)	0.213	0.036	-5.2
(h)	0.347		-1.5
			Total heat generated
			-93.0

Matte	Mole	HEAT REQUIRED	
		$H_{1177} - H_{25}$ (kcal/mole)	$H_{1177} - H_{25}$ (kcal)
$\text{Cu}_2\text{S}$	0.5	27.81	13.9
$\text{FeS}$	0.432	25.81	11.1
$\text{Fe}_2\text{O}_4$	0.041	89.95	3.7
			28.7

Slag	Mole	(to raise temperature of slag constituents to 1277°C)	
		$H_{1277} - H_{25}$ (kcal/mole)	$H_{1277} - H_{25}$ (kcal)
$\text{Fe}_2\text{SiO}_4$	0.174	74.30	13.0
$\text{Fe}_2\text{O}_4$	0.03	92.35	2.8
$\text{FeS}$	0.008	26.62	0.2
$\text{SiO}_2$	0.167	21.31	3.6
Others			3.3
			22.9

Gas	Mole	(to heat outgoing gases to exit gas temperature of 1250°C)	
		$H_{1250} - H_{25}$ (kcal/mole)	$H_{1250} - H_{25}$ (kcal)
$\text{SO}_2$	1.06	15.24	16.1
			Total heat required
			Excess heat available to overcome heat loss
			25.3 kcal
			67.7 kcal

Table 7.4 Specific Smelting Rates in Different Copper Smelting Reactors

Smelting reactor	Furnace volume (m <sup>3</sup> )	Concentrate feed rate (tons/day)	Specific smelting rate (tons/day/m <sup>3</sup> )
<b>Reverberatory smelter</b>			
Green charge	1160	1040	0.89
Calcine charge	1030	860	0.83
<b>Outokumpu flash furnace</b>			
Air (preheated)	460	1200	2.61
Oxygen enrichment	250	970	3.88
Mitsubishi continuous smelter	170	580	3.41
Noranda continuous smelter	290	1300	4.48
INCO flash furnace	590	1500	2.54
New INCO flash burner	7.4	130	17.56

continuous unit operations. The concentrate particles possess a large surface area which helps in accelerating the reactions with a gas, liquid, or another solid. The WORCRA process also seeks to reduce the capital and operating cost by eliminating the handling of solids and liquids in batches.

In the WORCRA process, a single furnace combines the following operations so that they occur in separate but interconnected zones:

- (1) continuous smelting,
- (2) continuous converting,
- (3) continuous slag cleaning by conditioning and settling.

Figure 7.9 presents the traditional approach used in copper production *vis-à-vis* the WORCRA approach.

Several variations of the WORCRA process have been suggested with the sole aim of achieving the compartmentalization of the three unit operations in a horizontal plane. Figure 7.10 shows two types and Fig. 7.11 depicts an idealized vertical section of a straight horizontal form of the WORCRA reactor.

The WORCRA process is characterized by the following features:

- (1) The process directly produces the metal, rather than a matte, from the concentrate.
- (2) The heat of the exothermic oxidation reaction is utilized in the reactor itself.

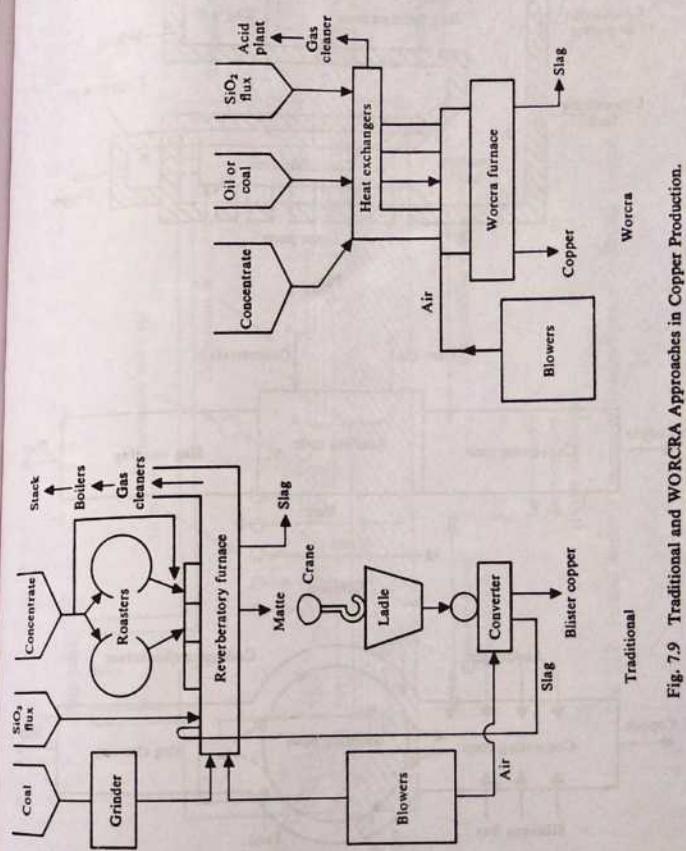


Fig. 7.9 Traditional and WORCRA Approaches in Copper Production.

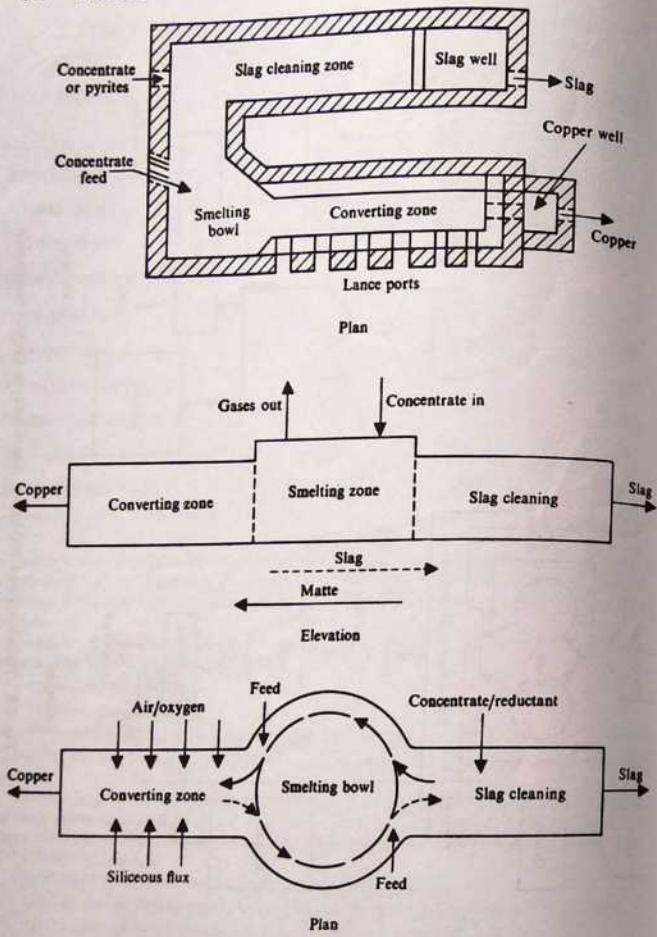


Fig. 7.10 Two Shapes of WORCRA Reactor.

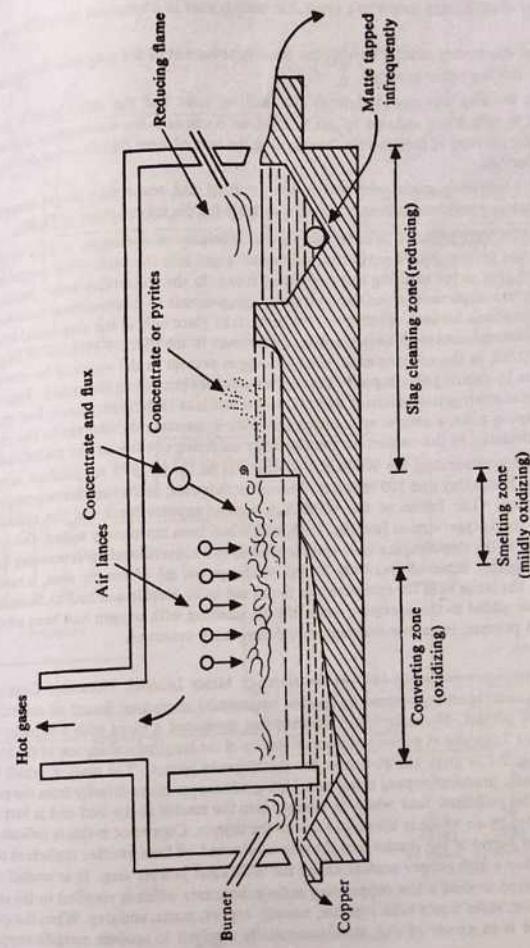


Fig. 7.11 Vertical Sectional Diagram of Straight Form of WORCRA Reactor.

(3) In the smelting and converting zones, the bath is kept in a constant state of motion and turbulence.

(4) In the converting zone, generally, the countermovement of the slag and the matte takes place; the slag moving under gravity.

(5) After the slag has passed through the smelting zone and the slag-cleaning zone, its copper content is sufficiently reduced to allow it to be discarded. No subsequent treatment is necessary for the recovery of copper from the slag as in the case of some other continuous processes of copper production.

(6) The SO<sub>2</sub>-bearing gases generated in the smelting and converting stages combine and leave the reactor in a continuous stream which is suitable for the manufacture of H<sub>2</sub>SO<sub>4</sub>.

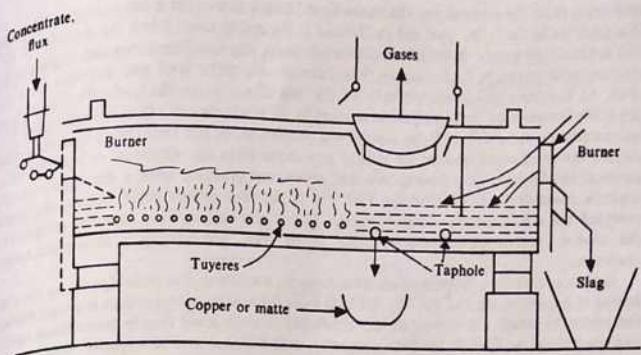
Several factors were expected to contribute to the efficiency of operation of the WORCRA process. First, the process injects particulate solids and gases into the bath. This maximizes the reaction surface area in the smelting and converting zones. In the converting zone, particularly, smelting, the reactions between the slag and the matte take place only at the slag-metal interface. Second, the countermovement of the slag and the matte leads to the effective removal of impurities such as iron. Third, in the smelting zone, valuable copper present in the slag can be reverted to the matte phase by reacting the slag with the ferrous sulphide present in the matte. Fourth, the process maintains appropriate oxidizing and reducing conditions in different zones. For example, in the slag-cleaning zone, a neutral or reducing condition is maintained, whereas in the smelting zone and, particularly, in the converting zone strongly oxidizing conditions are maintained.

A pilot plant incorporating the WORCRA process was set up in 1970 to produce copper on two scales, i.e., 5 tons/day and 100 tons/day. Thereafter, however, no further developmental work has been reported. The future of the WORCRA process appears bleak for the reasons now mentioned. In the U-type version (see Fig. 7.10), which had been extensively tested, the quantity of fuel required in the slag-cleaning zone was the same as in a conventional reverberatory furnace. Also, the throughput achieved was only 3 tons of charge per m<sup>2</sup> of hearth area, a rather low value. Finally, the lance used for oxidation was found not to be durable and had to be constantly replaced, which added to the operating costs. If flash smelting with oxygen had been adopted in the WORCRA process, these disadvantages could have been overcome.

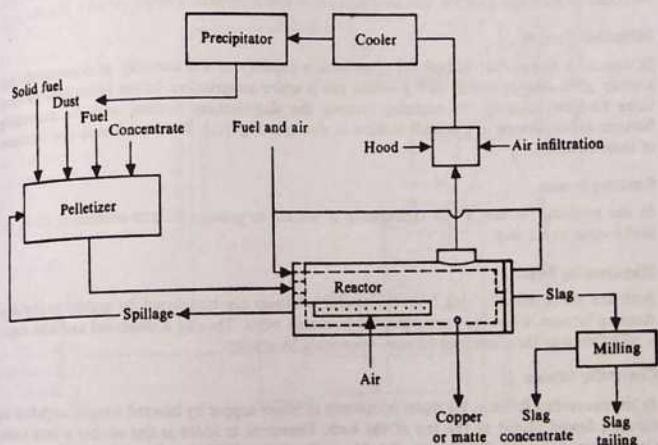
#### Noranda Process

The Noranda reactor, installed in 1973 at the Noranda Mines Limited, Noranda, Canada, was the first continuous smelting process to go into commercial operation. Based on several years' trial on a pilot project, Noranda Mines Limited has developed a plant with a capacity of 800 tons/day. Figure 7.12a shows a schematic representation of the longitudinal section of the Noranda reactor and Fig. 7.12b gives the flowsheet for the Noranda process. The reactor, which is fuel-fired at both ends, produces copper metal or a high-grade copper matte directly from the sulphide concentrate. The pelletized feed which is charged into the reactor at the feed end is first melted and then oxidized by air which is blown in through the tuyeres. Copper or matte is collected from a taphole in the barrel of the reactor and the slag is skimmed off from another taphole at the slag end. This slag has a high copper content unlike the WORCRA process slag. It is cooled slowly, milled, and floated to yield a low copper slag and a concentrate which is recycled to the reactor.

In the reactor, three layers exist together, namely, copper, matte, and slag. When the quantity of air available is in excess of that stoichiometrically required to produce metallic copper and



(a) Schematic diagram of Noranda reactor



(b) Flowsheet

Fig 7.12 Noranda Process.

iron oxide from the concentrate, the excess air oxidizes a part of the matte to copper. This results in a decrease in the matte level and an increase in the copper level. When the quantity of air is not sufficient to satisfy the stoichiometric requirement, any unoxidized iron and sulphur tend to combine with copper to form a matte. This increases the matte level and decreases the copper level. At the exact stoichiometric ratio of the concentrate to air, the levels of both copper and concentrate in order to yield the desired end product. Jeffes and Diaz (1971) have theoretically studied the continuous process for copper production from the viewpoint of heat balance and chemical equilibrium. They have shown that, on thermal grounds, when a dry high-grade chalcopyrite concentrate is used as the feed, the continuous process could become autogenous, provided the air employed contained about 30 per cent oxygen. They have also estimated that the copper content of the slag is likely to be high, necessitating a subsequent recovery operation.

In the continuous process reactor, there is always metallic copper present, and, as the distribution of impurities such as As, Sb, and Bi is more favourable to copper than to copper sulphide, the extent to which the impurities are eliminated is much lower than in conventional smelting and converting. As a result, we obtain an anode with a higher level of impurity, which requires additional care during electrorefining. In fact, when the impurity level is high in the concentrate, the continuous process becomes unsuitable. Therefore, a two-step process, with the first step producing white metal ( $Cu_2S$ ) and the second step producing copper, has to be resorted to. The Noranda process has adopted this modification as also Kennecott Copper (Utah), U.S.A.

#### Mitsubishi Process

In Japan, a commercial Mitsubishi plant with a capacity of 650 tons/day of concentrate has already gone into operation and a second one is under construction. In the Mitsubishi process, three furnaces, namely, the smelting furnace, the slag-cleaning furnace, and the converting furnace, are connected in a cascade fashion as shown in Fig. 7.13. We now discuss the functions of these furnaces.

#### Smelting furnace

In the smelting furnace, a wet concentrate is smelted to produce a matte containing 60–65 per cent copper and a slag.

#### Slag-cleaning furnace

Both the matte and the slag from the smelting furnace are transferred by gravity to the slag-cleaning furnace, where they are separated from each other. The slag is discarded and the matte is transferred to the converting furnace, once again by gravity.

#### Converting furnace

In the converting furnace, the matte is oxidized to blister copper by injected oxygen enriched air through lances placed at the top of the bath. Limestone is added as flux so that a lime ferrite slag is formed instead of the conventional iron silicate slag. This is to ensure that a blister copper with a low sulphur content is produced and to decrease copper transfer to the lime ferrite slag. This slag is granulated and later transferred to the smelting furnace for copper recovery. The blister copper is continuously tapped.

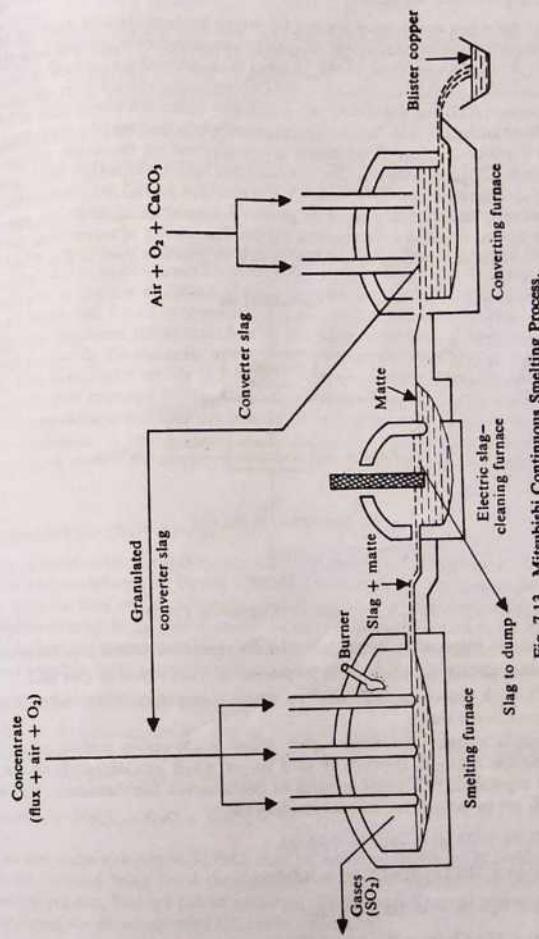


Fig. 7.13 Mitsubishi Continuous Smelting Process.

## TORCO SEGREGATION PROCESS

The TORCO (treatment of refractory copper ores) process has been specially designed to extract copper concentrates from oxidized copper ores, such as aluminosilicates, because normal leaching or flotation methods are unsuitable. In this process, the comminuted ore (ground to 60 per cent minus 50 µm) which generally assays 2-6 per cent Cu is first mixed with 0.5-2 per cent coke or coal and 0.5-1 per cent NaCl and then heated in a segregation reactor at a temperature of 700-800°C for about 30-60 minutes. It may be noted that the reactor is in the form of a vertical kiln. When the process is completed, most of the copper gets precipitated on the carbon surface and the gangue are separated from each other by flotation. The segregate and the gangue are then discharged into a flotation circuit to produce a concentrate of 30-50 per cent metallic copper. The product is sent to a reverberatory smelter. The recovery of copper from the TORCO process is 85-90 per cent. A flowsheet for the segregation process is given in Fig. 7.14.

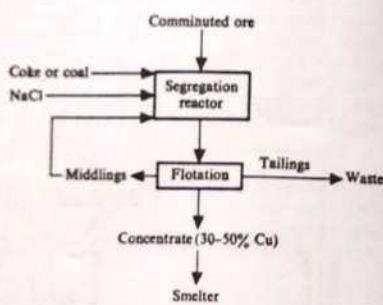


Fig. 7.14 Oxide Ore Segregation Process.

The mechanism suggested by Wright (1973) for the segregation process is as follows:

- (1) Sodium chloride is hydrolyzed in the presence of water vapour to give HCl.
  - (2) HCl reacts with copper oxide to give a volatile copper chloride believed to be predominantly cuprous chloride trimer.
  - (3) Cuprous chloride and water vapour diffuse to the carbon surface, where cuprous chloride undergoes hydrogen reduction to yield copper which gets deposited on the carbon surface. The regenerated HCl is used up again for chloridization. Simultaneously, H<sub>2</sub>O vapour is reduced to H<sub>2</sub> gas by carbon. The relevant reactions are
- $$2\text{CuO}(\text{s}) + \text{CO}(\text{g}) = \text{Cu}_2\text{O}(\text{s}) + \text{O}_2(\text{g})$$
- $$\text{Cu}_2\text{O}(\text{s}) + 2\text{HCl} = \frac{1}{2}\text{Cu}_3\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$$
- $$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) = \text{H}_2(\text{g}) + \text{CO}(\text{g})$$
- $$\text{H}_2(\text{g}) + \frac{1}{2}\text{Cu}_3\text{Cl}_2(\text{g}) = 2\text{Cu}(\text{s}) + 2\text{HCl}(\text{g})$$

In Mauritania, a commercial TORCO plant capable of handling 3500 tons of ore per day is under operation.

The roasted sulphide ores of copper should be amenable to copper recovery by the segregation process. Marcuson (1980) has observed that the segregation process when applied to roasted copper sulphide concentrates possesses the potential to recover copper in a manner that is relatively pollution-free, energy-conserving, and cost-effective.

## 7.5 ENERGY CONCEPTS IN COPPER SMELTING

Kellogg (1974) has determined, after detailed computations, the energy consumption of different copper smelting processes. He has defined a term PFE (process fuel equivalent) as

$$\text{PFE} = F + E + S - B,$$

where  $F$  is the quantity of fuel directly consumed by the process,  $E$  the fuel equivalent of electrical energy (taken as 2650 kcal/kWh which is the normal energy needed to generate power from fossil fuel),  $S$  the fuel equivalent of major supplies used in smelting such as reagents, oxygen, and fluxes, and  $B$  the fuel equivalent of byproducts and useful surplus heat.

Kellogg and Henderson (1976) have observed that when the air used in a smelting process is enriched by oxygen to the maximum extent possible, the energy required to produce copper is minimized. This is evident from Fig. 7.15 which shows that the INCO oxygen smelter (using 95 per cent oxygen) consumes the least amount of energy. Both the Outokumpu flash smelter and the Noranda continuous smelter can be made less energy-intensive by increasing the degree of oxygen enrichment. It may be noted that although conventional reverberatory smelting consumes a large amount of energy, electric furnace smelting is the most energy-intensive process.

## 7.6 HYDROMETALLURGY OF COPPER

At present, pyrometallurgy accounts for about 85 per cent of the world's total production of copper and hydrometallurgy for the rest. Hydrometallurgy is mainly employed in the extraction of copper from oxidized ores or low-grade sulphide ores. However, extensive research on the use of hydrometallurgy in the case of normal sulphide concentrates has led to the development of some new processes. Except in special circumstances, these processes have proved to be far more energy-intensive than the pyrometallurgical processes and require a higher amount of capital.

## FERRIC CHLORIDE LEACHING

It is well known that chalcopyrite is a difficult mineral to leach. However, as a result of experiments, Haver and Wong (1971) have found ferric chloride to be an ideal leaching reagent. Ermilov *et al.* (1969) have found the reaction between FeCl<sub>3</sub> and chalcopyrite



to be of the first order with respect to FeCl<sub>3</sub> with an activation energy of 12.3 kcal/mole. Not only does this reaction bring about the dissolution of copper but it also produces elemental sulphur as a byproduct. This is a distinct advantage over pyrometallurgical processes that emit SO<sub>2</sub>, necessitating the use of expensive SO<sub>2</sub> recovery equipment.

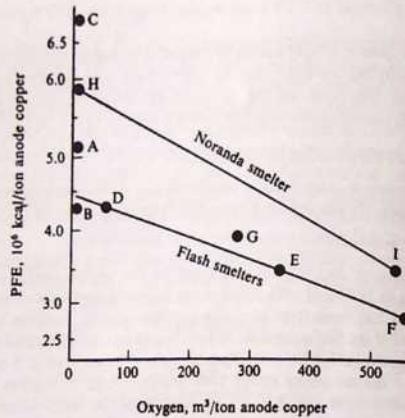


Fig. 7.15 Oxygen Enrichment Effect on Energy used in Copper Smelting (A, wet concentrate-charged reverberatory furnace; B, calcine-charged reverberatory furnace; C, electric furnace smelting; D, Sagonesaki (Outokumpu) flash smelter; E, Outokumpu flash smelter; F, INCO flash smelter; G, Mitsubishi continuous smelter; H, Noranda with no oxygen enrichment; I, Noranda with oxygen enrichment).

On the basis of their groundwork, Haver and Wong (1971) have proposed a flowsheet (shown in Fig. 7.16) for the extraction of copper. According to their scheme, copper is recovered by cementation and fire refining. As shown in the flowsheet,  $\text{FeCl}_3$  is regenerated by the chlorination of the ferrous chloride solution produced as a result of leaching.

The route depicted by the foregoing flowsheet is a rather involved one, and, to simplify the procedure, efforts have been directed towards the direct electrowinning of copper from the leach liquor. During electrowinning, the production of a smooth cathode copper at economical current densities is rendered difficult due to the excessive quantity of iron present in the leach liquor. If electrowinning proves successful, the regeneration of  $\text{FeCl}_3$  will become much simpler. An alternative to electrowinning is the crystallization of  $\text{CuCl}$  from the leach liquor and the reduction of  $\text{CuCl}$  by hydrogen to produce copper powder. This alternative is also under investigation.

The foregoing hydrometallurgical routes are yet to produce a variety of copper that can meet wire bar specifications. Also, the leach residue contains valuable precious metals. To recover these metals, special cyanidation treatment is required. Further, the total energy required for a hydrometallurgical process is much higher than that required for a pyrometallurgical process.

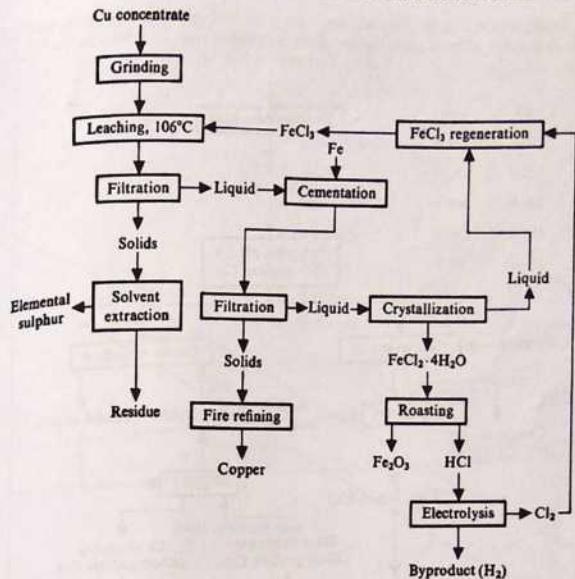


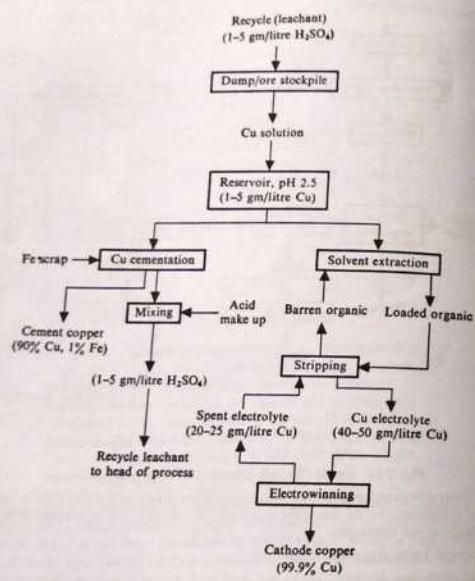
Fig. 7.16 Ferric Chloride Leaching of Copper Concentrate.

In view of these disadvantages, the use of hydrometallurgy can be justified only in isolated cases, i.e., where a competitive market does not exist or where tonnage treated is so small that pyrometallurgy is not applicable.

#### LEACHING OF LOW-GRADE ORES

It has been established that for a low-grade copper ore, hydrometallurgical treatment, especially the *in situ* leaching technique, is the best suited. A typical flowsheet employed in the dump or heap or *in situ* leaching of a low-grade ore is shown in Fig. 7.17. In dump leaching or heap leaching, the low-grade ore is accumulated in the form of a heap and dilute acid is percolated through it. After percolation, the leach solution is either treated with scrap iron to recover cement copper or subjected to solvent extraction to extract copper and also to provide a solution suitable for electrowinning. To accelerate the leaching rate *Thiobacillus ferroxidans* bacteria can be employed. (For a detailed discussion of bacterial leaching, see Section 4.18.)

In the case of an oxidized copper ore, leaching is carried out in vats (leaching tanks) employing a spent copper electrowinning electrolyte that contains about 100 gm/litre  $\text{H}_2\text{SO}_4$ . The resultant leach liquor that contains about 50 gm/litre copper is used for electrowinning metallic copper.

Fig. 7.17 Dump/Heap/*in situ* Leaching of Low-Grade Copper Ores.

## LEACHING OF ROASTED SULPHIDE CONCENTRATES

A sulphide concentrate of copper is roasted prior to leaching in order to obtain a sulphate that can subsequently be extracted by a dilute acid solution.

Figure 7.18 shows the stability regions in the Cu-O-S system. In a fluid bed roaster, a roasting temperature higher than 650°C is required to achieve good roasting kinetics. From Fig. 7.18, we see that a temperature of approximately 700°C is optimum when  $p_{SO_2}$  lies in between 0.04 and 0.09 and  $p_{O_2}$  lies in between 0.04 and 0.10, which is the case in the roaster. The operating conditions for several roasters at different locations essentially satisfy these conditions as seen

from the data points shown in Fig. 7.18. In some cases, the problem of CuO formation has been reported, which is probably due to the operation taking place outside the region of  $CuSO_4$  stability.

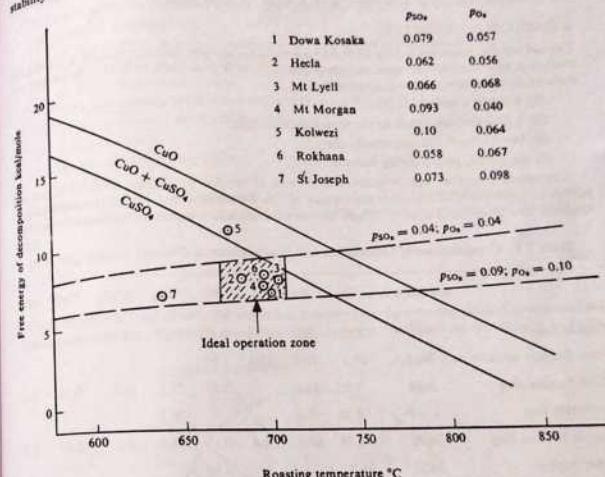
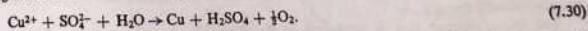


Fig. 7.18 Sulphation Roasting of Copper Sulphide.

During the subsequent electrowinning of the  $CuSO_4$  solution (obtained from the dilute acid leaching of the roasted concentrate),  $H_2SO_4$  is generated. The reaction is



The sulphuric acid in the spent electrolyte is normally used for the vat leaching of copper oxide ores. If such copper ores are not available,  $H_2SO_4$  is neutralized with either lime or limestone and rejected as gypsum.

## 7.7 PRODUCTION OF COPPER IN INDIA

In 1967, Hindustan Copper Limited (HCL) was set up by the Government of India for the

exploration and the extraction of copper. HCL took over the already existing copper extraction plant at Ghatsila (Bihar) from the Indian Copper Company. Under its aegis, it also installed in 1975 another copper extraction plant, namely, the Khetri Copper Complex, at Khetri (Rajasthan). The combined capacity of both these plants is 47,000 tons per annum.

#### INDIAN COPPER COMPLEX

The old smelter, commissioned in 1927, had conventional smelting facilities, namely, a multibearth roaster, a reverberatory furnace, and three great falls type converters. In 1971, this smelter was replaced by a modern smelter that consists of

- (1) a rotary concentrate dryer,
- (2) a flash furnace based on the Outokumpu design,
- (3) two Pierce-Smith converters, and
- (4) an electric slag-cleaning furnace.

The modern smelter can produce 16,000 tons of copper per annum from a 22-per cent copper concentrate. The typical compositions of the concentrate and process intermediates at Ghatsila are given in Table 7.5. Since this concentrate has a higher nickel content than most

Table 7.5 Compositions of Concentrate and Intermediates in Ghatsila Smelter (per cent)

	tons/month	Cu	Fe	S	Ni	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Concentrate	4972	22.2	29.0	27.8	0.49	14.7	0.53	0.25	0.87
Flash furnace matte	2463	50.5	22.5	22.3	1.10				
Flash furnace slag	2188	1.65	44.0		0.35	27.1	6.8	0.51	1.23
Converter slag	1160	4.30	45.5			28.6			
Electric furnace slag	3600	0.78	44.6	1.4	0.15	29.7	7.8	0.61	0.52
Blister copper	1450	98.3			0.50				

other copper concentrates, the Indian Copper Complex has been equipped with a nickel sulphate plant in order to recover any nickel that might enter the refinery along with the anode copper. However, most of the nickel and any cobalt present in the concentrate are lost as they are in association with the slag.

The blister copper that is produced in the Pierce-Smith converters is refined in anode furnaces and deoxidized by poling. The cast anodes are electrolytically refined to produce wire bar grade copper. From the resulting anode slime, selenium and precious metals such as silver and gold are recovered.

#### KHETRI COPPER COMPLEX

There are two copper mines at Khetri, namely, the Khetri mine and the Kholihana mine. The

former has an estimated ore reserve of 47 million tons of 0.9 per cent copper and the latter an estimated reserve of 29 million tons of 1.6 per cent copper. The Khetri plant can produce 31,000 tons of copper per annum and was inaugurated in 1975. This plant consists of

- (1) a concentrator designed to handle 9600 tons of ore per day;
- (2) a smelter equipped with
  - (a) rotary dryers capable of handling 1100 tons of wet concentrate per day,
  - (b) an Outokumpu type flash furnace,
  - (c) Pierce-Smith converters,
  - (d) a slow-cooling plant to handle furnace and converter slags,
  - (e) anode furnaces and a casting wheel;
- (3) a refinery having
  - (a) electrolytic refining tanks,
  - (b) a wire bar casting plant.

The final product of the Khetri plant is refined copper. The anode slime produced as a result of electrolytic refining is sent to Ghatsila for the recovery of selenium and the precious metals.

#### 7.8 LEAD

##### USES

The consumption of lead all over the world has steadily gone up over the years. The present level of global consumption, excluding the Soviet bloc, is about 5 million tons per annum. In India,

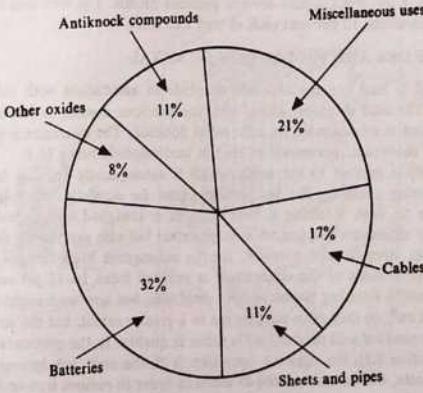


Fig. 7.19 Various Uses of Lead.

the consumption in 1979 was only about 65,000 tons and the production even lower, i.e., about 10,000 tons. The deficit had to be plugged by importing the metal, leading to a drain on the foreign exchange reserves.

Lead is used mainly in the manufacture of batteries, cables, pigments, and flexible sheets and pipes. The approximate breakdown is shown in Fig. 7.19. From this figure, it is evident that a large chunk of the total lead consumption is taken up by batteries. Also, lead is the most preferred material sheathing power cables in the medium voltage range (1–11 kV). In the lower voltage range (i.e., up to 1 kV), lead has been replaced to a great extent by plastics and in the higher voltage range (above 11 kV) it has been replaced to some extent by aluminium. It should be noted that such replacement is for economic reasons rather than for technical ones. Research work is now in progress to counteract the trend for replacement. As a result, new alloys of lead have been developed which are used in the manufacture of thinner but stronger sheathings. Attempts are also under way to use a combination of lead and plastic.

Sheets and pipes made of lead are used in chemical industries because they offer excellent resistance to corrosion by chemicals. Lead, both as sheet metal and as a component of fabricated composite materials, finds application in sound damping and vibration damping in structural engineering. Lead alloys are extensively used in the manufacture of solders, printing metal, and bearings.

## 7.9 EXTRACTION OF LEAD

### OCCURRENCE

In nature lead exists either in the form of sulphide or oxide. The common minerals are galena ( $PbS$ ), cerrusite ( $PbCO_3$ ), and anglesite ( $PbSO_4$ ). The most common ores contain galena associated with  $ZnS$ ,  $FeS$ ,  $CuS$ ,  $PbCO_3$ , and several precious metals. The lead ores from Zawar mines (Rajasthan) contain about 10 per cent each of lead and zinc.

### TREATMENT OF ORE AND PRODUCTION OF METAL

As just mentioned, a lead ore contains lead sulphide in association with other sulphides and precious metals. The lead sulphide, along with the precious metals, is first separated from the other sulphides and is concentrated by differential flotation. The concentrate may contain 60–80 per cent lead; the theoretical percentage of lead in lead sulphide being 86.8.

The concentrate is roasted to the oxide which is subsequently reduced by carbon to yield metallic lead. During roasting, the temperature must be carefully controlled because above 800°C,  $PbS$  tends to fuse. Roasting is best done in a Dwight-Lloyd sintering machine. This machine not only eliminates sulphur to a large extent but also produces a sinter with requisite properties, such as strength and porosity, for the subsequent blast furnace operation, during which, the sulphur content of the concentrate is reduced from 16–18 per cent to 1–2 per cent. Initially, downdraught sintering machines were employed, but now updraught machines are preferred because not only do they drive out  $SO_2$  gas to a greater extent, but the stream of  $SO_2$  driven out (subsequently used for acid production) is richer in quality. In the pyrometallurgical extraction of copper (see Section 7.3), the roasting operation is deliberately left incomplete to enable the formation of a matte, which is converted to metal in order to remove iron and to oxidize sulphur before copper can be recovered. On the other hand, in the case of lead the presence of iron is of no consequence as lead and iron are completely immiscible. Even if some iron sulphide present

first gets oxidized during roasting and then gets reduced in the subsequent blast furnace operation, it does not alloy with lead.

A Dwight-Lloyd sintering machine operates at around 800°C and produces 200–1600 tons of sinter per day. The reactions that take place during roasting are



The metal is ultimately produced by the carbon reduction of the sinter in a lead blast furnace. This furnace is rather small when compared with the furnaces used for producing pig iron. Its total height is around 8 m, top diameter 3 m, crucible depth  $\frac{1}{2}$  m, and stack height 5 m. (The stack is usually a vertical shaft.) The temperature at the bosh seldom exceeds 1200°C; in fact, the bosh is often water-cooled to ensure that the bosh temperature and, therefore, the temperature of the outgoing gases remain low. This is to reduce the loss of lead due to vaporization. A cold blast of air is blown in through 15 tuyeres (15 to 20) around the bosh to oxidize the carbon charged with the sinter which produces the required heat.

At the top of the furnace, either bag houses or electrostatic precipitators are provided so as to recover the lead fumes from the outgoing gases. Cutaway views of bag houses and electrostatic precipitators are shown in Figs. 7.20 and 7.21, respectively. As just mentioned, the temperature of the outgoing gases is kept low.

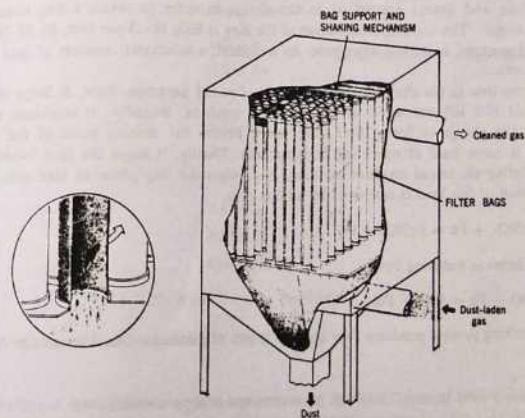


Fig. 7.20 Cutaway View of Bag Filter (Boldt and Quenau, 1967).

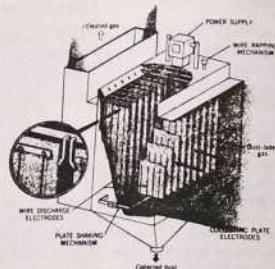


Fig. 7.21 Electrostatic Precipitator (Boldt and Queneau, 1967).

Figure 7.22 shows a flowsheet for the smelting of lead in a blast furnace. The blast furnace charge consists of sinter obtained from the sintering machine, coke (10 per cent), limestone (5–10 per cent), scrap iron (about 1 per cent), and quartz. Occasionally, limestone is introduced at the sintering stage itself. A lead blast furnace produces 200–600 tons of metal per day.

Limestone and quartz are added to the charge in order to obtain a slag containing the gangue material. The normal composition of the slag is  $\text{SiO}_2$  18–35 per cent,  $\text{Fe}$  30–38 per cent,  $\text{CaO}$  10–20 per cent, and  $\text{Pb}$  2–4 per cent. As is evident, a substantial amount of lead goes into the slag.

The scrap iron in the charge serves a number of useful purposes. First, it helps in reducing any residual  $\text{PbS}$  left unroasted in the sintering machine. Secondly, it combines with silica present in the charge to form  $2\text{FeO} \cdot \text{SiO}_2$ , which lowers the melting point of the slag, thus rendering it more fluid at operating temperatures. Thirdly, it keeps the lead losses low. For instance, during the initial stages of smelting, lead enters the slag phase as lead silicate, and a major portion of this lead is recovered by adding iron:



Finally, it helps in reducing  $\text{PbO}$ :



The smelting process produces four distinct layers of products. These layers are demarcated as follows:

First layer Slag (sp. gr. maintained at approximately 3.6)

Second layer Matte containing copper (sp. gr. approximately 5) and other elements

Third layer Spess (especially if As is present in the charge)

$\text{FeAs}_4 +$  impurities (sp. gr. approximately 6)

Fourth layer Lead (sp. gr. 11); also called base bullion

#### Treatment of Base Bullion

The lead-rich layer produced in the blast furnace, namely, the base bullion, is rich in several other valuable elements as indicated in Fig. 7.22. Each of these elements is recovered during a

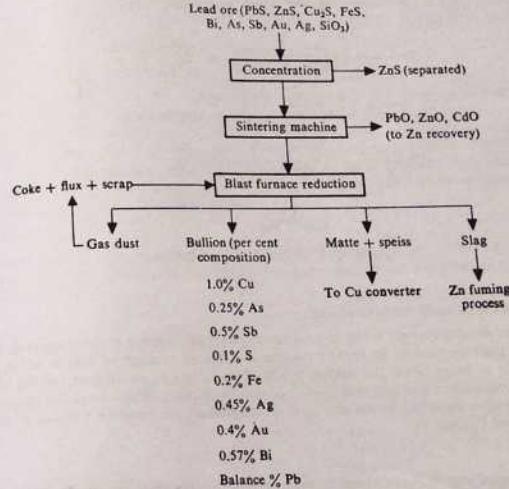


Fig. 7.22 Blast Furnace Smelting of Lead Ore.

series of steps as now described (see Fig. 7.23).

#### Drossing

The base bullion is first subjected to drossing at around  $350^\circ\text{C}$ . (Drossing is a combination of liquation and oxidation and is usually carried out in a reverberatory furnace.) At this temperature, many metals get oxidized and are skimmed off. Subsequently, the temperature is raised to  $500$ – $550^\circ\text{C}$  and sulphur is added to eliminate copper in the form of copper sulphide.

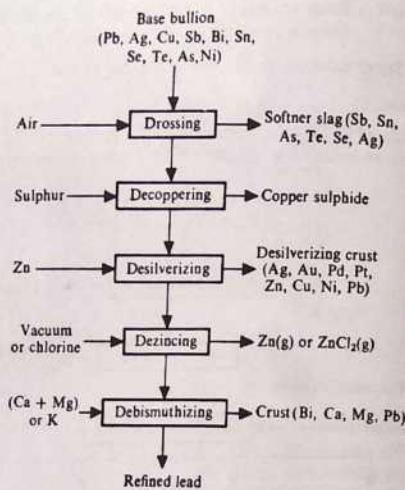


Fig. 7.23 Refining of Lead Bullion.

#### Parke's process for desilverization of lead

Drossing and decoppering are followed by a treatment for the removal of precious metals, mainly silver, from the base bullion. In Parke's process, a sufficient quantity of zinc is added to the molten metal to bring about the desilverization of lead. This process is based on the fact that the mutual solubility of zinc and lead is low and that silver dissolves more readily in zinc than in lead. The silver absorbed by the zinc layer is subsequently recovered by distilling off the zinc (for details, see Chapter 9).

#### Dezinzing

It should be noted that in Parke's process, some zinc inevitably dissolves in the lead and vice versa. (Lead dissolves 0.6 per cent zinc and zinc dissolves 1.6 per cent lead, both metals being in the molten state.) The lead containing zinc is subjected to cupellation, where zinc is removed by oxidation. Zinc can also be separated either by the application of a vacuum or by preferential chlorination with chlorine.

#### Debismuthizing

In the base bullion, if bismuth is present in a large quantity, it can be separated by the addition of an alloy of calcium and magnesium which forms an insoluble intermetallic compound with bismuth.

#### Electrolytic refining

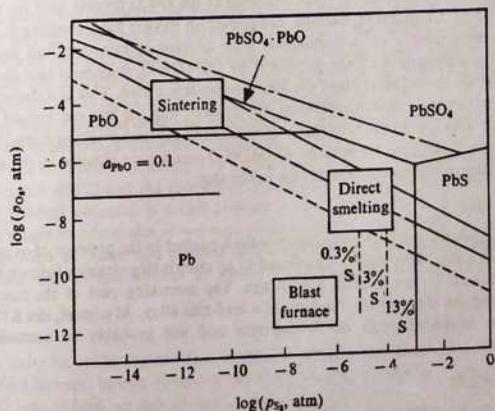
Most attempts to refine the base bullion by electrolysis have proved futile because there are not many water-soluble salts of lead. However, an electrolyte that proves successful is made up of  $H_2SiF_6$  (70 gm/litre and 66 gm/litre of lead as  $PbSiF_6$ ). In the electrolytic cell, the cathode is made of pure lead and the anode of the base bullion. Lead by itself can be selectively electrodeposited because the deposition potential required is low. During electrolysis, impurities such as bismuth, arsenic, antimony, and the precious metals collect at the bottom of the cell in the form of an anode slime from which they can be readily recovered. If the impurity content of the base bullion is very high, electrolytical refining is preferable to conventional refining because the recovery is more complete and easier. COMINCO in Canada and Cerro de Pasco in Peru have adopted the electrolytic route on a large scale.

#### 7.10 MODERN DEVELOPMENTS IN LEAD SMELTING

At present, about 90 per cent of the world's primary lead is produced by the conventional process, i.e., sintering followed by blast furnace reduction, and about 10 per cent by the Imperial Smelting process (see Section 7.1). Recent environment protection laws, which seek to control the emission of lead fumes into the atmosphere, coupled with a shortage of energy needed for lead production have necessitated the development of processes that are both cleaner and less energy consuming. In this regard, the one-step (continuous) smelting process appears attractive. Here,  $PbS$  is oxidized to yield lead according to the reaction



Figure 7.24 shows the equilibrium phases in the  $Pb-S-O$  system at  $1200^\circ C$ . At this temperature, metallic lead, with 1-3 per cent sulphur, can be produced in the presence of pure  $SO_2$ .

Fig. 7.24 Predominance Area Diagram at  $1200^\circ C$  for  $Pb-S-O$  System.

The main difference between the blast furnace slag and the slag obtained by the one-step process is that the latter has a higher lead content because the oxygen potential is higher, leading to a higher PbO activity. Therefore, the slag has to be treated for the recovery of Pb.

Several novel direct smelting processes for lead have been tested only up to the pilot-plant stage. We now discuss these processes individually.

#### **OUTOKUMPU FLASH SMELTING**

In the Outokumpu flash smelter, the lead concentrate is flash smelted in the presence of air as in the case of copper flash smelting. Sufficient air is provided to oxidize all the sulphur present in the concentrate and produce a lead bullion and a molten slag (see Bryk *et al.*, 1966). A temperature of 1200°C is maintained in the furnace in order to keep the slag in a molten and fluid state. However, an arrangement for cooling by water is provided at the bottom of the furnace to keep molten lead at about 500°C. This is done to reduce the loss of lead due to volatilization. Although successful pilot testing had been carried out in 1966, no further progress has been reported since then.

#### **DIRECT SMELTING IN CONVERTER**

Fuller (1968) has described a test conducted by St. Joe, in the U.S.A., for the direct smelting of a lead concentrate to lead in a Pierce-Smith converter. This test was eventually abandoned because of excessive refractory wear. To overcome this wear, Quarm (1974) has suggested the injection of a lead concentrate, fluxes, powdered coal, and air into a water-jacketed vessel. In this case, the frozen slag that accumulates on the water-jacketed vessel acts as a container which can shield the refractory from corrosion.

#### **FLASH SMELTING WITH OXYGEN**

Flash smelting with oxygen is an obvious follow-up to the INCO process used for the extraction of copper and nickel. COMINCO, Canada, has piloted an oxygen flash smelting process for lead, but has not implemented it on a commercial scale because of excessive lead loss to the slag. According to the schematic diagram published by COMINCO, it appears that the lead concentrate and oxygen are flash smelted and the flux is separately added. This is a departure from the INCO practice where the copper concentrate, the oxidant, and the flux are burned together and then the reaction with the flux is brought to completion in the flash smelting flame. The procedure adopted for lead concentrate burning by COMINCO could have resulted in the over oxidation of the lead, leading to the excessive lead loss to the slag.

#### **KIVCET PROCESS**

In the KIVCET process, the lead concentrate is flash smelted in the presence of oxygen to produce metallic lead and a slag. This slag is transferred to an electric slag-cleaning furnace where most of the zinc is recovered in the form of zinc fumes. The remaining part of the zinc and any lead present in the slag are recovered in the form of a lead-zinc alloy. At present, the KIVCET process has reached an advanced stage of development and will probably be soon adopted on a commercial basis.

#### **WORCRA PROCESS**

Initial trials in the WORCRA pilot unit for the smelting of the lead concentrate were reported to

be successful, but extensive testing remains to be done. The same unit subsequently switched over to copper smelting.

#### **Q-S PROCESS**

The Q-S (Queneau-Schuman) process involves an essentially worthwhile concept; i.e., flash smelting, converting, and slag cleaning being carried out in a single long converter type unit with an arrangement for the countercurrent flow of the metal and the slag. At present, trials are under way to carry out the operations of flash smelting, converting, and slag cleaning in a single vessel, and unless this is achieved, the Q-S process will not become commercially feasible.

#### **TBRC (TOP-BLOWN ROTARY CONVERTER) SMELTING**

Recently, Boliden in Sweden has demonstrated that lead can be directly flash smelted in the presence of oxygen-enriched air in top-blown rotary converter with high lead recovery. There is a proposal to enlarge the scale of operation, and, if successful, the TBRC smelting process would become the first direct smelting process to find commercial application.

#### **7.11 PRODUCTION OF LEAD IN INDIA**

At present, the sole producer of lead in India is the Hindustan Zinc Limited (HZL), a Government of India undertaking. HZL operates two plants: one at Tundoo (Bihar) and the other at Visakhapatnam (Andhra Pradesh). The former has a capacity of 8000 tons and the latter has a capacity of 10,000 tons of lead per year. The smelters at the plants not only extract and refine lead from indigenous ores but also yield a substantial quantity of silver as a byproduct. We now discuss the Tundoo plant in some detail.

#### **TUNDOO PLANT**

In the Tundoo plant, the procedure for lead production entails roasting and sintering of the lead concentrate in pots provided with an updraught system for the supply of air for roasting. The exothermic reactions that take place during roasting and sintering can render the process autonomous, provided the sulphur content in the concentrate is between 8 per cent and 10 per cent. An excess of sulphur would cause fusion leading to insufficient roasting.

The roasting section consists of several hemispherical cast iron sinter pots, each of which has an inlet at the bottom through which air is blown in. Suction is created by hoods present above the pots which can be raised or lowered. The maximum temperature attained in the bed during operation is around 800°C and the time taken for roasting and sintering varies from 7 hours to 12 hours. The product obtained is called primary sinter. This sinter is first cooled and then crushed in two stages to a final size of -6 mm. After crushing, the primary sinter is mixed with a suitable proportion of water and charged back into the sinter pots where secondary roasting brings down the sulphur content to about 2 per cent. The product obtained is called secondary sinter.

#### **Tundoo Blast Furnace**

The secondary sinter has to be crushed to a size of 75–100 mm size before it can be fed into the Tundoo lead blast furnace. In fact, there are two blast furnaces at Tundoo, each capable of producing about 25 tons of lead per day. It may be noted that each of these two furnaces consumes about 65–70 tons sinter per day.

A lead blast furnace differs from an iron blast furnace in several respects. For example, the cross-section of the bosh in a lead blast furnace is not circular but rectangular and the stack of a lead furnace is much shorter than that of an iron blast furnace.

Since lead has a rather low melting point, i.e., 327°C, melting hardly poses any problem. The slag, however, melts only at 1200°C. Even this temperature can be easily attained without the blast being preheated. While the blast furnace is in operation, all the gases from the top are sucked in through the cooling and settling chamber into a baghouse where a series of special woollen bags collect the metallic dust. The flue pipes and the cooling chamber are cooled by water spray. The blast furnace product is called hard lead because of the hardness imparted by impurities such as copper, antimony, zinc, and silver. After these impurities have been removed, a soft metal with a purity of 99.99 per cent is obtained during subsequent refining.

#### Lead Refining

During lead refining, copper is removed from the hard lead by a two-stage drossing process in 30-ton kettles heated by oil burners and then again in 60-ton kettles. The temperature of the refined lead obtained after drossing is allowed to drop to about 340°C and then rock sulphur is added on the basis of 1 kg per ton of hard lead. After 2 hours of stirring, the black powdery dross formed is skimmed off. This dross contains about 80 per cent of the copper originally present in the hard lead.

Like copper, antimony, too, is removed in stages. The main bulk is removed after copper drossing by raising the temperature of the kettle to 650°C and blowing air under pressure for about 6 hours. Some caustic soda is also added to precipitate a high antimony slag. The remaining antimony is removed after desilverization and dezincing.

Like copper and antimony, silver, too, is removed in stages by the conventional Park's process. In the first stage, zinc and low zinc crust from the previous charge are added and stirred. The fresh crust formed is taken out and mechanically pressed to remove any entrained lead and to obtain a press crust which contains silver and zinc. In the second stage, some more zinc is added and the temperature is allowed to drop gradually to the freezing point of lead. As zinc separates, it removes with it silver, gold, and residual copper. This crust, known as low zinc crust, is kept in circulation. Silver is subsequently recovered by a retort process.

Dezincing or the removal of residual zinc (about 0.55 per cent) from the lead is accomplished by blowing air for 3–4 hours at 650°C, when a zinc dross is formed. The addition of caustic soda at this stage removes the residual antimony.

The approximate consumption of materials per ton of lead is as follows: zinc 16–17 kg, sulphur 1–1.2 kg, and caustic soda 2–2.5 kg.

A typical analysis of the products obtained during lead refining is given in Table 7.6.

#### 7.12 ZINC

##### USES

The annual global consumption of zinc (excluding the U.S.S.R. and China) is comparable with that of lead, i.e., about 5 million tons. The metal is most extensively used as a protective coating for steel (galvanizing) because it resists atmospheric corrosion by forming an impervious basic zinc carbonate layer. From the electrochemical point of view, too, a zinc coating protects steel because the former is more electropositive. Zinc is also widely used in the fabrication of alloys

Table 7.6 Typical Analysis of Lead-Refining Products (per cent)

Material	Pb	Cu	Sb	Ag	Fe	Zn	Ni	S
Hard Pb	98.6		0.39	0.15	0.03	0.02	0.01	0.32
Cu dross	81.3		0.35	0.04	0.66	0.45	0.16	10.1
Sn dross	70.1		9.4	0.01			1.1	
Zn dross	73.1		15.1	0.005				
Low Zn crust	37.5				0.42		10.2	
Press crust	75.9				2.0		13.5	
Refined Pb	99.996	0.0006	0.0009	0.0018	0.0003	0.0008		

such as Cu-Zn brasses. A low melting point, a relatively high structural strength, a good dimensional stability, and a relatively low cost per unit weight render zinc ideal for die casting. Rolled zinc plates are used in dry cell batteries. The formability of the metal makes it suitable for forging and extrusion. Finally, zinc is used in combination with other compounds in the manufacture of paints and pigments.

In India, galvanizing consumes the maximum amount of zinc (about 60 per cent). This is followed by the metal's use in the manufacture of brass and zinc oxide. Die casting accounts for only about 10 per cent of the metal.

#### 7.13 EXTRATION OF ZINC

Zinc stands out as a unique metal in that there are at least six different processes in full commercial operation for its production. Table 7.7 gives a comparative estimate of the percentages of production of zinc by several processes.

Table 7.7 World Zinc Production

Process	Year of commercial adoption	Per cent share	
		1958	1975
Horizontal retort	1800	32	15
Vertical retort	1930	7	13
Electrothermic	1936	3	3
Electrolytic	1915	50	58
Imperial smelting	1950	8	11

The first three processes listed in Table 7.7 are essentially retort processes, and tackle the difficult, but vital, problem of condensation by preventing the dilution of the retort gases by combustion products. The horizontal retort process has made a major contribution to zinc production in the past and is now giving way to newer processes.

The electrolytic process, introduced in 1915, has proved to be highly successful mainly because it produces a zinc with a high degree of purity (normally 99.95 per cent). This process requires an extremely pure solution because the ultimate result of the process depends on the maintenance of a high hydrogen overvoltage, which is profoundly affected even by trace impurities. Over the years, a sufficient number of purification methods have been developed which have helped the electrolytic process to get firmly established. Recently, further improvements have been made. For example, silicon rectifiers have been incorporated in electrolytic cells in order to reduce power consumption and higher current densities have been applied in order to achieve higher production.

A recently developed blast furnace process for the production of zinc is the Imperial Smelting Process (ISP) (for details, see Section 7.16). In this process, the zinc vapours generated by reducing the zinc smelter are shock-cooled in molten lead. This process may eventually prove to be the most successful, especially in the case of complex lead-zinc ores. The Imperial Smelting process has many of the advantages of a blast furnace. We now list some of these advantages. A large furnace can be constructed and run at competitive capital and operating costs. The fact that a considerable quantity of lead can be simultaneously smelted along with zinc at practically no additional cost makes the ISP furnace, in many cases, a more economical producer of lead than the standard lead blast furnace. The process enables the recovery of almost the entire amount of silver, gold, copper, antimony, and bismuth present in the zinc concentrate in a single operation. The ISP also eliminates differential flotation. Perhaps the most important single attribute of the ISP is its ability to smelt low-grade concentrates with a high iron content *vis-à-vis* the competing processes which are restricted to the chief high-grade ores.

#### SOURCES OF ZINC

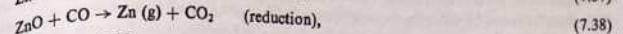
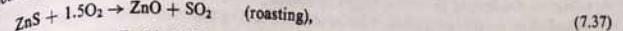
Some of the important naturally occurring minerals of zinc are: sphalerite ( $ZnS$ ), zincite ( $ZnO$ ), franklinite [ $ZnO(Fe, Mn)_2O_3$ ], calamine [ $Zn_2(OH)_2SiO_3$ ], and smithsonite ( $ZnCO_3$ ). Of these minerals, sphalerite is the commonest. The zinc ores are usually associated with several compounds, mainly sulphides of Pb, Cu, and Cd. The main zinc-producing countries are Canada, the U.S.A., Belgium, Australia, and Mexico.

Zinc ores are often of a low grade. Differential flotation can, however, be used to separate the sulphides of Pb, Cu, and Zn from a typical zinc ore. This produces a zinc concentrate containing as much as 50 per cent zinc. As already mentioned, both pyrometallurgical and hydrometallurgical techniques are currently being employed in the extraction of zinc. The former is distinctly successful if the concentrate is of a very high grade.

#### 7.14 PYROMETALLURGICAL EXTRACTION OF ZINC

The technique of smelting and converting, applied in the case of copper sulphide, is not practicable with regard to zinc sulphide because the latter does not melt even at a temperature as high as  $1500^{\circ}\text{C}$ . Consequently, different methods have to be adopted. In one particular method, the zinc sulphide concentrate, which contains about 55 per cent zinc, is roasted at a temperature of about  $800^{\circ}\text{C}$ . The resultant roasted oxide is first ground and agglomerated and then sintered at

$1200^{\circ}\text{C}$  so as to provide a feed in the form of lumps for retort reduction. In the retort, the  $ZnO$  is reduced by carbon at about  $1200^{\circ}\text{C}$ . The zinc which distils off is collected in condensers. The reactions are



It should be noted that the partial pressure of CO in the retort gases has to be maintained

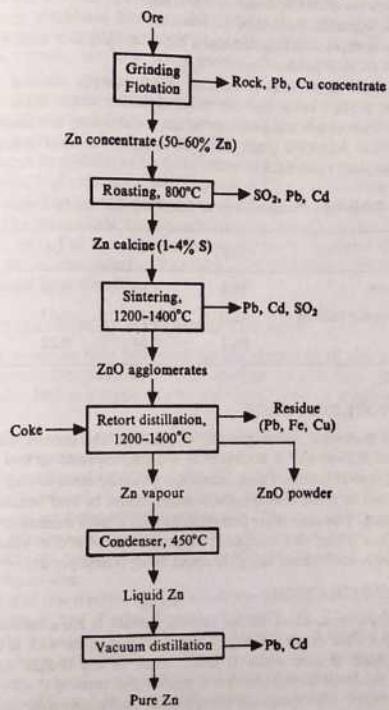


Fig. 7.25 Extraction of Zinc by Reduction of  $ZnO$  by Carbon.

at a high level in order to prevent the oxidation of Zn to  $ZnO$  by the  $CO_2$  present in these gases. The flowsheet for the extraction of zinc by carbon reduction is given in Fig. 7.25. The zinc sulphide concentrate always contains some lead sulphide. In order to eliminate this lead sulphide to a large extent during the initial stages of roasting, i.e., by volatilization, a hearth roaster is employed. The remaining lead sulphide is removed during sintering which is carried out at rather high temperatures. In order to prevent the distillation of any lead present in the zinc concentrate along with the zinc and to obtain a high-grade zinc, it becomes essential to ensure that the feed for retort distillation has a low lead content.

In most cases, roasting is carried out in a fluid bed roaster rather than in a conventional hearth roaster because the former has certain advantages. For instance, the roasting process in a fluid bed roaster is autogenous. Further, a fluid bed roaster provides a good control over the temperature, ensures a rapid roasting rate and a high throughput of zinc calcine, and generates  $SO_2$  which is suitable for acid production.

The calcine obtained as a result of roasting is subsequently sintered in a Dwight-Lloyd sintering machine to provide lump feed for retort reduction and to eliminate residual sulphur, cadmium, and lead. The typical compositions of the concentrate, the roaster calcine, and the sintered product for the ASARCO plant are given in Table 7.8. Such elimination of Pb, S, and Cd is typical of other plant operations as well.

Table 7.8 Compositions in ASARCO Smelter (per cent)

	Zn	Pb	Cd	S
Concentrate	56.5	1.07	0.49	31.24
Hearth roaster calcine	62.0	0.54	0.63	4.7
Sinter	66.2	0.24	0.02	0.01

#### HORIZONTAL RETORT REDUCTION

We now discuss the horizontal retort process in detail. In this process, 2-m-long retorts, each having a diameter of 0.25 m and a thickness of 5–6 cm, are lined up in a gas-fired furnace in batches of several dozens at a time. These retorts are generally made of clay and last for about 35 operations. It should be noted that a metallic retort cannot be used because most metals alloy with zinc when heated. The retorts are first charged with a loose mixture of  $ZnO$  and an excess of coke breeze and then heated to a maximum temperature of  $1400^\circ C$  to volatilize zinc which is subsequently condensed. Each retort can yield about 50 kg of zinc per day.

#### VERTICAL RETORT REDUCTION

Vertical retorts are usually made of silicon carbide because it has a conductivity that is about five times higher than that of clay. Consequently, in comparison with a horizontal retort, a vertical retort has much thicker walls, is much larger in size (height approximately 10 m, diameter 0.7 m, and thickness 30 cm), and has a much higher capacity (7–10 tons of zinc per day). Most retorts are provided with automatic charging and discharging mechanisms which facilitate the handling of raw materials and products.

A vertical retort can be also used for electrothermic reduction. In this case, the retort is normally 15 m high with an internal diameter of 2.4 m and produces about 100 tons of zinc per day. In the process used by St. Joe, electrodes of graphite are introduced through the silicon carbide walls at two places—near the bottom of the retort and at a zone about 9 m from the bottom. The charge in this zone forms the resistance and the electrical energy supplied provides the heat necessary for the reduction of the charge instead of the fossil fuel employed in conventional horizontal and vertical retorts.

The gas liberated due to the reduction of the charge contains 40–45 per cent Zn, 45 per cent  $CO$ , 5–8 per cent  $H_2$ , 5–10 per cent  $N_2$ , and minute quantities of  $CO_2$ . In the St. Joe process, this gas (i.e., zinc vapour) is bubbled through an U-tube arrangement whose exit is maintained under a vacuum to enable the suction of the retort gases through the molten zinc. The zinc condensation has to be carried out quickly in order to avoid the formation of the blue oxide of zinc ( $ZnO + Zn$ ) in another process, namely, the New Jersey process, the zinc vapour is condensed in a splash zinc condenser.

The residues of the foregoing retort processes contain 3–4 per cent zinc, all the input iron, gangue, copper, and precious metals. The zinc recovery from these processes is over 95 per cent.

The zinc product obtained from the foregoing retort processes is known as *sphalerite* and contains other elements in addition to zinc. On melting, it forms three distinct layers, namely, a bottom layer of molten lead containing some zinc (about 1.5 per cent), a top layer of zinc containing some lead (about 0.8 per cent), and an intermediate layer of zinc and iron (15–20 per cent) called hard metal. The intermediate layer is recycled to the retorts and the lead layer is smelted in order to recover lead. The zinc layer is further refined by fractional distillation because the wide difference in the boiling points of Zn ( $907^\circ C$ ), Cd ( $780^\circ C$ ), and Pb ( $1620^\circ C$ ) facilitates the separation of one metal from the other.

#### 7.15 HYDROMETALLURGICAL EXTRACTION OF ZINC

Hydrometallurgical processes have been used for the extraction of zinc from a wide variety of ores, including extremely low-grade ores. These processes not only yield zinc with a high degree of purity but they also lead to a higher rate of recovery of valuable byproducts than pyrometallurgical processes.

In a hydrometallurgical process, the zinc concentrate is first roasted in the same manner as in the retort process. In this case, however, a greater control is exercised over the roasting operation in order to minimize the formation of the ferrite  $ZnO \cdot Fe_2O_3$ . As already mentioned, although this ferrite could be easily reduced, it was found to be virtually unleachable in the earlier hydrometallurgical processes, rendering it highly undesirable. This drawback has been overcome in the recently developed Jarosite and Goethite processes. The roasted zinc concentrate is dissolved in an acid and the valuable byproducts are precipitated out. The leach solution is finally electrolyzed for the recovery of zinc.

Since the position of zinc is rather high in the electrochemical series, it should be ensured that the foregoing solution is free of other elements such as Cd, Pb, Cu, Fe, As, and Ge. If not, the zinc deposited on the cathode of the electrolytic cell would be highly contaminated. Consequently, the removal of the aforementioned elements becomes an absolute necessity. (This is in contrast to the electrolytic recovery of copper, where the byproducts are recovered after electrolysis.) Further, the presence of Cu and Fe is known to reduce the current efficiency during electrolysis. Even minute traces of As and Ge (few parts per million parts of copper) could prove almost

disastrous because not only do these elements drastically reduce the current efficiency but they also render the deposit black and unsatisfactory.

The flowsheet for the hydrometallurgical extraction process for zinc is based on the following scheme:

- (1) Dissolution of the zinc calcine in sulphuric acid.
- (2) Precipitation of cadmium by adding zinc dust to the leach solution, i.e., cementation. (Some Co and Cu are also removed.)
- (3) Precipitation of cobalt from leach solution by adding  $\alpha$ -nitroso- $\beta$ -naphthol.
- (4) Adjustment of the pH of the leach solution to about 5.3 to hydrolyze aluminium and iron and addition of  $MnO_2$  to oxidize iron to the trivalent state and to produce a precipitate that is flocculent and can absorb the entire quantity of As, Sb, and Ge.

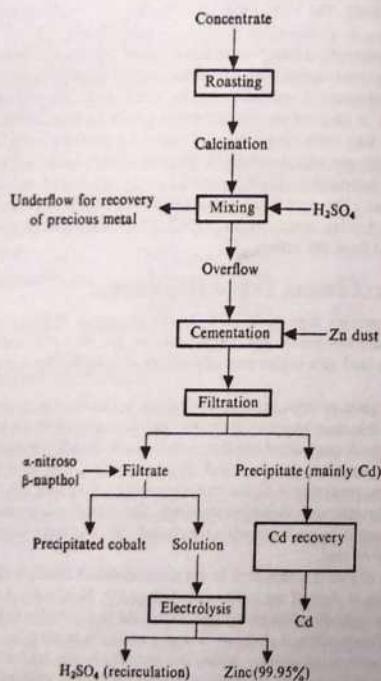


Fig. 7.26 Hydrometallurgical Extraction of Zinc.

(5) Electrolysis of the purified leach solution using a cell with a Pb-Ag anode and an aluminium cathode.

Figure 7.26 shows a simplified flowsheet for the hydrometallurgical zinc extraction process. As is evident from the flowsheet, the most important byproduct is perhaps cadmium. It should, however, be noted that the cadmium obtained by cementation normally contains some lead, copper, and residual zinc. To eliminate these constituents, the cadmium is first dissolved in sulphuric acid, when only zinc and cadmium go into solution. When this solution is subjected afresh to cementation by zinc dust, a purer variety of cadmium in the form of a sponge is precipitated. This sponge is redissolved in sulphuric acid, and the solution is electrolyzed in order to obtain pure cadmium.

#### 7.16 IMPERIAL SMELTING PROCESS (ISP)

In this section, we discuss the ISP (already referred to at various places) in detail.

In the ISP,  $ZnO$  is reduced by carbon to produce zinc. The reduction is carried out in an imperial Smelting blast furnace, in which, the zinc that is evolved in the form of a vapour is condensed by using molten lead.

Before taking up the actual process, we list some of the advantages that the ISP has over other processes:

- (1) It is possible to simultaneously smelt low-grade complex mixed charges of zinc and lead ores and concentrates in order to recover both zinc and lead.
- (2) Since the overall thermal efficiency is higher, the recovery of zinc becomes less expensive.
- (3) A wide variety of furnace sizes are available, the trend being towards units with larger capacities at lower operational costs.
- (4) The furnace operation is fully automated.
- (5) The mechanism is highly robust, i.e., it can withstand frequent shut-downs and restarts.

Figure 7.27 shows a simplified diagram of the Imperial Smelting blast furnace and Fig. 7.28 depicts the zinc recovery system.

The smelting reactions that take place in the blast furnace are



Besides the reduction of  $ZnO$  to  $Zn$ ,  $PbO$  is reduced to  $Pb$ ,  $Fe_2O_3$  to  $Fe$ , and certain sulphates to sulphides. Reaction (7.43) proceeds in the forward direction, but can be reversed in some regions of the furnace. The amount of reduction per unit of carbon consumed is governed chiefly by the heat balance for the unit operation.

After the reduction has been completed, the molten slag and lead are taken out of the furnace hearth at a temperature that is approximately equal to the melting point of the slag,

whereas the gases generated emerge from the top of the furnace at a temperature slightly higher than the equilibrium temperature for reaction (7.43). The latter temperature is raised to 1000°C

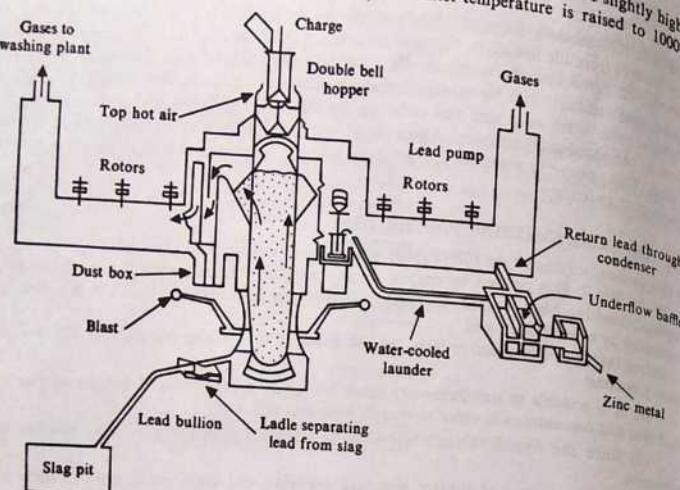


Fig. 7.27 Imperial Smelting Blast Furnace.

by admitting air above the top of the furnace charge in order to generate heat by the combustion of CO. At this temperature, zinc could be collected without back reaction. The heat balance for the blast furnace reduction of zinc oxide is much more favourable than that for the conventional retort reduction, i.e., the amount of zinc oxide smelted per unit of carbon consumed is much higher.

The basic process during the smelting of zinc oxide is the combustion of carbon in preheated metallurgical coke which produces gaseous carbon monoxide. This monoxide affects the reduction of ZnO and PbO in a sinter with a very low sulphur content.

Preheated coke (800°C) and sinter are charged into the top of the ISP furnace. The lead in the sinter, which is reduced to liquid metal, flows down to the bottom of the furnace. In so doing, it collects copper, silver, and gold together with other elements contained in the furnace charge. (This liquid lead is called lead bullion.) The other product that is removed from the bottom of the furnace is a relatively barren slag. This slag and the lead bullion are tapped together from the bottom of the furnace and are separated by the difference in their density values. This bullion is usually cast into one-ton ingots which are subsequently refined by conventional refining methods.

The ISP furnace is of a square cross-section and consists of a water-jacketed brick-lined shaft. Since the feed arrangement at the top of the furnace operates under a positive pressure,

it becomes necessary to introduce the preheated coke and sinter through a double bell charging system. The furnace gases generated during reduction, pass upward through the charge and are evenly divided between two condensers. These condensers serve two purposes, i.e., they very rapidly cool the furnace gases, resulting in the condensation of the zinc contained in these gases and they help in dissolving the condensed zinc in molten lead. Each condenser (see Fig. 7.28)

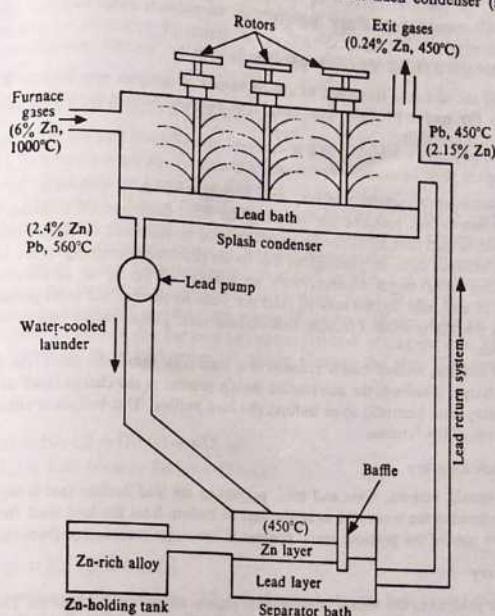


Fig. 7.28 Zinc Recovery System (after Pehlke, 1973).

consists of a bath of molten lead. Rotors capable of generating an intense spray of lead droplets over the entire volume of the condenser are immersed into the molten lead bath. When the furnace gases (containing zinc) pass through this spray, they are cooled very rapidly. (Such shock cooling minimizes the reoxidation of Zn by CO<sub>2</sub>.) As a result, the Zn vapour present in the furnace gases either goes directly into solution with the lead or forms liquid zinc, which, in turn, immediately dissolves in the lead.

The zinc-containing lead is constantly pumped out from the condensers at a temperature of about 550°C into water-cooled launders, where it is cooled to a temperature of about 440°C. During cooling, the lead becomes saturated with zinc, and any excess zinc emerges from the

lead and floats in the form of rivulets on the surface of lead because the density of zinc is less than that of lead. The supernatant zinc is separated and the lead is continuously returned to the condensers. The zinc is collected in a holding tank where it is treated with metallic sodium in order to remove arsenic. At this stage, the metal is of a high grade and is ready for casting.

At present, ISP furnaces operate in the U.K., Zambia, France, Germany, Rumania, Japan, and Canada. The construction of new units in other countries is under way.

#### PRODUCTION OF OTHER METALS BY ISP

The ISP is well suited to the treatment of a wide variety of complex ores because it combines in one operation the recovery of the zinc metal and the lead bullion containing precious metals, copper, and other elements.

#### Lead Recovery

In the ISP, a considerable quantity of lead can be produced along with zinc. In this process, additional carbon is not required for reducing the lead. Experimental evidence has indicated that the maximum lead content of the feed sinter should be restricted to 28 per cent; otherwise, the operation becomes difficult, presumably due to the premature softening of the charge.

The capacity of a single furnace, with an area of 27 sq. m., at Avonmouth, U.K., is 100,000 tons of zinc and 75,000 tons of lead per year. At present, the total global annual zinc production by the ISP is about 1 million tons and the total global annual lead production about 0.5 million tons.

In the ISP furnace, molten lead is reduced in a zone high up in the shaft. As this lead falls through the charge, it collects the nonvolatile metals present in the charge (such as silver, gold, copper, antimony, and bismuth) so as to form the lead bullion. This bullion is ultimately tapped from the bottom of the furnace.

#### Precious Metals Recovery

The precious metals, namely, silver and gold, present in the lead bullion that is tapped from the bottom of the furnace are recovered as in the case of bullion from the lead blast furnace. On an average, 95 per cent of the precious metal content of the sinter is recovered from the bullion.

#### Copper Recovery

All the copper present in the charge is essentially recovered by the lead bullion. The ISP furnace can treat a raw material in which the ratio of Zn to Cu is 5 to 1.

#### Arsenic, Antimony, and Bismuth Recovery

In the ISP furnace, arsenic volatilizes and collects in the condensers. It is more of a nuisance because it gives rise to a dross which returns to the furnace; this arsenic eventually leaves the furnace circuit in the form of speiss, and is either tapped from the forehearth or disseminated in the slag.

Antimony is collected in the lead bullion, as is bismuth, the rate of recovery in both cases is over 90 per cent.

#### Tin Recovery

Tin is an objectionable constituent of zinc for some uses. So, if zinc refining is not practised, tin

in the furnace feed should not be allowed to exceed 0.01 per cent. About 10 per cent of the tin input finds its way to zinc product and a separation can be made by the distillation of the zinc either by vacuum dezincing or reflux refining.

#### Cadmium Recovery

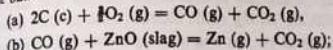
Cadmium is an important byproduct. During the sintering operation, cadmium compounds are volatilized and can be recovered by means of an ion exchange process from the leaching of sludges from gas cleaning. Further recovery of cadmium is effected if the zinc output is subsequently refined.

#### 7.17 ZINC FROM LEAD SLAGS BY SLAG FUMING

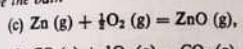
The slags produced in the lead blast furnace are high in zinc (15–18 per cent Zn) and are sent to the zinc fuming furnace for recovery. As zinc is almost always associated with lead, all the lead smelter slags containing zinc are treated for zinc recovery by slag fuming.

The initial development of zinc fuming was carried out by COMINCO in Canada. The molten lead blast furnace slag and the granulated blast furnace slag are charged into a slag fuming furnace. This furnace has no refractory, but has water jackets which ensure a solidified crust of slag to act as lining. Each furnace is 3 m wide, 3 m high, and 8 m long and has about 70 double inlet tuyeres located at a height of 178 cm from the bottom. The inner tuyere of diameter 19 mm is to inject coal and the outer tuyere of diameter 38 mm is for air injection. This furnace treats about 55 tons of slag per heat and about 700 tons of slag per day. In this process, pulverized coal and air at a fixed ratio are blown through the slag. The reactions taking place are:

*in the bath*



*above the bath*



Reaction (a) provides the reductant for ZnO reduction and also the heat needed to keep the bath molten. Reaction (b) is endothermic. Reactions (c) and (d) are exothermic and provide heat to the system. The excess heat is collected in boilers located in the gas collection system. The control of the coal to air ratio determines the extent of heat release and is used to maintain the bath at about 1200°C.

The zinc fumes from the slag are collected in bags/Cottrells as zinc oxide. The rate of zinc fuming is dependent on the amount of zinc in the slag as shown in Fig. 7.29. Zinc fuming is normally stopped when the zinc level is about 2 per cent, and the slag is discarded. The economic cut-off value of the zinc in the slag discarded depends on the prevailing zinc price and the operating cost.

The typical analysis of COMINCO slag fuming furnace feed products are shown in Table 7.9.

The recoveries of zinc and lead are 89 per cent and 98 per cent, respectively. The zinc fume is sent to a zinc plant for zinc recovery. In addition to lead and zinc, other trace elements such as

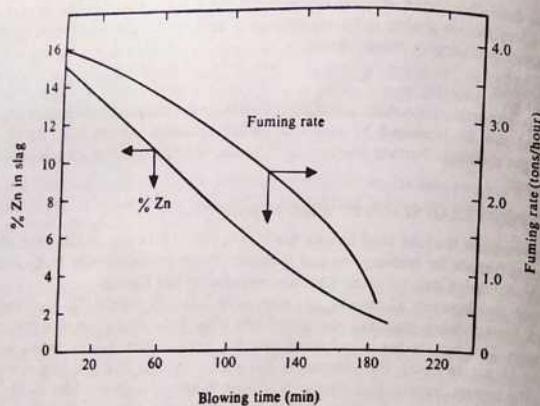


Fig. 7.29 Zinc Elimination During Slag Fuming.

cadmium, indium, tin, and silver are volatilized from the slag and are collected along with the dust.

It has been experimentally determined that the addition of lime to the furnace lead increases the zinc recovery. This is understandable because strong oxide formers such as CaO increase the activity of less stable oxides in ternary slags as per the slag model put forward by Richardson (1974).

Table 7.9 Slag Composition in Zinc-Fuming Furnace (per cent)

Feed/product	Zn	Pb	Cd	S	SiO <sub>2</sub>	CaO	Fe
Lead blast furnace slag	17.5	2.5	0.09	1.8	20.8	10.3	27.5
Cleaned slag	2.5	0.05					
Zn fume dust	63.0	9.8	0.10	1.8	0.5	0.2	0.2
Boiler cleaning	59.6	10.5	0.09	0.7	1.8		2.5
Boiler clinker	42.8	14.0	0.06	1.0	6.0		8.0

#### 7.18 PRODUCTION OF ZINC IN INDIA

The annual demands of zinc and cadmium in India are approximately 100,000 tons and 80 tons, respectively. More than half of the zinc demand is met by indigenous production. The entire

cadmium demand, however, is met by the byproduct metal obtained from the zinc plants. The Zawar mines (Rajasthan) have been a centre of zinc mining and smelting since the thirteenth century. The public sector undertaking Hindustan Zinc Limited (HZL) operates a smelter at Debari, near Udaipur (Rajasthan) with a capacity of 45,000 tons per year of zinc. This smelter, which uses locally available concentrate, also produces 80 tons of cadmium per year. It also produces about 90 tons per day of sulphuric acid and 220 tons per day of superphosphate fertilizer. It is estimated that on full exploitation of the reserves, it would be possible to produce 100,000 tons of zinc per year with an annual byproduct production of 35,000 tons of lead, 400 tons of cadmium, 35,000 kg of silver, and 500,000 tons of superphosphates.

HZL has another plant at Visakhapatnam with a capacity of 30,000 tons per year of zinc. Another zinc plant, belonging to COMINCO-BINANI, with a capacity of 20,000 tons per year of zinc, is located in Alwaye (Kerala). Both these plants use imported concentrates.

#### HZL DEBARI PLANT

The HZL plant at Debari uses the hydrometallurgical process to produce zinc with a purity of 99.99 per cent. This percentage is higher than that required for galvanizing, which is the primary use of zinc in India. The details of the process used are shown in Fig. 7.30 and Fig. 7.31.

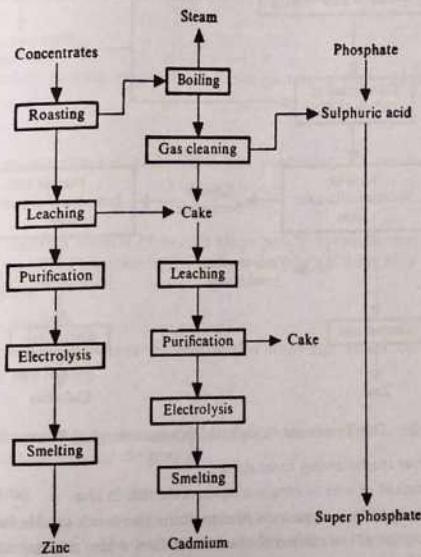


Fig. 7.30 Essential Steps in Zinc Plant at Debari.

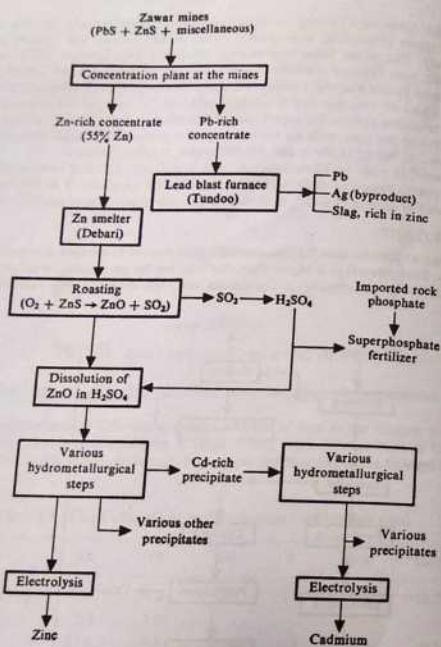


Fig. 7.31 Ore Treatment in Debari Hydrometallurgical Process for Zinc.

This process involves the following basic steps:

- (1) The treatment of ores to obtain a concentrate rich in zinc.
- (2) The roasting of the concentrate to convert the zinc into a soluble form.
- (3) The treatment of the roasted concentrate to form a zinc sulphate solution.
- (4) The purification of the zinc sulphate solution by precipitation of impurities.

(5) The removal of zinc from the purified solution by electrolysis.

(6) The melting of zinc sheets to form ingots.

#### 7.19 TREATMENT OF COMPLEX SULPHIDES OF LEAD, COPPER, AND ZINC

As zinc, lead, and copper often occur together, the separation of one metal from the other has presented problems to the nonferrous metallurgists. A large number of processes have been employed, some of which are now discussed.

##### Gravity Concentration

Gravity concentration methods can separate to a large extent the Zn, Pb, and Cu minerals from the gangue.

##### Differential Flotation

As already mentioned, the sulphide minerals can be floated selectively and separated, provided the metals are present as discrete minerals having a reasonable particle size, i.e., above 10 µm.

##### Retort Distillation

Retort distillation separates zinc from lead, copper and gangue. The zinc finally obtained contains some lead.

##### Electrolysis

Electrolysis can produce pure zinc from a leach liquor containing lead and copper in addition to zinc.

##### Liquation

The liquation of molten zinc-lead baths yields zinc containing 1.2 per cent lead and lead containing 0.5 per cent zinc.

##### Rectification

The rectification of zinc that contains Pb and Cd alloys permits the production of zinc containing less than 0.003 per cent Pb, Pb containing 0.5 per cent Zn, and a Cd-Zn alloy containing about 20 per cent Cd and 80 per cent Zn.

##### Lead Blast Furnace Smelting

In a lead blast furnace, copper enters the lead bullion while zinc enters the slag phase. This zinc is recovered by slag fuming.

##### Selective Roasting

Partial roasting under reducing conditions of zinc sulphide concentrates containing Pb and Cd separates Pb and Cd from zinc and the gangue.

##### Reverberatory Smelting

Copper/zinc concentrates can be treated in conventional copper reverberatory furnaces and converters to recover copper. The zinc present in the slag is subsequently recovered by slag fuming.

In any traditional circuit, a selective combination of the foregoing processes must be used in order to achieve the recovery of all metallic values from polymetallic ores. The ISP, however, can directly treat sinters from mixed ores.

For the winning of Pb, Cu, and Zn from sulphide ores by conventional methods, it is essential that these metals be beneficiated to yield high-grade concentrates. The ore minerals, it is essential, metallic and complex deposits are often found to be in close mutual association with each other and with the nonmetallic gangue. In many cases, attempts to concentrate these ores have run into problems because it is either difficult to obtain a suitable grade of the concentrate by conventional flotation methods or the recovery of metals in the respective concentrate is poor. Zinc that finds its way to a copper concentrate is always discarded in the slag as a waste, while copper in a lead concentrate leads to serious smelting problems. In such cases, the cost of production in a smelting process becomes unfavourable and new approaches to process these ores become more attractive. Hydrometallurgical processes, based on leaching and precipitation, or in combination with conventional pyrometallurgical methods, can meet the requirements of polymetallic ores. Hydrometallurgical processes can be adopted to small-scale operation more easily than conventional smelting and refining.

#### HYDROMETALLURGICAL TREATMENT OF COMPLEX SULPHIDES

The types of variation that are found in the hydrometallurgical flowsheets for the processing of complex sulphide ores depend on the nature of the gangue materials and the percentage composition of the various nonferrous metals present in the ores or in the bulk concentrates. The first major step in hydrometallurgical methods involves the absorption of the nonferrous metallic values in solution and leaving behind a major part of the iron in the leach residue. The next steps are solution purification, separation of the nonferrous metals from each other by cementation, precipitation, solvent extraction, or electrolysis. Fluosolid roasting helps in the selective conversion of the nonferrous values in the ores or concentrates to sulphates, which are soluble in dilute acids or water and thus permit a good separation of the iron which exists in the roaster calcine in the form of an insoluble ferric oxide. Due to the vigorous mixing of materials inside a fluosolid roaster, the temperature throughout the bed remains the same and can be easily controlled, assuming the formation of the desired sulphates. By fixing the proportion of air to solid feed in the roaster, calcine and gas compositions can be controlled and thus a selectivity in the sulphation can be achieved.

After selective sulphation, most of the copper or zinc can be dissolved in dilute  $H_2SO_4$ , leaving behind lead and iron in the residue. Copper may be recovered from leach solution by cementation. However, when the copper occurs in substantial amounts, a method based on the cementation for copper recovery from leach liquors containing both copper and zinc would prove uneconomical, and the copper recovery step would have to be modified. Some plants adopt a method based purely on electrolysis for the separation of copper and zinc. In such a case, the solution has to be neutralized and iron precipitated by the addition of lime before the solution can be purified for the electrolysis of zinc.

Pressure leaching for the treatment of complex sulphides has been suggested on a purely theoretical basis, and possible methods of separation of copper and zinc indicated. However, autoclaving under high pressures ( $>5$  atm) would take most of the iron in solution which would have to be removed by subsequent treatment.

#### Solvent Extraction

A process has been recently developed for obtaining a clean separation of copper from the zinc sulphate roasting and leaching is purified to remove iron, and zinc is selectively recovered by solvent extraction with a kerosene solution of ethylhexyl phosphoric acid and subsequently stripped from the loaded organic with sulphuric acid or spent electrolyte by conventional zinc electrolysis. If the copper content of the zinc raffinate is high, copper may be recovered directly by electrowinning.

#### 7.20 NICKEL

##### USES

Nickel and chromium are two strategically important alloying elements that are being increasingly consumed in the fields of chemical processing, space research, and nuclear reactor engineering. Accordingly, the present yearly world production of nickel has exceeded 0.5 million tons. India's nickel requirements are met by imports.

Many uses of nickel are dependent on the combination of the properties of strength and ductility, which the metal possesses. Nickel is also a valuable alloying constituent in more than 3000 commercial alloys which find wide application principally for their mechanical properties and resistance to corrosion and heat.

Steels that contain a high percentage of nickel and chromium are known for outstanding resistance to high-temperature oxidation and strong chemicals such as acids. Ductile nickel-alloyed steels are used in various structural applications. Electric heaters and thermocouples use heat-resistant alloys made of nickel, iron, and chromium.

Nickel forms an important group of alloys with nonferrous metals. Nickel-copper alloys, known as *monel metals*, are used in the chemical oil industry and the electrical industry in applications that require a combination of extraordinary corrosion resistance and strength. Nickel, copper, and zinc alloys, known as *German silver*, are easily formable and are accordingly used in the manufacture of ribbons, bands, and wires for various applications, for example, in medical instruments. Pure nickel is used as a catalyst in many reactions, for example, in the hydrogenation of vegetable oils.

#### 7.21 EXTRACTION OF NICKEL BY PYROMETALLURGY

Nickel ores occur both in the oxidic and sulphidic forms. As seen from Table 7.10, production from the sulphidic ores had predominated, but in the future, the oxidic ores will play an ever-increasing role.

#### EXTRACTION FROM SULPHIDE ORES

The principal sulphide mineral of nickel is pentlandite  $[(NiFe)_3S_4]$ . Nickel also occurs to a minor degree as violarite  $(Ni_2FeS_4)$  and as a solid solution in pyrrhotite  $(Fe_7S_8)$  which often occurs with pentlandite. As seen from Table 7.10, Canada is the principal nickel producer and INCO accounts for nearly 80 per cent of this production. The process flowsheet used by INCO for nickel extraction is shown in Fig. 7.32.

Table 7.10 World Production of Nickel Ores (in 1000 tons)

Location/source	1960		1975		1990 (estimated)	
	Sulphide	Oxide	Sulphide	Oxide	Sulphide	Oxide
Europe	2.1		5.0	8.6	5.0	65.0
Asia						
India		0.6				
Other Asian countries	3.2		40.7	25.1	75.0	5.0
Africa						
Canada	194.6		244.8		340.0	
U.S.A.		11.4		13.2		
South America and Central America			60.0	29.6	15.0	
Australia			53.5	110.0	50.0	135.0
New Caledonia					70.0	70.0
Sea nodules					225.0	
Total	199.9	65.5	350.5	186.5	470.0	745.0

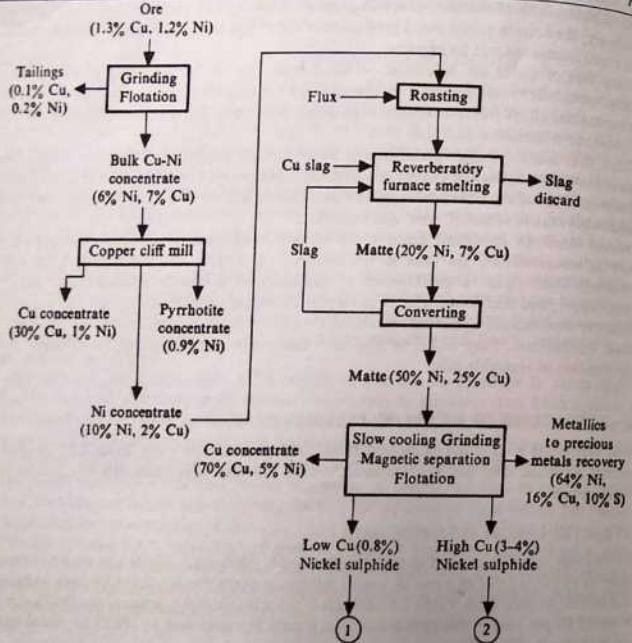


Fig. 7.32 Nickel Extraction (INCO process) (cont.).

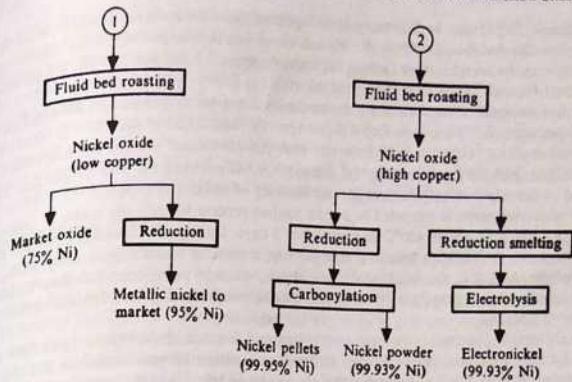


Fig. 7.32 Nickel Extraction (INCO process).

**Nickel Sulphide Ore Processing at Sudbury (Canada)**

The ore at Sudbury is a mixed copper-nickel ore with nearly equal amounts of copper (as  $\text{CuFeS}_2$ ) and nickel (as pentlandite and pyrrhotite). About 60,000 tons per day of 1–1.5 per cent Cu and 1–1.4 per cent Ni ore are mined from 14 mines and sent to four different mills. These mills employ grinding and froth flotation to produce a bulk concentrate which is sent to the Copper Cliff mill for separation into copper concentrate, nickel concentrate, and pyrrhotite concentrate. The copper concentrate is subjected to oxygen flash smelting described for copper extraction. The pyrrhotite concentrate, which is essentially iron sulphide with about 0.8 per cent Ni, is roasted in order to yield iron oxide, from which nickel is recovered by leaching. Subsequently, iron ore pellets are produced from the leached iron oxide. The nickel concentrate containing about 10 per cent Ni, 2 per cent Cu, 40 per cent Fe, and 30 per cent S is sent to a smelter for nickel extraction.

**Smelting of nickel concentrate**

As in the case of copper, nickel, too, has to be separated from the iron present in the sulphide concentrate. In the conventional process, this is done in both the smelting and converting stages. To aid iron rejection in the smelting stage, the concentrate is first partially roasted to selectively oxidize the iron sulphide. This is done either in a multiple hearth roaster or in a fluid bed roaster. The latter is preferred because of its high throughput and the rich  $\text{SO}_2$  gas stream it generates. During partial roasting in the temperature range 550–600°C, about 40 per cent of the sulphur is oxidized and enough heat is generated to make the roasting in the fluid bed autogenous.

The roasted calcine, which also contains the desired amount of siliceous flux, is smelted in a reverberatory furnace to produce a matte containing the Cu and Ni values and a slag containing the gangue and oxidized iron. The matte typically contains 20 per cent Ni, 7 per cent Cu, 40 per

cent Fe, and 27 per cent S. The converter slags from both the nickel and copper converters are returned to the reverberatory furnace. Hence, there is a copper pick-up in the circuit. The discarded slag from the reverberatory furnace typically analyzes 0.3–0.4 per cent Ni, 0.2 per cent Cu, 39 per cent Fe, and 35 per cent SiO<sub>2</sub>.

The furnace matte is converted in a Pierce-Smith converter to produce nickel-enriched matte with 50 per cent Ni, 25 per cent Cu, 0.7 per cent Fe, and 21.5 per cent S. The converting is completed at about 1150°C to produce matte with the aforementioned desired sulphur content. The slag, containing about 2 per cent Ni, 1.5 per cent Cu, 40 per cent Fe, and 25 per cent SiO<sub>2</sub>, is returned to the reverberatory furnace for the recovery of nickel and copper.

The converted matte is subjected to a slow cooling process wherein the matte is cooled from its melting point to about 400°C in a period of 3 days. During slow cooling, first Cu<sub>2</sub>S precipitates and grows. At 700°C, a second phase, namely, a metallic nickel-copper alloy phase, starts to precipitate. At 575°C, the third solid phase, Ni<sub>3</sub>S<sub>2</sub>, starts to precipitate. The slow cooling rate provides the necessary grain growth so that in subsequent processing the sulphides can be recovered by froth flotation.

The slow-cooled matte is subjected to grinding and flotation. Here diphenyl guanidine (DPG) is used both as a collector and a frother rather than xanthate because the former has been found to be more effective. Prior to flotation, the nickel-copper alloy, which contains over 95 per cent of the precious metals, is isolated by magnetic separation and sent for the recovery of precious metals. The copper sulphide concentrate produced by flotation contains about 70 per cent Cu, 5 per cent Ni, and 20 per cent S and is sent to the copper circuit. The nickel sulphide is recovered as a low copper-nickel sulphide with 74 per cent Ni, 0.8 per cent Cu, 0.8 per cent Fe, and 22 per cent S and as a high copper-nickel sulphide with 72 per cent Ni, 3–4 per cent Cu, 0.8 per cent Fe, and 21 per cent S. Both the nickel sulphide fractions are roasted after pelletization in fluid bed roasters in the temperature range 1100–1250°C to produce granular nickel oxide. The low copper-nickel oxide is marketed directly as nickel oxide under the brand name Sinter 75 or reduced to metal and sold as Utility nickel. The high copper-nickel oxide is sent to the refineries. Half of it is refined by the carbonyl process and the other half by electrolytic refining.

#### Carbonyl process for refining nickel

In 1889, Carl Langer and Ludwig Mond discovered a novel process for refining nickel. They found that carbon monoxide combined with metallic nickel in the temperature range 40–90°C to form gaseous nickel carbonyl [Ni(CO)<sub>4</sub>]. At higher temperatures, i.e., between 150 and 300°C, the nickel carbonyl decomposes to give pure nickel and carbon monoxide. The reactions are



Iron, too, forms a volatile carbonyl [Fe(CO)<sub>5</sub>], but the rate of reaction is slow. Cobalt forms a tetracarbonyl [Co<sub>2</sub>(CO)<sub>8</sub>] and a tricarbonyl [Co<sub>4</sub>(CO)<sub>12</sub>], but their volatility is low. Since copper and a majority of the other elements do not form carbonyls, the carbonyl process is a very selective one and can be advantageously used for nickel refining.

In the INCO atmospheric carbonylation process, the oxide is first reduced by circulating hydrogen at about 400°C, and the active nickel thus formed is subjected to carbonylation at

about 50°C. The nickel carbonyl produced is decomposed at about 230°C in either pellet decomposers to produce nickel pellets of about 1 cm diameter or in powder decomposers to produce powder with a mean particle size of about 3.5 μm.

In a newer process, i.e., the INCO pressure carbonylation process, an elevated pressure of about 70 atm is employed. As the carbonylation reaction has a 4 to 1 volume charge, a higher pressure aids the reaction and permits higher operating temperatures. In the commercial process, a temperature of 180°C and a pressure of 70 atm are used. Under these conditions, carbonyls of iron, nickel, and cobalt are formed. Nickel carbonyl is recovered by fractional distillation and later converted to metallic nickel in a pellet decomposer or a powder decomposer.

#### Electrolytic refining of nickel

The nickel oxide, as shown in Fig. 7.32, is reduction smelted with coke in a fuel-fired furnace or in an electric furnace and then cast into nickel metal anodes. These anodes are electrolytically refined in a bath containing 60 gm/litre Ni<sup>2+</sup>, 95 gm/litre SO<sub>4</sub><sup>2-</sup>, 35 gm/litre Na<sup>+</sup>, 55 gm/litre Cl<sup>-</sup>, and 16 gm/litre H<sub>3</sub>BO<sub>3</sub>. The electrolysis is carried out at 60°C at a current density of 170 A/m<sup>2</sup>. The electrolyte is purified as follows. Copper is removed by cementation with active nickel powder; iron and the other impurities are removed by the aeration of the electrolyte and the addition of small amounts of chlorine to ensure oxidation to form an iron hydroxide precipitate. Cobalt is removed as cobaltic hydroxide by further chlorine oxidation. At this cobalt removal stage, further removal of impurities such as As and Pb takes place. The purified electrolyte contains about 0.01 gm/litre Co, 0.001 gm/litre Cu, 0.001 gm/litre Fe, 0.0002 gm/litre As, and 0.0002 gm/litre Pb. The electrolyzed nickel analyzes about 99.93 per cent Ni, 0.05 per cent Co, 0.005 per cent Cu, 0.002 per cent Fe, 0.001 per cent S, 0.0002 per cent As, and 0.001 per cent Pb.

INCO has also established a process for directly electrorefining nickel sulphide to metallic nickel. Here, instead of resorting to roasting and reduction smelting to produce nickel anodes, the nickel sulphide is melted and cast as anodes. The anodes contain 76 per cent Ni, 0.5 per cent Co, 2.6 per cent Cu, and 20 per cent S. These are electrolyzed at a current density of 200 A/m<sup>2</sup> in an electrolyte similar to that used for nickel anode refining. The procedure for the purification of the electrolyte is also similar. The main difference is that the anode is enclosed in a bag in order to collect the luminous anode slime that is produced. This slime contains 95 per cent sulphur and is processed to recover elemental sulphur and precious metals. The electronickel finally obtained contains 99.95 per cent Ni.

#### 7.22 EXTRATION OF NICKEL FROM OXIDE ORES

As pointed out in Section 7.20, the reserves of nickel as oxide ores greatly exceed those as sulphide ores. Also, the extraction of nickel from oxide ores is likely to become important in the future.

The oxide ores of nickel are referred to as *nickeliferous laterites*. The laterite ore body is formed by a process of weathering and occurs mainly in the tropical regions. A typical laterite ore body contains a higher iron overburden containing less than 1 per cent Ni and 40 per cent to 50 per cent Fe. Below the overburden lies a limonitic ore which contains 1 per cent to 1.5 per cent Ni with 40 per cent to 45 per cent Fe. The limonite is essentially a goethite [(FeNi)O(OH)<sub>n</sub>H<sub>2</sub>O] which has nickel in solid solution with iron oxide. The layers below the limonite contain nickeliferous silicates which are essentially serpentines [Mg<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>] in which MgO has been substituted in varying degrees by nickel, iron, and cobalt. The serpentinitic ores, or saprolitic

ores, as they are sometimes called, contain 1.5 per cent to 4 per cent Ni with 10 per cent to 15 per cent Fe. Below these layers is rock containing less than 1 per cent Ni and 10 per cent to 15 per cent Fe.

In India, limonitic ore containing 0.8 per cent to 1.2 per cent Ni and 40 per cent to 50 per cent Fe has been discovered in Sukinda (Orissa), and a plant to produce 4000 tons of nickel per year utilizing this ore has been envisaged. It may be noted that the serpentinitic ore zone is absent in this ore body.

In the limonitic ore and the serpentinitic ore, nickel is present in the form of a solid solution. Hence, physical upgrading methods are not applicable. The only method which has been employed is tumbling followed by screening. This method separates the more friable serpentine from the harder base rock. Therefore, in laterite ore processing, the feed to the extraction plant is low grade with 1 per cent to 3 per cent Ni compared with the 8 per cent to 15 per cent Ni in sulphide concentrates fed to the sulphide ore processing plants. In addition, when processing sulphide concentrates, the heat generated by sulphide oxidation can be used advantageously, whereas no such internal fuel is available in the case of laterite ores. Further, the laterites contain a large amount of free and combined water, and the removal of this water requires a lot of energy. Therefore, the recovery of nickel from oxide ores requires two to six times the energy needed for the recovery of nickel from sulphide concentrates.

The lateritic ores can be processed by the following methods to recover the nickel values:

- (1) pyrometallurgical processing,
- (2) pyrometallurgical processing followed by hydrometallurgical processing,
- (3) pyrometallurgical processing followed by carbonylation, and
- (4) hydrometallurgical processing.

#### PYROMETALLURGICAL PROCESSING

Pyrometallurgical processing consists of drying the ore to eliminate free moisture, heating the ore to a temperature of 800°C to 1000°C in an oxidizing or a reducing atmosphere to drive off combined water which is released above 500°C (and to selectively reduce the ore when a reducing atmosphere is used), and smelting the ore to recover a metal/matte phase containing over 90 per cent of the nickel and a slag containing the unwanted oxides. Pyrometallurgical processing is applicable in the case of ores with less than 25 per cent Fe.

Over 75 per cent of the nickel produced from the oxide ores of nickel is currently being extracted by total pyrometallurgical processing which is ideal because the more economical high-grade ore bodies have a low iron content. However, in the future, the lower-grade high iron ore bodies are likely to be important sources of nickel and methods (2)-(4) just mentioned are likely to attract more attention.

#### DTA (Differential Thermal Analysis) of Lateritic Ores

Differential thermal analysis, when carried out on lateritic ores, gives a good indication of the expected behaviour of the ore during pyrometallurgical processing. Such an analysis carried out on an ore containing 1.7 per cent Ni and 25 per cent Fe is shown in Fig. 7.33. The small endothermic peak *W* below 100°C is due to the evolution of a small amount of water from an already dried sample. The as mined ore contains up to 40 per cent moisture, and a large amount of heat is needed to dry it. The second endothermic peak *G* at about 230°C is due to goethite decomposition according to the reaction

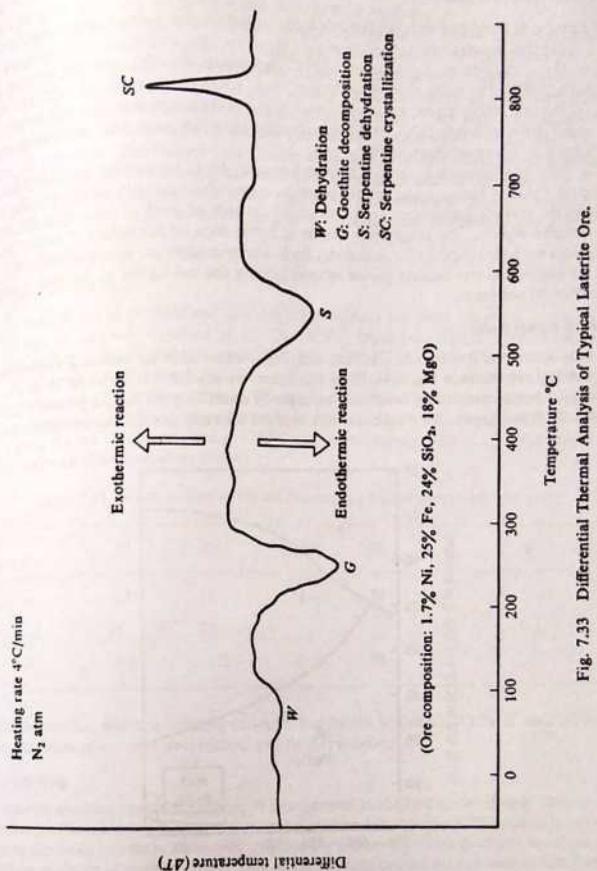
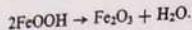


Fig. 7.33 Differential Thermal Analysis of Typical Laterite Ore.



The nickel oxide associated with the goethite is liberated from the goethite lattice and becomes active above this temperature. (7.47)

The third endotherm  $S$  at about 530°C represents the dehydration of serpentine [ $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_2$ ]. The oxide in the serpentine becomes active above 600°C. The next exothermic peak  $SC$  (around 800°C) represents the recrystallization of the magnesium silicate (liberated from serpentine) into olivine ( $\text{Mg}_2\text{SiO}_4$ ). At this temperature, the nickel oxide gets locked up in olivine, and is not easy to reduce above 800°C.

The DTA of a limonitic ore with a high iron content (40–45 per cent Fe) would not have the serpentine peaks, whereas a serpentinic ore with a low iron content (8–10 per cent Fe) would not have the goethite dehydration peak because of the lack of goethite mineral in the ore. In some laterite deposits, the magnesium silicate is in the form of talc instead of serpentine and, hence, does not have the peaks for serpentine. Such laterite deposits are generally easier to reduce than the serpentinic ores because olivine recrystallization and locking up of the nickel oxide in the olivine do not occur.

#### Selective Nickel Reduction

The stability regions for Ni,  $\text{NiO}$ , Fe,  $\text{FeO}$ , and  $\text{Fe}_3\text{O}_4$  under different reducing conditions and temperatures are shown in Fig. 7.34. From this figure, we observe that it should be theoretically possible to reduce nickel and keep iron as oxide by controlling the oxygen potential ( $\text{CO}/\text{CO}_2$  ratio) in the reducing gas. This simple analysis does not take into account the interaction between

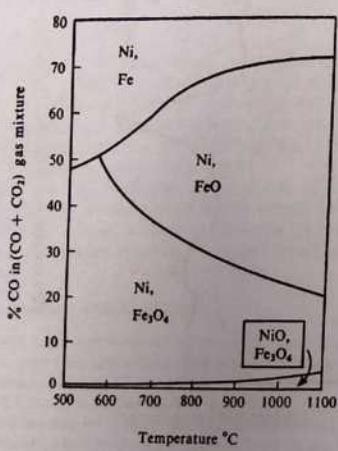


Fig. 7.34 Thermodynamics of Reduction of Lateritic Ores.

metallic Ni and Fe and between  $\text{NiO}$  and the iron oxides. It, however, provides a practical basis for selecting the operating temperature and the reduction potential.

In practice, reducing conditions can be produced by the partial combustion of hydrocarbon fuel which results in a mixture of  $\text{H}_2$ , CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . By controlling the combustion to yield a desired  $\text{CO}/\text{CO}_2$  ratio (or  $\text{H}_2/\text{H}_2\text{O}$  ratio), the targeted oxygen potential can be achieved. As  $\text{H}_2$  and CO are consumed during reduction, the reducing gas should have an adequate number of moles of the reductant. These requirements are generally met by employing a reducing gas with a  $\text{CO}/\text{CO}_2$  ratio of 0.4 to 0.5 before reduction and a  $\text{CO}/\text{CO}_2$  ratio of about 0.2 after the completion of reduction. This implies that metallic nickel and magnetite would be the predominant phases. In reality, the metallic phase contains 30–50 per cent Ni and 50–70 per cent Fe and the oxide phase always contains FeO in addition to  $\text{Fe}_3\text{O}_4$ . The amount of reduction varies between 80 per cent and 95 per cent of nickel, depending on reduction time and the reducing conditions.

#### Reduction Smelting

**Ferronickel production**  
The hot reduced ore or calcined ore, to which the reductant has been added, is smelted in the normal way in an electric furnace at 1550 to 1650°C. During smelting, the reduced nickel and iron melt to form a ferronickel bath with 25–40 per cent Ni. The gangue silicates form a molten slag. The ferronickel is tapped from the furnace and is sent for further refining in order to oxidize phosphorus and remove sulphur. The slag is discarded. The typical compositions of ore, slag, and ferronickel produced by Le Nickel in its New Caledonia plant are shown in Table 7.11. In this case, the ore is only calcined at 1000°C and not selectively reduced. (All the reduction is carried out in an electric smelting furnace.)

Table 7.11 Composition of Nickel Stream (Le Nickel operation) (per cent)

	Ni	Fe	MgO	SiO <sub>2</sub>	C	S	P
Ore	2.8	13	24	37			
Ferronickel	24	72			2	0.3	0.03
Slag	0.2	5.5	38	53			

The ferronickel, which is normally desulphurized by the addition of  $\text{CaC}_2$ , is used directly in the manufacture of stainless steel without any further refining.

#### Matte smelting

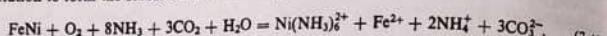
In the matte smelting operation, sulphur is incorporated in the feed to the electric furnace. This operation produces a matte instead of ferronickel in the electric furnace. This matte is later converted to eliminate iron as in the case of sulphide ore processing which produces converter matte essentially made up of nickel sulphide. This nickel sulphide can be roasted and reduced to produce metallic nickel. This practice is followed by INCO in its operations at Guatemala and Indonesia.

**PYROMETALLURGICAL PROCESSING FOLLOWED BY HYDROMETALLURGY**

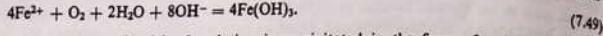
An ore with a high iron content cannot be readily treated by total pyrometallurgy because in the smelting stage the grade of ferronickel/matte produced is low and the high iron content of the slag renders it very highly corrosive towards refractories at smelting temperatures of 1500°C and above. For such an ore, an alternative processing method has to be resorted to. One of the alternative methods involves the leaching of metallic nickel after selective reduction and the subsequent recovery of nickel from the solution.

**Ammoniacal Leaching**

The advantage of using an ammoniacal solution for leaching was first demonstrated by H. Caron (1950). In this process, nickel combines with ammonia in an ammonia-ammonium carbonate solution to form the stable hexammine complex. The reaction is



The  $\text{Fe}^{2+}$  formed is further oxidized and precipitated over ore particles according to the reaction



The nickel in ammoniacal leach solution is precipitated in the form of a basic carbonate  $[\text{Ni}(\text{OH})_2 \cdot 2\text{NiCO}_3]$ . On calcination at 700–800°C, the carbonate decomposes to nickel oxide which can be reduced to yield the metal.

Caron's process was first adopted at Nicaro (Cuba) in 1944. This process is suitable for medium- and high-iron laterites including those found in India.

**Other Leachants**

Although laboratory- and pilot plant-tested processes have been reported for leaching selectively reduced nickel ores with dilute  $\text{H}_2\text{SO}_4$ , dilute  $\text{HNO}_3$ , and dilute  $\text{HCl}$ , these processes have not been adopted on a commercial scale. These leachants dissolve nickel, and some of them even attack the unreduced iron oxides present in large quantities in the ore. The leach solutions contain nickel and iron, and the simple iron-nickel separation that is carried out in ammoniacal solutions by iron oxidation is not feasible and, therefore, elaborate processing is required. These leachants may find application in places where they are readily available and in newer plants in which the authorities have restricted the discharge of  $\text{NH}_3$ -containing streams into the water sources.

**PYROMETALLURGICAL PROCESSING FOLLOWED BY CARBONYLATION**

INCO has developed (see Canterford, 1975) a process for the carbonylation of nickel contained in reduced laterite at CO pressures of 1–10 atm. The carbonylation reaction, as discussed in Chapter 5, is favoured by higher pressures. For carbonylation to occur, the reduced metal surfaces must be active. It has been reported that a reduction temperature of less than 750°C is ideal for the subsequent carbonylation of nickel. During reduction, 0.1–1 per cent sulphur is introduced into the feed. This sulphur aids reduction as well as nickel carbonylation. Carbonylation is carried out at 65°C. Nickel carbonyl and any iron carbonyl that is formed are subsequently separated by fractional distillation. Nickel carbonyl is then decomposed by heating to 230°C to produce either nickel pellets or nickel powder. Similarly, iron carbonyl is decomposed

to give iron powder as a byproduct. The CO formed during the carbonyl decomposition is recycled to the carbonylation step.

The carbonyl process acts both as an extraction as well as a refining process. The nickel carbonyl, except for iron contamination, is free of impurities and the purest grade of nickel can be produced from it. Although this process is very attractive, only INCO has the technology to handle carbonyls (which are extremely poisonous). After INCO's plans to set up a plant in New Caledonia were disallowed by the French Government, no further steps have been taken to employ the carbonyl process on a commercial scale.

**HYDROMETALLURGY**

Although a number of hydrometallurgical processes have been studied, the process that is used in commercial practice—and is receiving ever-increasing attention—is the high-pressure sulphuric acid leaching process. This process is suited for high-iron (> 40 per cent) ores with a low serpentine content. Serpentines consume a large amount of acid; therefore, for high-serpentine ores, this process is not attractive.

The foregoing process is in commercial use at a plant in Moa Bay (Cuba). In this plant, the limonitic ore is first screened to remove rock and serpentine and then subjected to sulphuric acid leaching at 250°C. In order to maintain water in a liquid state, a pressure of about 40 atm is applied. The nickel dissolution taking place during leaching is according to the reaction



A typical analysis of the ore and leach products in the Moa Bay operation is given in Table 7.12.

Table 7.12 Composition of Nickel Streams (Moa Bay operation)

Substance	Ore (per cent)	Leach residue (per cent)	Leach solution (gm equivalent)	Extraction (per cent)
Ni	1.35	0.06	5.95	96.0
Co	0.146	0.008	0.64	95.0
Fe	47.50	51.00	0.80	0.4
$\text{SiO}_2$	3.70	3.50	2.00	12.0
MgO	1.70	0.70	2.00	60.0
$\text{SO}_4^{2-}$		8.1	6.7	

As is evident from Table 7.12, the limonitic ore contains an appreciable amount of cobalt which can also be extracted. The metals in the leach solution are precipitated in the form of sulphides by precipitation with  $\text{H}_2\text{S}$  at 120°C and 10 atm. The reaction taking place is

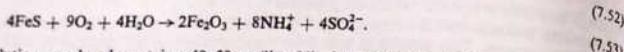
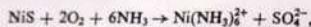


This reaction produces a sulphide precipitate with (wt %) 55 Ni, 5.9 Co, 1.7 Zn, 0.3 Fe, and

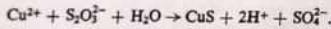
36 S. This precipitate has to be dissolved and the solution refined to produce refined nickel and cobalt. This sulphide precipitate can be dissolved by high-pressure ammonia leaching and the resultant solution can be purified as in the Sherit-Gordon process described in the next section.

### 7.23 HYDROMETALLURGY OF NICKEL SULPHIDE CONCENTRATES

Sherit-Gordon in Canada was the first to employ hydrometallurgical processing for nickel sulphide concentrates. The concentrate is leached with a strong ammonia solution in an autoclave at 80°C and 7–10 atm. The reactions can be represented as



The solution produced contains 40–50 gm/litre Ni, 1 gm/litre Co, 5–10 gm/litre Cu, 120–180 gm/litre  $(\text{NH}_4)_2\text{SO}_4$ , and 90 gm/litre  $\text{NH}_3$ . The copper is removed by thiosulphate addition which precipitates  $\text{CuS}$  according to the reaction



The copper-free solution is heated to 200°C and reduced in another autoclave with hydrogen at 32 atm. (For details, see Chapter 4.)

### 7.24 OTHER METALS FROM SULPHIDE ORES

Besides the metals discussed, a large number of other metals are also obtained from sulphide ores. We now briefly describe the extraction of some of these metals.

#### COBALT

About three-fourths of the cobalt produced all over the world is used for metallurgical purposes (alloying) and one-fourth as oxides and other compounds in the ceramic and paint industries. Steels containing Co, Cr or Co, Cr, and W are used in the manufacture of cutting tools and dies. Often, the entire article is not made of the alloy, but only the surface is coated by a special process of hard facing. The alloys are also used for making surgical instruments, because of their inertness towards the human system. Co-Cr-Mo alloys are used in turbine blades because they possess extraordinary strength properties and, at high temperatures, offer excellent resistance to corrosion.

The mixed copper-cobalt ores of Zaire and Zambia form the largest source of cobalt. These ores occur both in the oxide and sulphide forms. The copper oxide ore which contains 5–6 per cent Cu and 0.2–0.3 per cent Co is concentrated by flotation with palm oil,  $\text{Na}_3\text{CO}_3$ , and sodium silicate to yield a concentrate with 26–27 per cent Cu and 1 per cent Co at a Co recovery of 82–85 per cent. The oxide ores with 3.5 per cent Cu and 1.7 per cent Co are also concentrated by flotation to yield a concentrate with 10.4 per cent Cu and 7.9 per cent Co. The mixed sulphide-oxide ores contain 4–5 per cent Cu and 0.2–0.3 per cent Co. These ores are also concentrated by flotation with an alkaline sulphate. In this case, a sulphide concentrate with 46 per cent Cu and 0.4–2.5 per cent Co and an oxide concentrate with 20 per cent Cu and 1.7 per cent Co is produced. The leach-electrowinning circuit adopted to extract copper and cobalt from their oxide concentrates is shown in Fig. 7.35. The cobalt is essentially leached in an acid solution, precipitated

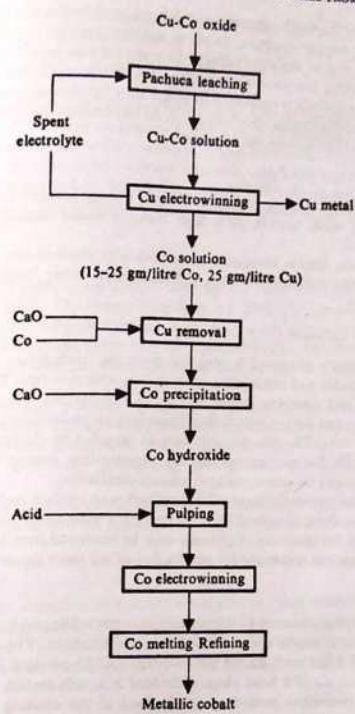


Fig. 7.35 Extraction of Cobalt from Cu-Co Oxide Concentrate.

after Cu removal, and the cobalt hydroxide fed to electrolytic cells to electrowin metallic cobalt. The sulphide concentrates are first roasted in a fluid bed roaster at 675°C to produce soluble sulphates. Next, the sulphate calcine is leached with acid and the solute subjected to a process similar to that described for oxide concentrate leaching.

The sulphide and oxide nickel ores account for the second-largest source of cobalt. During the electrolytic refining of nickel, cobalt is precipitated as cobaltic hydroxide, which is subjected to leaching and then electrowinning in order to produce metallic cobalt.

Cobalt is also present in small amounts (0.1–0.2 per cent) in the slag discarded from nickel smelters and from some copper smelters. In these smelters, the converter slags are enriched in cobalt (0.4–1.0 per cent) and in some operations, these slags are reduced in an electric furnace to produce an alloy containing 3–5 per cent Co with nickel, iron, copper, and sulphur constituting the remainder of the alloy. Cobalt is recovered from the alloy by conventional hydrometallurgical processing. During hydrometallurgical processing, solvent extraction, electrowinning, and hydrogen reduction steps are used. (For details, see Chapter 4.)

#### CADMUM

Cadmium is mainly used in the manufacture of alkali storage batteries and for decorative and anticorrosive plating on other metals. It is also used, in minor amounts, for making anti-friction alloys.

Cadmium minerals are almost invariably associated with those of zinc and lead. During the differential flotation of zinc and lead fractions, cadmium enters either fraction and is, therefore, recovered as a byproduct.

#### Production of Byproduct Cadmium

Much of cadmium currently produced is obtained from the leach liquor produced during the leaching of zinc concentrates and subsequent precipitation with zinc dust. The precipitate obtained is generally impure and contains metals such as Zn, Cu, and Pb. The common practice is to redissolve the precipitate and then remove these impurities by precipitation. Finally, cadmium is reprecipitated with zinc dust. The zinc impurity may be removed by distillation.

In the retort processes for zinc extraction, the vapours that emerge first are often rich in cadmium, and the metal can be recovered by fractional distillation.

All the flue dust in the pyrometallurgy of zinc or lead may contain cadmium. It is advantageous to recycle this dust through a lead blast furnace or a zinc sinter plant until cadmium is sufficiently concentrated for recovery. Cadmium may be recovered from the dust by dissolution and electrolysis after chemical treatment for purification of the leach liquor.

#### ANTIMONY

Antimony is used in varying amounts (2–15 per cent) in alloys (for cast types) to strengthen and harden the alloys and to decrease contraction during solidification. The metal is also used in bearing metals (around 5 per cent Sn, 10 per cent Sb, and 85 per cent Pb). These metals are characterized by the presence of a hard phase embedded in a soft matrix so that the antimony alloy bearings adjust themselves according to the load of the rotating shaft resting on these bearings. The 4–12 per cent Sb, used in lead battery plates for hardening, constitutes the largest consumption of the metal. Antimony is also used in alloy lead when the latter is used as sheets and pipes and in various components for use in chemical industries.

#### Extraction of Antimony

At the outset, antimony ores are upgraded by gravity and flotation techniques. The concentrate containing the sulphide is roasted at 450°C in a controlled atmosphere to yield  $Sb_2O_3$ . The oxide is volatile and, therefore, easy to separate from the gangue. (During roasting, it is necessary to avoid the formation of the higher oxide  $Sb_2O_4$ , which is nonvolatile.) The  $Sb_2O_3$  obtained is reduced by charcoal in the presence of a suitable flux, for example,  $Na_2CO_3$ . Concentrates of a

very high grade may be directly reduced by iron to metallic antimony, the resulting FeS forming a matte with other sulphides. The reaction is



Ordinarily, a clean separation of matte and slag is difficult to achieve because of the small difference in their densities. The separation is, however, facilitated by the addition of fluxes such as common salt, soda ash, and sodium sulphate, which dissolve in the matte and lower its density.

The metallic phase may contain up to 10 per cent iron, which can be removed through liquation. Crude antimony is purified by fire refining. Copper and iron are removed by sulphur addition and arsenic by drossing. The dissolved oxygen is finally removed by poling, as in the case of deoxidation of copper.

#### BISMUTH

Bismuth is extensively used, in association with Sn, Cd, and Pb, in the manufacture of alloys with a low melting point. The ternary eutectic in the Bi-Sn-Pb system (52.5 : 15.5 : 32) melts at only 96°C. However, the addition of cadmium produces a quaternary eutectic which melts at 70°C. Alloys with even lower melting points may be produced by the addition of Ga and In. These so-called fusible alloys are used in automatic safety devices for fire alarms, heating equipment, and solders.

Bismuth has the unusual property of expanding on cooling; the volume increases by 3.3 per cent during solidification. Consequently, the addition of bismuth to tin and lead improves their casting properties. Master patterns in foundry work are produced from an alloy containing 57 per cent Bi and 43 per cent Sn (melting point 124°C) which has a zero coefficient of contraction.

Bismuth also finds miscellaneous applications in the ceramic and pharmaceutical industries. Powdered bismuth with or without powdered lead is impregnated into rubber to produce X-ray-proof goods.

#### Extraction of Bismuth

The procedures for the extraction of bismuth are similar to those adopted for antimony. A rich sulphide ore may be upgraded by liquation. Impurities such as arsenic and antimony are removed by volatilizing roasting. The sulphide ore is oxidized and finally reduced by charcoal reduction. Iron may also be used for the direct reduction of the sulphide. The crude metal is refined by either fire refining or electrorefining.

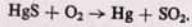
#### MERCURY

The present world production of mercury is about 10,000 tons per year, of which the major amount comes from Spain and Italy. A metal known from ancient times (as quicksilver), mercury finds more than 3000 end uses today. It is chiefly used in the manufacture of drugs, chemicals, insecticides, and explosive compounds in detonators. As a metal, it is used in a wide range of scientific instruments such as vapour lamps, arc rectifiers, and electrolytic cells. It is also used as a coolant in fast plutonium fuel reactors.

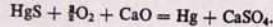
#### Extraction of Mercury

The chief mineral of mercury is cinnabar ( $HgS$ ). Since the mineral is generally associated with a

high quantity of gangue, the ores contain less than 1 per cent mercury. The usual practice is to directly charge the ore into a furnace without any concentration. Calcination at about 600°C decomposes the sulphide and volatilizes mercury. The reaction is



Sometimes, when SO<sub>2</sub> recovery poses problems, the sulphur may be absorbed in lime. The reaction is



The metal vapours are cooled in water-cooled condensers. The crude metal thus obtained can be refined by repeated distillation.

#### MOLYBDENUM

The use of molybdenum as ferromolybdenum has been discussed in Chapter 6. Molybdenum occurs mainly as molybdenite (MoS<sub>2</sub>) in disseminated porphyry deposits. They are characterized by their low grade and large volume. In these deposits, the molybdenum content varies from 0.1 per cent to 0.5 per cent, and the ore is associated with pyrite and small amounts of tungsten, tin, topaz, and uranium (brannerite). Molybdenite also occurs in some copper porphyry deposits, but its content is low at 0.005 per cent to 0.1 per cent. Nevertheless, the copper porphyry deposits presently account for over 40 per cent of the world's molybdenum production.

In the extraction process, the molybdenite in the ore is concentrated by flotation, because it possesses excellent flotation characteristics. A comparison of the contact angle measurements of common sulphide minerals given in Table 7.13 shows that MoS<sub>2</sub> has a higher flotation capability than other common sulphide minerals.

Table 7.13 Contact Angle for Some Sulphide Minerals

Mineral	Contact angle
Molybdenite	145°
Pyrite	135°
Chalcopyrite	131°
Galena	90°

Because of the excellent floatability of molybdenite, it is possible to float it with hydrocarbon addition, and the addition of xanthate or thiophosphate is not necessary.

From molybdenum porphyry ores, over 90 per cent of the molybdenum can be recovered by comminution and flotation in a concentrate containing over 90 per cent MoS<sub>2</sub>. From the copper porphyry ores, the recovery of MoS<sub>2</sub> is lower, i.e., 30–60 per cent due to the lower MoS<sub>2</sub> content in the ore. Figure 7.36 gives the general flowsheet followed for the extraction of molybdenite

from copper porphyry ores. In the first stage, both copper and molybdenum are recovered by flotation with reagents such as xanthate. In the next stage, the xanthate is eliminated by oxidation

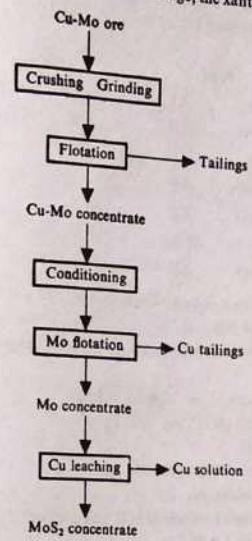


Fig. 7.36 Recovery of Molybdenite from Copper Porphyry Ores.

to render copper nonfloatable, and molybdenum is floated with hydrocarbon addition. Copper is further eliminated from the MoS<sub>2</sub> concentrate by leaching with ferric chloride.

#### Molybdenite Roasting

The MoS<sub>2</sub> concentrate is roasted to MoO<sub>3</sub> to provide the raw material for molybdenum and ferromolybdenum production. Although the roasting of MoS<sub>2</sub> to MoO<sub>3</sub> is chemically simple, it requires a good temperature control. This is because at temperatures below 600°C, the kinetics of roasting is poor and at temperatures above 650°C the calcine starts to sinter, leading to molybdenum loss due to volatilization of the oxide. The desired temperature control is achieved by employing a Nichols-Herreshoff multiple hearth roaster. The desired sulphur content in the oxide product, i.e., 0.1–0.5 per cent, is achieved in commercial practice by good temperature control.

Molybdenum metal is ultimately produced by the hydrogen reduction of MoO<sub>3</sub>, in the form of briquettes, at 1000°C. The metallized briquettes are then pressed into consumable electrodes for melting into molybdenum ingots.

## PROBLEMS

1. A mixture of ores is roasted in a multiple hearth furnace, the roasting being effected by the heat of oxidation. The following data are given:

(a) Percentage analyses

	<i>Feed</i>	<i>Calcine</i>	
Cu	7.1	Cu	7.8
SiO <sub>2</sub>	21.4	S	12.0
Fe	34.5		
Al <sub>2</sub> O <sub>3</sub>	4.6		
CaO	4.4		
S	25.7		
H <sub>2</sub> O	2.3		

(b) Copper is present in the calcine as Cu<sub>2</sub>S, iron as FeS and Fe<sub>2</sub>O<sub>3</sub>.

(c) Sulphur burns to yield SO<sub>2</sub>.

(d) The flue gases from the furnace contain 11 per cent oxygen (dry basis).

Calculate:

- (i) Weight of calcines produced per 1000 kg of feed.
- (ii) Air used in cubic metres (NTP) per 1000 kg of feed.
- (iii) Percentage of excess air.
- (iv) Volume of the flue gases (NTP) per 1000 kg of feed.
- (v) Percentage sulphur elimination.

[Hint 1 gm mole of gas occupies 22.4 litres at NTP; air contains 21 per cent oxygen by volume; atomic weights O 16, S 32, Fe 56, Cu 64.]

2. With the help of the phase diagrams for the Cu-Cu<sub>2</sub>S and Cu-Cu<sub>2</sub>O systems, explain why it is not possible to use a bottom-blown converter to produce blister copper from matte.

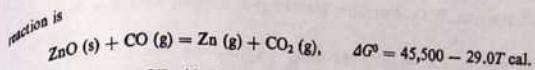
3. Discuss whether lead can be produced by direct smelting of lead sulphide concentrates with air and/or oxygen.

4. What are the harmful impurities in electrical grade copper and how are they eliminated during copper electrorefining?

5. Describe the carbonyl process for nickel refining. Are higher pressures and temperatures beneficial in the carbonyl process?

6. Outline a procedure for the differential flotation of a copper-zinc sulphide ore containing pyrite, sphalerite, and copper sulphides. Give reasons for your choice of collectors, depressants, and activators.

7. The gas leaving the top of the charge of a zinc blast furnace at 1000°C and 1 atm has a CO/CO<sub>2</sub> ratio of 2.4 and contains 60 vol per cent N<sub>2</sub>. If it is in equilibrium with solid zinc oxide, calculate the vol per cent of zinc in the gas. Assuming the CO/CO<sub>2</sub> ratio remains constant at 2.4, calculate the temperature at which liquid zinc would form on quenching the gas. The



The vapour pressure of liquid zinc is given by the relationship

$$\log p_{Zn}(\text{atm}) = -\frac{6850}{T} - 0.755 \log T + 11.24.$$

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## 8 Extraction of Metals from Halides

### 8.0 INTRODUCTION

As pointed out in Chapter 4, halogens, particularly chlorine, are playing an ever-increasing role in the extraction and refining of metals. This is attributed to the specific advantages gained by following the halide reduction route. In addition, the availability of bulk chlorine from chlor-alkali plants and the fact that advances in materials technology have minimized materials handling problem in corrosive atmospheres have led to the adoption of chloride reduction techniques for the extraction of the metals covered in this chapter.

This chapter is divided into two parts. The first part deals with the extraction of nuclear reactor metals, namely, uranium, plutonium, thorium, beryllium, and zirconium. All these metals occur as refractory mixed oxide minerals which cannot be treated by conventional beneficiation or smelting techniques. Consequently, the halide route is used both for the extraction and the refining to produce high-purity metals. The second part deals with the extraction of magnesium, alkali metals, alkaline earth metals, and titanium. These metals occur in nature usually as halides, complex oxides, and carbonates. The extraction of magnesium from the carbonates has already been described in Chapter 6. The affinity of these metals for oxygen and, in some instances, for carbon, dictates a halide reduction technique in order to obtain them in the pure state.

### PART I

#### 8.1 EXTRACTION OF NUCLEAR REACTOR METALS

In view of the present energy scarcity, nuclear energy is becoming increasingly important. In nuclear power generation, uranium, plutonium, and thorium act as fuels and beryllium and zirconium are used as a neutron moderator and a fuel cladding metal, respectively. Both sodium and potassium find roles as coolants in nuclear reactors and their extraction is described in Part II of this chapter.

As mentioned in Section 8.0, the nuclear reactor metals occur as refractory complex oxide minerals. Therefore, they are difficult to reduce, and carbon reduction results in carbide formation because of the high stability of the carbides of these metals.

The foregoing complex ores often necessitate elaborate processes for the breakdown and separation of metal values. Often the aim is to effect a considerable degree of purification of the ore and to finally produce a pure compound for conversion to metal. The preliminary treatment, which leads to the production of a pure compound, often involves hydrometallurgical processes and chemical engineering plants. These processes and plants are sometimes required to treat ores which may initially contain the metal in concentrations as low as 0.01 per cent.

It should be noted that some of these metals are relatively more abundant in the earth's crust than the common metals such as copper, zinc, and nickel. They are not so commonly used because of the absence of high-grade deposits, diverse problems encountered in their extraction

and conversion to usable form, and the consequent high cost of production.

Generally, the flowsheet for the production of nuclear reactor metals from the complex ores has the following main steps:

- (1) the initial physical and/or chemical beneficiation to produce a concentrate,
- (2) the purification of the concentrate for the production of a pure intermediate and for the recovery of valuable byproducts,
- (3) the reduction of the pure intermediate under controlled conditions for the production of the metal,
- (4) final refining and consolidation of the metal.

For some metals, special problems may be encountered during one or more of the foregoing steps. For example, it is extremely difficult to separate chemically similar metal pairs such as zirconium and hafnium. In such cases, techniques such as solvent extraction and ion exchange may have to be used.

The nuclear reactor metals are generally extremely reactive towards oxygen. Also, even a very low level of impurity pick-up may greatly affect their physical, chemical, and mechanical behaviour. It is, therefore, often profitable to follow a halide route for extraction in order to altogether avoid oxygen. For this purpose, the oxides are converted to halides through halogenation. Subsequently, the pure halides may be reduced to obtain the pure metal. The reduction may be achieved by either metallocermic reaction or fused salt electrolysis.

In recent years, many major national laboratories and universities in India have undertaken research and development programmes on nuclear reactor metals extraction. In India, the Bhabha Atomic Research Centre (BARC), Bombay, in particular, has played a pioneering role. The pilot plant operations successfully developed there have paved the way for the establishment of production units for high-purity magnesium (for zirconium production), zirconium, hafnium, thorium, uranium, and plutonium and, on a smaller scale for titanium, tantalum, niobium, and tungsten. The processes that have been developed/adopted in India for the extraction of nuclear reactor metals can be broadly classified as follows:

#### Physical Ore Beneficiation

Physical methods of ore beneficiation, such as those being employed for the beach sands of South India, exploit the characteristic differences in the size, shape, density, and electromagnetic and electrostatic properties of the minerals.

#### Chemical Ore Breakdown

Chemical methods of beneficiation make use of selective leaching of minerals by acids or alkalies and other methods which aid selective leaching.

#### Solvent Extraction

The principles of solvent extraction have been described in Chapter 5. At present, solvent extraction is used in the extraction of several metals, for example, Th, U, Pu, Zr, Nb, and Ta.

#### Ion Exchange

The ion-exchange technique (described in Chapter 5) is extensively utilized for the concentration and purification of lean uranium leach liquors.

#### Halogenation

Halogenation processes have been devised to prepare chlorides and fluorides which are reduced in an oxygen-free atmosphere to obtain ductile metals. For example, the large-scale production of titanium, zirconium, and uranium depends on halide intermediates.

#### Reduction of Halide Intermediates

Extensive know-how is now available on the metallocermic reduction and electrolytic production of several metals. The details of the indigenous techniques are discussed later in this chapter.

#### Consolidation, Vacuum Refining, and Ultra-Purification

To further improve the properties of the metals, additional refining operations may become necessary. The techniques for these operations are also discussed later in this chapter.

#### 8.2 BENEFICIATION OF COMPLEX ORES

It is not possible to suggest general methods for the beneficiation of complex ores. Nevertheless some isolated examples which emphasize the well-tested procedures and the diversity of problems are given in this section.

#### PHYSICAL METHODS

Physical methods include the electrical sorting of the ores based on electrostatic properties, electromagnetic separation, heavy-media separation, other gravity methods, and flotation. In the electronic sorting of uranium-bearing minerals, the radioactive properties of the minerals are made use of in order to reject waste below a prescribed grade. The magnetic separation of some uranium minerals is based on the fact that while these minerals may possess a medium magnetic susceptibility, the gangue containing ferruginous materials may be relatively more magnetic. When uranium minerals are liberated at coarse size, heavy-media separation may be successfully employed. Both sink-and-float type separators as well as the cyclone type of heavy-media separators have been employed.

Uranium does not occur as sulphide and, therefore, cannot be concentrated by the usual sulphide flotation process. Flotation, however, may be employed to float the associated sulphide minerals with a view to enriching the uranium fraction or to eliminating those nonmetallic minerals which are undesirable during leaching.

Thorium is produced mostly from monazite. In order to recover high-grade monazite from the minerals associated with it in the as mined ores in the form of sands, physical beneficiation is carried out. The processes adopted depend on the nature and extent of mineral association. For instance, in Malaysia, monazite is associated with cassiterite, in Florida (U.S.A.) with ilmenite and zircon, and in India and Brazil, mainly with ilmenite, zircon, rutile, silica, and sillimanite.

We may consider, as an illustration of the separation process, the practice adopted at the Indian Rare Earths Limited (IREL), for the processing of beach sands that are rich in several heavy minerals. The approximate composition is: ilmenite 60–75 per cent, garnet 5–7 per cent, zircon 5–6 per cent, rutile 2–4 per cent, monazite 0.5–5 per cent, silica and others 8–28 per cent. The beach sands are first sun-dried and passed through 26 mesh screens in order to remove oversized lime shells and trash. The screened material is next subjected to low-intensity magnetic separation which removes the highly magnetic constituent ilmenite. The tailings are then subjected to a high-intensity magnetic field for the recovery of weakly magnetic monazite. Further bene-

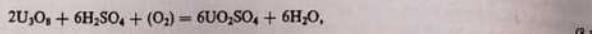
ficiation of the concentrate is carried out by electrostatic separators and air tables. In the Brazilian practice of treating ores with a smaller (10–15 per cent) extent of heavy minerals, the sands are first treated on Humphrey spirals to sort out the heavy minerals. Ilmenite and rutile are then removed on electrostatic separators and, finally, monazite is separated from zircon on high-intensity magnetic separators.

#### CHEMICAL METHODS OF BENEFICIATION

Purely physical methods can lead to only a limited extent of beneficiation because they are directly dependent on the degree of liberation of minerals in the ore body. Fine grinding, for example, would be helpful in the liberation of mineral fractions for better selectivity during magnetic or electrostatic separation. It is, however, obvious that there is always some associated gangue. On the other hand, the recovery can be poor if mineral values happen to be coated by gangue material. For a high recovery of metallic values, it becomes necessary to subject the ore to chemical treatment, for example, leaching and precipitation reactions.

#### Dilute Acid Leaching

Some complex ores are satisfactorily leached by dilute acids. The primary minerals of uranium include pitchblende and uraninite; the composition approximating  $U_3O_8$  or a mixture of oxides intermediate between  $U_3O_8$  and  $UO_2$ . These oxides are easily leached by dilute sulphuric acid, provided a suitable oxidant which can oxidize uranium to the hexavalent state is available. The oxidation of lower valence states of uranium is automatically achieved during the bacterial leaching of uranium ores. A typical reaction is



where the parentheses indicate bacterial leaching. However, as a result of other reactions, the leach liquor may also contain  $UO_2(SO_4)_2^{2-}$  and  $UO_2(SO_4)_4^{4-}$  ions.

Uranium ores may be leached, without the need for any oxidant, by dilute nitric acid. Nitric acid, however, is costlier. It also requires better corrosion-resistant plant equipment. Besides, the leach liquors may not be suitable for subsequent treatment.

Various leaching systems have been experimented with in order to minimize acid consumption (see Chapter 4). It is generally known that often better acid economy is achieved by using a constant pH leaching system. In this technique, the acid is added at a controlled rate, i.e., at a rate equal to the consumption rate so that the pH in the leaching system remains constant. It should be noted that if the entire amount of acid is added at the same time, then leaching takes a longer time and the acid consumption is also greater.

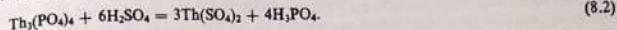
Some minerals of thorium, for example, thorite or thorium silicates, are also leached by dilute acids. For dilute acid leaching of thorium ores, nitric acid is generally preferred because the nitrate leach liquors are more suitable for subsequent purification treatment.

#### Concentrated Acid Leaching

Concentrated acids have to be resorted to when dilute acids fail to attack the ore. Concentrated acids, however, are likely to attack the gangue materials too, leading to acid wastage. Further, corrosion problems would be of a more serious nature. Leaching by concentrated acids, therefore, would be advisable only when the ores are of a high grade and when suitable plant equipment is available. Obviously, concentrated acids are usually employed only for those refractory ores which

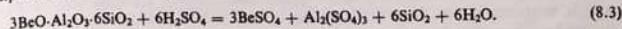
do not respond to less severe breakdown procedures.

A good example of concentrated acid leaching is the sulphuric acid leaching of monazite which is obtained as a virtually pure mineral after the physical beneficiation of beach sands. Monazite mainly consists of phosphates of rare earths and thorium. Acid leaching brings all the metals into solution for subsequent separation by precipitation reactions and solvent extraction. The reaction for thorium may be written as



The reactions for rare-earth phosphates are similar to reaction (8.2). Oxalic acid may be subsequently used to precipitate salts of thorium or rare earths. The sulphates can be obtained by adding hot concentrated sulphuric acid followed by evaporation or by crystallizing the double sulphates after the addition of sodium sulphate.

Another example of the use of concentrated acid treatment is the sulphuric acid leaching of beryl ( $3BeO \cdot Al_2O_3 \cdot 6SiO_2$ ). Beryl is heated to  $1700^\circ C$  and then quenched in water in order to separate some of the mineral constituents and to increase the reactivity for subsequent reaction with sulphuric acid. The leaching reaction is

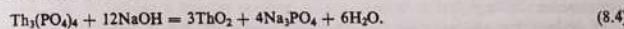


In the actual process, the acid ore slurry is sprayed as a jet on the preheated inner surface of a mild steel mill at a temperature  $250\text{--}300^\circ C$ .

#### Alkali Leaching

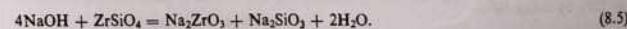
Occasionally, it may be preferable to leach the complex ore with an alkali. Generally, sodium hydroxide is used either in the molten condition (melting point  $318^\circ C$ ) or as a concentrated solution at elevated temperatures (around  $200^\circ C$ ). The phosphate or silicate ores, upon leaching, produce the oxide, the hydrated oxide, or the hydroxide of the metal, which can be further purified by dilute acid leaching and precipitation. Alkali leaching also produces sodium phosphate, which serves as a valuable raw material for fertilizer production. On the other hand, acid leaching of phosphates generally gives a product which cannot be used for the production of fertilizers.

The best-known example of alkali leaching is, perhaps, the alkali breakdown of monazite. The reaction for thorium is



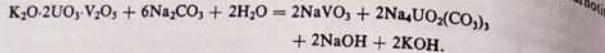
For this reaction, a concentrated NaOH solution is preferable to fused NaOH because the latter renders  $ThO_2$  somewhat inert towards acid treatment in subsequent stages. The same is true for other metal oxides as well. Beryl, too, can be leached by aqueous solutions of sodium hydroxide at elevated temperatures.

The alkali breakdown of zircon provides another example of alkali leaching. The silicate mineral, however, is not appreciably attacked by aqueous solutions of alkalies. Therefore, a fused hydroxide has to be used. Normally, NaOH at  $550\text{--}650^\circ C$  is employed. A typical reaction is



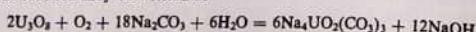
Other alkali leaching processes may involve alkali carbonate solutions. Ores of vanadium and uranium are sometimes leached by a carbonate solution. For instance, on leaching with a sodium carbonate solution, vanadium dissolves to form sodium vanadate and uranium forms a soluble

double carbonate. In the case of ores containing both uranium and vanadium, e.g., carnotite ( $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$ ), both products are simultaneously formed:

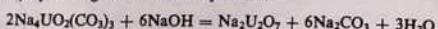


Obviously, the solution after leaching is more alkaline in nature.

Ores containing only uranium, e.g., pitchblende or uraninite, may be leached by a carbonaceous solution, provided an oxidant which can oxidize all the uranium to the hexavalent state is available. The reaction may be written as



It is interesting to note that uranium is reprecipitated if the solution is made highly alkaline ( $pH \approx 11$ ) by adding more sodium hydroxide:

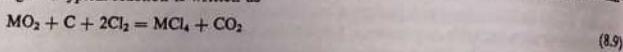


It should be noted that alkalies are weaker leaching agents than acids. Alkali leaching may, therefore, require very fine grinding of the ore (to make available a greater surface area) and also a high temperature. On the other hand, acids, especially the concentrated acids, can attack coarser particles—even lumpy ore—at a sufficiently high reaction rate.

#### Chlorination Breakdown

It has already been pointed out that for the extraction of most nuclear reactor metals it is necessary to produce a chloride as an intermediate. Such chlorides may sometimes be produced directly from the ore by suitable chlorination reactions. (For details, see Chapter 4.)

Oxides of many reactive metals, e.g., those of titanium, zirconium, hafnium, and uranium, may be chlorinated by chlorine gas in the presence of carbon, provided the temperature is sufficiently high. A typical reaction is written as



or



If sufficient carbon is present, then the  $CO/CO_2$  ratio in the product gas is governed by the temperature.

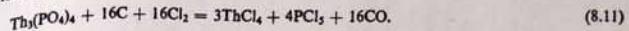
Relatively less stable oxides are sometimes directly chlorinated without any carbon. Stable oxides such as those of metals, however, necessitate the use of carbon in indirect chlorination. The advantage of the use of carbon is explained in relation to titanium extraction in Chapter 9. The same principles apply to the chlorination of U and Zr.

Zircon ( $ZrSiO_4$ ) is chlorinated in the presence of carbon to produce silica which is present in zircon and similar ores either as free silica or within the mineral in combined state, forms  $SiCl_4$  which has a very low boiling point ( $58^\circ C$ ). The  $SiCl_4$  is separated by differential condensation. Fluorination reactions are similar to chlorination reactions. For example,  $UO_2$  may be fluorinated to  $UF_4$  by using HF.

#### Halogenation Reactions for Breakdown of Complex Minerals

The high-temperature chlorination of monazite in the presence of carbon has been suggested as a method for breaking down the mineral. The selective chlorination of thorium at about  $1000^\circ C$

is written as

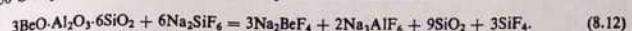


phosphorus may evolve either as trichloride or oxychloride. The other metallic values may be selectively chlorinated. This procedure, however, has not been adopted commercially.

Beryl may be decomposed by indirect chlorination to produce chlorides of beryllium, aluminum, silicon, and iron, all of which are collected separately by selective condensation.

#### Fluoride Breakdown

Sometimes, a different kind of halogenation reaction may be adopted to form halide compounds. For example, each ton of beryl may be mixed with two tons of silicofluoride and sintered at  $750-850^\circ C$  to produce a double fluoride of beryllium. The reaction is



The product beryllium compound can be leached out and treated for the recovery of the metal.

Zircon may be sintered with potassium silicofluoride to produce a double compound of zirconium at around  $700^\circ C$ . The reaction is



The impurity element in zirconium, namely, hafnium, undergoes a reaction similar to reaction (8.13). The two double compounds may be subsequently fractionally crystallized for the separation of the elements.

The use of chlorine in the metal industry bears a special significance in India, since a large percentage of the chlorine produced in soda-cells remains unutilized.

#### 8.3 REDUCTION OF METAL HALIDES

The metallothermic reduction of halides allows operation in an oxygen-free environment, leading to a superior metallic product, especially in the case of metals of a reactive nature. (The principles of metallothermic reduction have already been discussed in Chapter 4.) Generally, the reduction reaction is carried out in closed bombs, where intense exothermic heat produces two clear phases of metal and slag. Sometimes a booster reaction is incorporated to supply additional heat for better slag-metal separation as well as to help form a more fusible slag. In certain cases, i.e., where the end product is required in a finely divided form, the heat of the reaction is dissipated by using heat sinks in order to prevent coalescence of particles or grain growth.

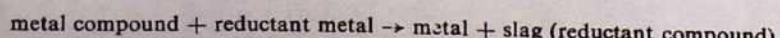
The choice of the reduction method and the details of the operational procedure are governed by the following factors:

- (1) the thermodynamic feasibility and the kinetics of the reduction reaction,
- (2) the heat balance,
- (3) the melting and boiling points of the constituents of the reaction,
- (4) densities of the reduced metal and slag.

The details of the methods used for the production of individual metals are discussed later in this chapter. Table 8.1 gives the physico-chemical data on thermit reactions yielding some selected metals. This table also includes data on the reduction of some oxides.

Table 8.1 Thermal, Physical, and Chemical Data Relevant to Metallothermic Reduction of Selected Rare Metals  
(Sundaram and Saratchandran, 1972)

*Reaction:*



Metal	Metallothermic reduction	Heat of reaction $\Delta H$ (kcal per gm mole) of metal compound at reaction temperature	Melting point (°C)				Boiling point (°C)		Product (and further treatment)
			Metal compound	Metal reductant	Metal	Slag	Metal compound	Metal reductant	
Beryllium	$\text{BeF}_2(\text{l}) + \text{Mg}(\text{l}) \xrightarrow[923-1573 \text{ K}]{\quad} \text{Be}(\text{l}) + \text{MgF}_2(\text{l})$	-43	803	650	1283	1263	1159	1105	Coarse powder and flakes (Vacuum induction melted)
Titanium	$\text{TiCl}_4(\text{g}) + 2\text{Mg}(\text{l}) \xrightarrow[1100 \text{ K}]{\quad} \text{Ti}(\text{c}) + 2\text{MgCl}_2(\text{l})$	-102	-30	650	1668	714	136	1105	Sponge (99.5%)—consumable (Electrode vacuum arc melted)
Zirconium	$\text{ZrCl}_4(\text{g}) + 2\text{Mg}(\text{l}) \xrightarrow[1100 \text{ °C}]{\quad} \text{Zr}(\text{c}) + 2\text{MgCl}_2(\text{l})$	-78		650	1852	714	331 (sublimation point)	1105	
	$\text{ZrO}_2(\text{c}) + 2\text{Ca}(\text{c}) \xrightarrow[1173 \text{ K}]{\quad} \text{Zr}(\text{c}) + 2\text{CaO}(\text{c})$ (using $\text{CaCl}_2$ as heat sink)	-43	2677	851	1852	2600	4300	1482	Micron-size powder (98.5%) (Sized)

Table 8.1 Thermal, Physical, and Chemical Data Relevant to Metallothermic Reduction of Selected Rare Metals  
(Sundaram and Saratchandran, 1972) (cont.)

*Reaction:*



Metal	Metallothermic reduction	Heat of reaction $\Delta H$ (kcal per gm mole) of metal compound at reaction temperature	Melting point (°C)				Boiling point (°C)		Product (and further treatment)
			Metal compound	Metal reductant	Metal	Slag	Metal compound	Metal reductant	
Thorium	$\text{ThF}_4(\text{c}) + 0.3\text{ZnCl}_2(\text{c}) + 2.6\text{Ca}(\text{c}) \xrightarrow[873 \text{ K}]{\quad} \text{Th}(0.3)\text{Zn}(\text{l}) + 2\text{CaF}_2(\text{l}) + 0.3\text{CaCl}_2(\text{l}) + 0.3\text{Ca}(\text{l})$	-140	1027	851	1750		1727		Th(5-7%)-Zn alloy (Vacuum retorted and arc melted)
Uranium	$\text{UF}_4(\text{c}) + 2\text{Ca}(\text{c}) \rightarrow \text{U}(\text{l}) + 2\text{CaF}_2(\text{l})$ (electrically ignited with Mg ribbon at 873 K)	-134	1036	851	1132	1418	1417	1482	Ingots (Vacuum induction melted)

Table 8.2 Some Features of Fused Salt Electrowinning of Reactive Metals (Sundaram and Saratchandran, 1972)

Metal	Cell	Bath composition	Temperature (°C)	Current efficiency (%)	Cell voltage (volts)	Energy required (kWh/kg)	Product
Aluminium	Steel, carbon, cryolite; anode, carbon; cathode, Al; internally heated	Cryolite ( $\text{Al}_2\text{O}_3$ )	950–980	85–90	4.5–5.3	17.6	Liquid Al, 99.6–99.9%
Magnesium	Anode, carbon; cathode, steel; internally or externally heated	$\text{MgCl}_2\text{-NaCl-CaCl}_2$	700–790	80–90	6.5–7.5	18.7	Liquid magnesium, 99.9% (traces of Si, Fe, Al, Mn, $\text{Cl}_2$ )
Misch metal	Cathode, graphite crucible; anode, graphite; inert atoms	$\text{ReCl}_3$ (alkali or alkaline earth chlorides)	800–900	45	14	16	Liquid rare-earth metals, 99.9%
Sodium	Anode, graphite; cathode, steel; internally heated	$\text{CaCl}_2\text{-NaCl}$	590	80	6.9	10.5	Liquid sodium (0.04% Ca); $\text{Cl}_2$ gas; 98% pure
Tantalum	Cathode, molybdenum; anode, graphite pot; vacuum or argon	$\text{K}_2\text{TaF}_7$ (alkali metal chloride)	800–950	na	na	na	Dendrites; 500 ppm impurities
Titanium	Anode, graphite lining; cathode, steel; inert atoms	$\text{K}_2\text{TiF}_6\text{-NaCl}$	740–760	na	4.5	na	Dendrites; Ti, 99.5–99.8%
Zirconium	Anode, graphite lining; cathode, steel; inert atoms	$\text{K}_2\text{ZrF}_6\text{-NaCl}$	800–850	na	4.5	na	Dendrites; Zr, 99–99.9% (0.029–0.047% C, 0.002–0.011% $\text{N}_2$ , 0.038–0.074% $\text{O}_2$ )
Beryllium		$\text{BeCl}_2\text{-NaCl}$	350	na	na	na	Flakes; vacuum melted product contains 0.4% BeO

na not available.

to a Boltzmann velocity distribution. If there are various molecular species with varying molecular weights, then the average velocities of the various species are inversely proportional to the square roots of their masses. In other words, the heavier molecules have a lower average speed of movement. In an enclosed chamber, therefore, the lighter molecules bombard a given wall with a greater frequency. If this wall consists of a porous membrane with very fine holes then the lighter molecules escape to the other side more frequently. Heavier and lighter isotopes are thus partially separated. Figure 8.1 illustrates this principle. Obviously, for effective separation, a

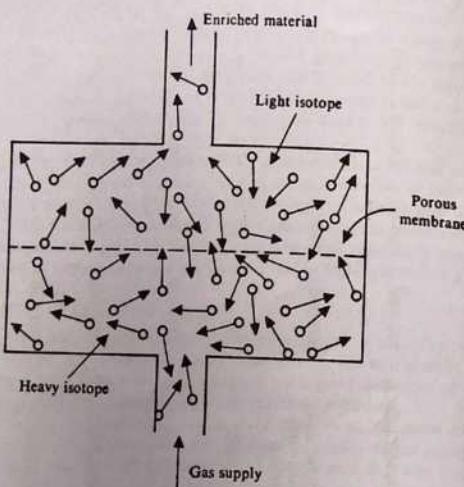


Fig. 8.1 Separation of Isotopes Based on Gas Diffusion.

single stage will not suffice and multiple stages become necessary. Multistage operations have been successfully used in the separation of the isotopes of neon, hydrogen, carbon, and tungsten on a small scale. Further, some large-scale isotope separation plants for uranium are entirely based on the aforesaid principle. Usually, 90 per cent or more of  $U_{235}$  present may be recovered using uranium in the form of  $UF_6$ .

Some separation processes are based on centrifuging, the principle of which is well-known.

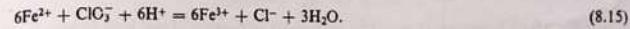
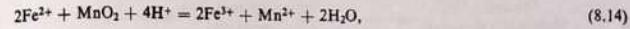
#### Processing of Uranium Ores

Both dry and wet methods have been used in the processing of uranium ores. The former refer to methods which use no liquid medium; such as grinding, screening, use of air classifiers, electrostatic separation, and magnetic separation. In this regard, the radioactivity of uranium minerals has also been made use of. Dry methods also include chemical steps such as chlorination and the

decomposition of compounds. The wet processes involve the use of leaching reagents. For instance, sulphuric acid, nitric acid, and hydrochloric acid have all been used for the leaching of uranium ores. Of these, the first is considered most economical. From the point of view of solvent extraction, in subsequent stages after leaching, nitric acid is preferable. However, both nitric acid and hydrochloric acid present corrosion problems. Sodium carbonate solution is another suitable leaching reagent under certain conditions.

It has already been mentioned that uranium goes into solution readily only when it is present in the hexavalent state. This may be considered to be a common feature in both acid and alkali leaching. If uranium is present in the tetravalent state, it must first be oxidized. The oxidation of the tetravalent uranium may be effected by either trivalent iron or pentavalent vanadium both of which are usually associated with uranium ores. Oxidizing agents such as  $MnO_2$  and  $KClO_3$  are added to maintain high valency states of iron and vanadium. The reactions may be written as follows.

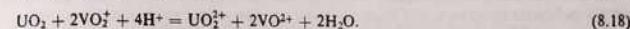
For the oxidation of iron:



For the oxidation of vanadium:

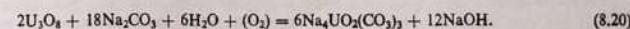
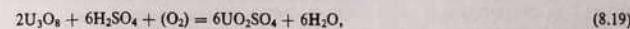


For the oxidation of uranium:

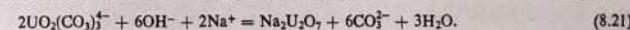


Solutions of ferric, vanadic, or similar oxidizing ions are used because oxidizing agents such as  $MnO_2$  are insoluble in sulphuric acid.

The reactions for acid leaching and alkali leaching, respectively, are



During alkali leaching, it is necessary to add an acid cation, such as bicarbonate, in order to neutralize the hydroxyl ion which may precipitate uranium out of the solution. For example,



#### Acid Leaching Versus Carbonate Leaching

Acid leaching usually leads to a higher recovery of uranium than carbonate leaching. However, acids cannot be used in cases where the ores contain calcium or magnesium carbonates or other compounds which consume an excessive amount of acid. Again, because of corrosion problems, the equipment and procedures required for acid leaching are more expensive. On the other hand, alkali leaching minimizes corrosion and also allows reagent recovery. For example, sodium carbonate can be regenerated from the hydroxide by passing carbon dioxide. Alkali leaching, however, is not suitable in the case of ores with a high gypsum or sulphide content or ores of a refractory nature.

solvent by a 10 per cent soda ash solution, the stripped solvent being recycled to the extraction unit. About 99 per cent of uranium is recovered by the neutralization of the soda ash solution with acid followed by precipitation with ammonia. [See also reaction (5.7).] Economically, solvent extraction compares well with ion exchange.

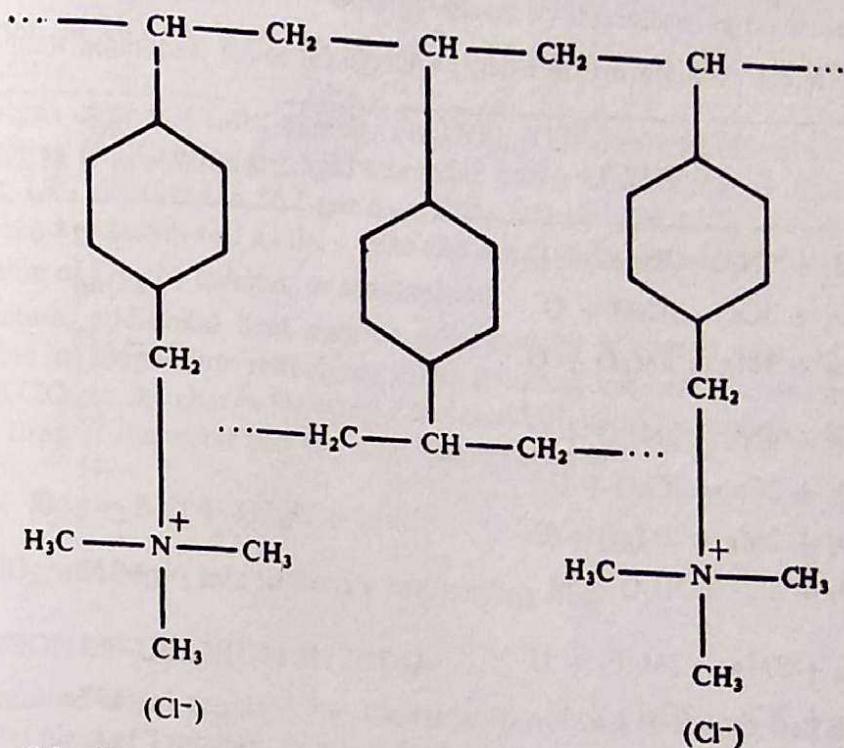


Fig. 8.2 Structure of Quaternary Ammonium Anion Exchange Resin.

The raw material obtained as a result of the foregoing methods for uranium recovery from a leach liquor is in the form of a yellow powder containing 80–85 per cent  $\text{UO}_2$ . Purification is carried out by dissolving the powder in nitric acid and then filtering the solution, the resulting uranyl nitrate being extracted with ether. Washing with water gives uranium in the aqueous phase from which it is precipitated by ammonia as pure ammonium diuranate  $[(\text{NH}_4)_2\text{U}_2\text{O}_7]$ . This is dried and reduced to the dioxide ( $\text{UO}_2$ ) by heating to  $650^\circ\text{C}$  with hydrogen. The dioxide may be converted to uranium tetrafluoride by heating in a stream of hydrogen fluoride gas.

Besides those mentioned, there are several other methods of treatment of the leach liquor for uranium recovery (for details, see "Suggested Reading" at the end of this chapter).

#### Production of Uranium Metal from Pure Compounds

Uranium was first produced by the potassium reduction of the tetrachloride. Various other methods that have been applied or attempted may be classified as follows:

- (1) Reduction, i.e., the reduction of uranium oxide by C,  $\text{CaH}_2$ , and various metals and the reduction of uranium halides by calcium or sodium.
- (2) Decomposition, i.e., the thermal decomposition of uranium halides.
- (3) Fused salt electrolysis.

Free energy data for certain reduction reactions are given in Table 8.3. These values are valid for 298 K only and may change appreciably at elevated temperatures. Yet, these values would

serve as a rough index to the feasibility of reactions. The data indicate that calcium and magnesium are the most powerful reducing agents. Hydrogen is not a suitable reductant. Aluminium is also a strong reducing agent, although the value for reduction is not given in Table 8.3.

Table 8.3 Standard Free Energy Change for Some Reduction Reactions

Reaction	$\Delta G^\circ$ (kcal/mole of U at 298 K)
$UO_3 + 6Na = 3Na_2O + U$	+12
$UO_3 + 3Ca = 3CaO + U$	-146
$UO_3 + 3Mg = 3MgO + U$	-122
$UO_2 + 4Na = 2Na_2O + U$	+67
$UO_2 + 2Ca = 2CaO + U$	-41
$UO_2 + 2Mg = 2MgO + U$	-25
$UO_2 + 2H_2 = 2H_2O + U$	-138
$UF_4 + 2Mg = 2MgF_2 + U$	-84
$UF_4 + 2Ca = 2CaF_2 + U$	-137
$UF_4 + 4Na = 4NaF + U$	-101
$UF_4 + 4K = 4KF + U$	-95
$UF_4 + 2H_2 = 4HF + U$	+162
$UCl_3 + 1.5Mg = 1.5MgCl_2 + U$	-18
$UCl_3 + 1.5Ca = 1.5CaCl_2 + U$	-73
$UCl_3 + 3Na = 3NaCl + U$	-81
$UCl_3 + 3K = 3KCl + U$	-101
$UCl_4 + 2H_2 = 4HCl + U$	+139

The calcium reduction reaction is the most highly exothermic. It produces sufficient heat to heat the charge, melt both the slag and the metal for a good clean liquid separation. In practice, however, there is the dissipation of heat and a pyrophoric metallic powder dispersed in the slag phase is produced. Sodium and potassium reductions are less exothermic. Also, the low boiling points of these metals (respectively, 880°C and 760°C) necessitate the use of high pressures, especially if uranium is to be produced in the liquid state (melting point of uranium 1130°C).

Uranium has also been produced by reducing  $UO_2$  or  $U_3O_8$  with graphite powder under vacuum. The process consists of two separate vacuum induction heating steps. The first step

involves heating a stoichiometric mixture of the oxide and carbon in a graphite crucible to a temperature in the range 1550–1950°C. This is in order to prepare an electrically conducting intermediate product. The final step, i.e., the refining step, in which the metal is obtained, consists of heating the intermediate product by self-induction at around 2200°C in an uranium crucible.

On a commercial scale, the metal has been produced by the following processes:

(1) Reduction of  $UO_2$  by  $CaH_2$  in an open nickel-chrome crucible at about 950°C in a hydrogen atmosphere.

(2) Electrolysis of double salts, namely,  $Na_2UCl_6$ ,  $KUF_5$ , or  $UF_4$ , dissolved in  $CaCl_2$ ;  $NaCl$  mixtures (80 : 20) at 900°C using a graphite crucible and a molybdenum cathode. Also, electrolysis of  $UCl_3$  or  $UF_4$  dissolved in 36.7 per cent  $KCl$ , 30.0 per cent  $LiCl$ , and 33.3 per cent  $UCl_3$  at 350–450°C using a uranium rod as the anode and a  $Mo_2B$  rod as the cathode.

(3) Reduction of  $UF_4$  by calcium or magnesium.

During reduction, additional heat may be generated by a booster reaction. This would be specially advisable for magnesium reduction, which produces less heat. For example, the addition of one mole of  $KClO_3$  to the charge for every 7 moles of  $UF_4$  provides enough extra heat to ensure the complete melting of the metal and the slag. The reaction is



$MgO$ ,  $KCl$ ,  $KClO_3$ , and  $MgF_2$  mix to form a low melting slag.

#### 8.5 PRODUCTION OF URANIUM IN INDIA

Initially, the uranium metal required for the research reactors at BARC, had been produced in the uranium metal plant at Trombay, Bombay, from monazite sands available from the beaches of Kerala. The decisions to subsequently install nuclear power stations at other places in the country created a demand for uranium metal in bulk quantities.

As early as 1955, uranium ore had been located at Jaduguda (between Jamsheedpur and Ghatshila) in Bihar. The ore was examined at BARC, and a process for its treatment and the production of the metal was developed. The capacity of the ore-processing mill had been fixed at 1000 tons throughput of ore per day. With 300 working days in a year, this would amount to processing 300,000 tons of uranium ore per year, yielding about 180 tons of uranium oxide or about 150 tons of uranium per year.

The mineralogical and chemical analysis of a typical Jaduguda ore sample is given in Table 8.4.

Table 8.4 Mineralogical and Chemical Analysis of Jaduguda Ore  
(a) Mineralogical analysis

Mineral	wt %	Mineral	wt %
Quartz	60	Magnetite	9
Chlorite	20	Sulphide	2
Apatite	3	Ilmenite	1
Tourmaline	3.50	Others	1.50

Table 8.4 Mineralogical and Chemical Analysis of Jaduguda Ore  
(b) Chemical analysis

Chemical	wt %	Chemical	wt %
$\text{U}_3\text{O}_8$	0.06-0.07	$\text{TiO}_2$	0.7
$\text{SiO}_2$	67.2	$\text{MnO}$	0.3
$\text{FeO}$	6.4	$\text{CaO}$	5.4
$\text{Fe}_2\text{O}_3$	7.9	$\text{MgO}$	2.2
$\text{Al}_2\text{O}_3$	5.5	$\text{P}_2\text{O}_5$	1.0
		S	0.8

Although other ore deposits have been located in Bihar and Rajasthan, only the Jaduguda ore has been hitherto used. The concentration of this ore by physical methods results in a rather high loss of uranium values and, therefore, chemical methods have been preferred. The ore is leached by sulphuric acid according to the flowsheet shown in Fig. 8.3. About 1000 tons of ore are processed per day. The lump ore is crushed and ground until 55 per cent is -200 mesh. The ore pulp containing 60 per cent solids is leached at a constant pH of about 1.8, the oxygen required being supplied indirectly by adding pyrolusite (65-70 per cent  $\text{MnO}_2$ ). (About 30 kg of sulphuric acid and about 6 kg of pyrolusite are consumed per ton of ore.) About 90 per cent of the uranium in the ore is leached out at 40°C in about 12 hours in rubber-lined mild steel conical base vessels (pachucas) in which air currents maintain continuous agitation.

The Jaduguda liquor contains  $\text{U}_3\text{O}_8$  (0.4 gm/litre) and also appreciable amounts of vanadium, aluminium, iron,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ , and a large amount of sulphate ions. An anionic exchanger is used to selectively adsorb the sulphate complex ions of uranium. The uranium content in the eluate is brought up to 5 gm/litre of  $\text{U}_3\text{O}_8$  prior to the precipitation of the diuranate cake.

Of the various methods available for the purification of uranium salts by chemical reagents, none has been adopted on a commercial scale. However, the diuranate which contains  $\text{U}_3\text{O}_8$  is dissolved in nitric acid and purified by solvent extraction using tributyl phosphate (TBP). Extraction, scrubbing, and stripping are all carried out using countercurrent flows in a number of stages. The pure uranyl nitrate is converted to uranium dioxide, which is fluorinated to  $\text{UF}_4$  for calciothermic or magnesiothermic reduction.

The uranium concentrate produced at the Jaduguda mill is processed at Trombay to produce uranium metal of nuclear purity. Another plant for producing uranium dioxide from the concentrate has been set up at Hyderabad. The complete process being used for the production of the metal from the ore is outlined in Fig. 8.4.

In the uranium metal plant at Trombay, uranium is produced by calcium reduction. Calcium has been preferred to magnesium because it produces more heat and gives a better slag-metal separation. High-purity  $\text{UF}_4$  powder is intimately mixed with calcium granules and the mixture is charged into a leakproof tapered stainless steel bomb reactor which is initially lined with dry  $\text{CaF}_2$  powder by vibratory packing. A magnesium ribbon embedded at the top of the charge is electrically ignited to trigger off the calciothermic reduction which then spreads rapidly and generates sufficient heat to produce liquid metal, which collects at the bottom of the reactor.

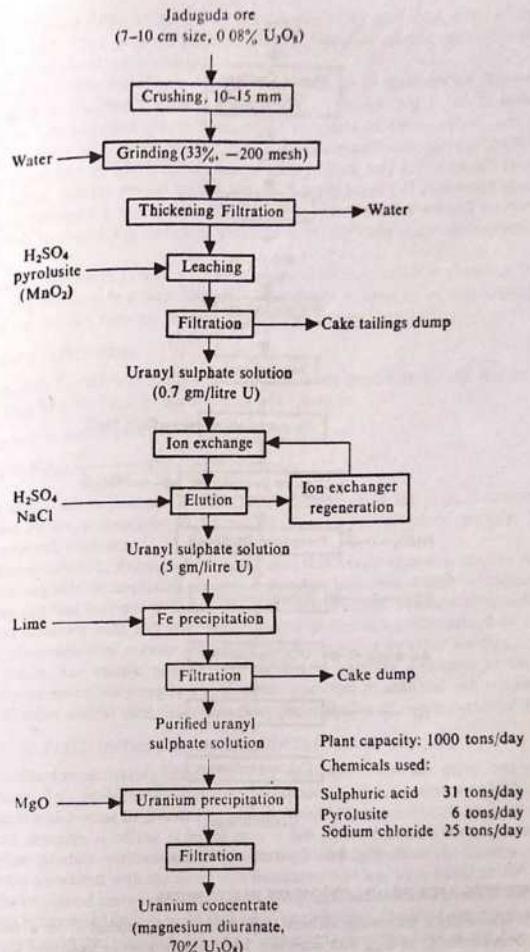


Fig. 8.3 Chemical Beneficiation of Jaduguda Uranium Ore.

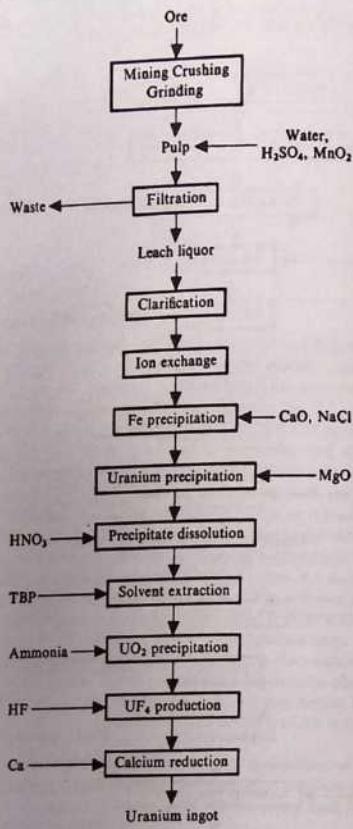


Fig. 8.4 Production of Uranium.

### 8.6 PROPERTIES AND PRODUCTION OF PLUTONIUM

Plutonium is essentially a man-made element, obtained as a byproduct from a nuclear reactor during the bombardment of  $U_{238}$  with neutrons. The fuel reprocessing technique has been developed for the extraction of plutonium from irradiated natural uranium fuels.

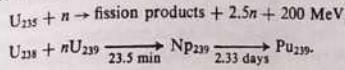
Plutonium is available in nature in very minute quantities; less than one part in  $10^{11}$  parts of pitchblende and other uranium minerals. Thus, plutonium having metallurgical importance cannot be obtained directly from nature.

Plutonium is a unique metal with unusual characteristics. It contracts on heating. It has six allotropic modifications from the room temperature to the melting point. It is the most toxic element known. The principal isotope  $Pu_{239}$ , which is mainly an alpha-emitter, can cause extensive damage to body tissues if adsorbed into a human system through the lungs or the blood stream. Alpha-particles do not penetrate even a rubber glove, yet, a few gm of the isotope can constitute a lethal dose for several million people. A body burden of plutonium exceeding 0.6 of a microgram is beyond the permissible limit. Consequently, plutonium and its compounds are always handled in closed dry chambers to avoid contamination of the atmosphere and contact with the skin.

As a potential source of power, plutonium is one of the most valuable elements. It is estimated that the use of plutonium in power reactors of the future is capable of multiplying the energy contained in the world's uranium reserves by a factor of more than  $10^{100}$ .

### SOURCES OF PLUTONIUM

In nuclear reactors fuelled with natural uranium, neutrons produced by the fission of  $U_{235}$  are captured in  $U_{238}$  to yield  $Pu_{239}$  by the so-called pile reactions:



The isotope of plutonium produced is stable with a half-life of 24,360 years. The atomic numbers of U, Np, and Pu are, respectively, 92, 93, and 94. The last two elements, namely, Np and Pu, are thus transuranic elements.

The Italian scientist, E. Fermi, first demonstrated that heavy elements such as uranium and thorium were capable of capturing neutrons, thereby becoming highly radioactive. It first appeared that this was only due to the synthesis of heavier atoms. Subsequently, however, it was observed that elements with half the atomic weight of the heavy elements were also present. These initial observations of nuclear fission were soon confirmed by other workers.

During fission, the atomic products are rejected in opposite directions at extremely high velocities carrying enormous energies. For instance, one atom of uranium can release an energy nearly  $4 \times 10^7$  times greater than that released by the explosion of one molecule of TNT.

### RECOVERY OF PLUTONIUM FROM IRRADIATED URANIUM

The major problem in recovering plutonium is its separation from the associated uranium and fission products. This problem is enormously complicated by the presence of highly radioactive fission products which must be handled by remote control. The amount of plutonium present in the irradiated uranium is of the order of only a few grams in several tons. Yet, to handle the final plutonium product without shielding, it is necessary to reduce the concentration of the fission products associated with the metal and irradiated uranium by a factor of  $10^7$ . This is done by storing the irradiated material till the radioactivity diminishes to the desired level.

Plutonium is recovered by processes that often use extensive chemical engineering techniques. These processes may be classified into two categories, namely, normal or low-temperature methods and high-temperature methods.

Low-temperature methods necessarily involve very dilute concentrations of aqueous solutions for reprocessing the spent fuel. This is to ensure that the concentrations are well below the critical value which can trigger off a chain reaction. Prior cooling of the fuel is also done to avoid the decomposition of the reagents by the radiation and possible explosions. Accordingly, a processing plant must have a large floor area to handle large bulk of solutions. On the other hand, high-temperature methods can use high concentrations of fissionable materials and can be operated with small volumes. Prior cooling of the fuel is also avoided because the inorganic substances employed are more stable compared with the organic reagents used in the low-temperature methods. Despite these advantages, the high-temperature processes have not been adopted beyond the laboratory scale.

Figure 8.5 shows the flowsheet for recovering  $\text{PuO}_2$  from spent uranium fuel elements. The fuel, if clad in aluminium, is chemically decladded with caustic soda; otherwise, when zirconium alloys are used, mechanical decladding is performed. The decladded fuel is dissolved in nitric acid. The nitrate solution containing  $\text{U}^{4+}$  and  $\text{Pu}^{4+}$  ions is contacted with TBP in kerosene. The uranium and plutonium ions are loaded in the organic and the solution containing the other fission products is discarded. During nitric acid dissolution, some sodium nitrite is added to ensure that Pu remains as  $\text{Pu}^{4+}$ . The  $\text{Pu}^{4+}$  ion loads preferentially as the distribution coefficients in the organic to aqueous solution for  $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$ , and  $\text{Pu}^{6+}$  are 0.001, 5, and 1, respectively.

The plutonium is stripped from the organic by contacting it with a solution containing ferrous sulphamate. The ferrous sulphamate reduces the valency of Pu to three. The organic containing uranium is sent for uranium recovery. The aqueous solution is subjected to ion exchange (Dowex-I). The ion-exchange columns are eluted with dilute  $\text{HNO}_3$  to remove plutonium, which is precipitated as an oxalate and then calcined to give reactor grade  $\text{PuO}_2$ .

#### CONVERSION OF PLUTONIUM COMPOUNDS TO METALLIC STATE

The choice of the starting compound and the subsequent route is governed by various considerations such as the ease of preparation of the pure compound, the availability and ease of handling of the reductant, the possibility of alloy or compound formation with the reductant, and the recovery obtainable. Since plutonium is fissionable at every stage, utmost care is taken to ensure that a critical assembly is not accidentally produced. This problem ultimately also governs the type and size of equipment to be used. Plutonium fluorides are nonhygroscopic and, therefore, easier to handle. However, their preparation needs HF. Fluoride slags are also comparatively insoluble. On the other hand, chlorides can be prepared more easily and can be easily dissolved in other solvent chlorides. They are, however, extremely hygroscopic.

Various reduction reactions have been examined for the preparation of plutonium. The hydrogen reduction of plutonium compounds theoretically requires a temperature in excess of 3000°C, whereas carbon forms stable plutonium carbides. These may, therefore, be ruled out as reducing agents. The thermal decomposition of the hydride produces only a powder and the electrolysis of plutonium halides produces globules of metal dispersed throughout the salt phase. However, alkali or alkaline earth metals may be used for the reduction of suitable plutonium compounds.

#### METALLOHERMIC REDUCTION OF PLUTONIUM HALIDES

During the Second World War, the atomic power project of the U.S.A. first developed [at Los Alamos (New Mexico)] the calciothermic reduction of plutonium halides. This reduction may be

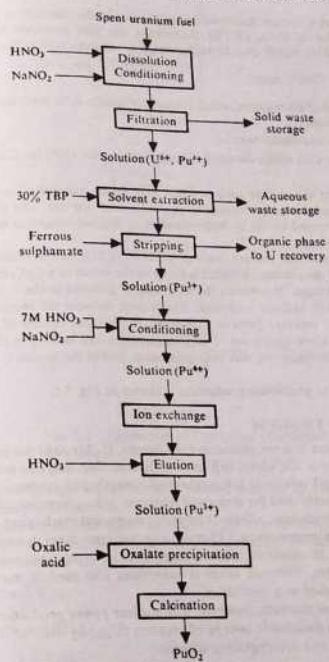
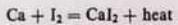


Fig. 8.5 Recovery of Plutonium from Spent Fuel  
(Sundaram and Gupta, 1980).

carried out inside a bomb in an inert atmosphere. The reactions are



It may be noted that both these reactions are exothermic and that the melting point of  $\text{CaF}_2$  ( $1360^\circ\text{C}$ ) is higher than that of  $\text{CaCl}_2$  ( $772^\circ\text{C}$ ). Sometimes, the heat generated may not be sufficient to melt the metal and the halide slag. In such cases, a booster reaction of the type



may be incorporated. This reaction, which is specially beneficial for the fluoride reaction, performs the following functions:

- (1) It supplies additional heat.  
 (2) It produces  $\text{CaI}_2$  which dissolves the reaction product  $\text{CaF}_2$  (or  $\text{CaCl}_2$ ) and forms a melting slag.

The use of an inert atmosphere such as argon aids in the slag-metal separation and gives a cleaner slag by not allowing the formation of oxides and nitrides. The raw material, namely,  $\text{PuF}_4$  or  $\text{PuCl}_3$ , is prepared by the hydrofluorination or hydrochlorination of  $\text{PuO}_2$  and it should be completely oxygen-free.

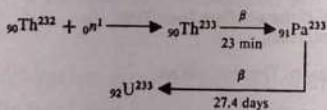
It has been shown that the booster reaction [reaction (8.27)] may be eliminated if a compacted mixture of calcium and the plutonium halide is taken in the bomb in a  $\text{CaF}_2$  crucible. Compaction provides several advantages. It prevents the scattering of powders in the vacuum system and the swelling of mixtures when vacuum is applied. The contact between the components is better and the amount of retained residual gases is minimized. Further, the volume of the mass is reduced by at least 50 per cent, allowing the use of smaller crucibles and leading to the release of greater heat per unit volume. Consequently, the heat generation within the system is better and the heat losses are minimized.

A general flowsheet for plutonium production is shown in Fig. 8.6.

## 8.7 EXTRACTION OF THORIUM

In the earth's crust, thorium is more abundant than Sn, As, U, Mo, and the precious metals. The metal is as abundant as Be or Co, about half as abundant as zinc, and one-tenth as abundant as copper. Because of thorium's relatively low mechanical strength and inadequate corrosion resistance, the metal is not directly used for structural purposes. It has, however, found some applications in alloys. In magnesium-base alloys, it imparts exceptional mechanical strength, stability, and creep resistance at high temperatures. The metal also has some other nonnuclear applications, for example, as a catalyst in chemical industries and as a refractory material in ceramics and metallurgy in the oxide form. Thorium oxide is sometimes also used in making gas mantles. Thorium is also sometimes used as a deoxidizer.

The most important use of thorium, however, is in nuclear power production. Nonfissionable thorium is converted into a fissionable isotope of uranium ( $U_{233}$ ) by neutron irradiation according to the following reaction and disintegration scheme:



In this scheme, the superscripts denote atomic weight and the subscripts the atomic number.

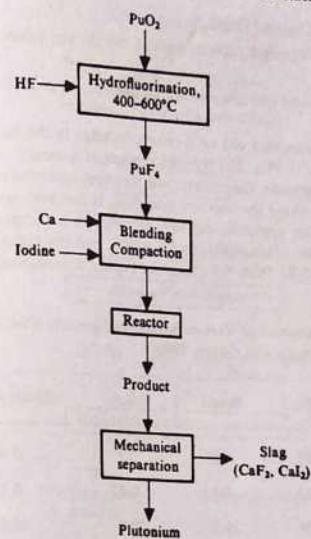


Fig. 8.6 Production of Plutonium (Sundaram and Gupta, 1980).

$U_{233}$  can be subsequently separated from the irradiated thorium by chemical processing because it is chemically dissimilar to thorium.

For reactor applications, the value of  $\eta_{ta}$ , i.e., the number of neutrons emitted by a fissionable nucleus per neutron absorbed, is an important fundamental parameter. The  $\eta_{ta}$  values for the different isotopes of uranium and for  $\text{Pu}_{239}$  are

$$U_{\text{obs}} = 2.30 \pm 0.02,$$

$$U_{235} = 2.06 \pm 0.02,$$

$$P_{\text{U}_{219}} = 2.03 \pm 0.02.$$

From these values, it is evident that the U<sub>233</sub>-thorium fuel cycle is highly promising as far as thermal breeders are concerned.

SOURCES OF THORIUM

The major thorium-bearing minerals can be categorized as follows:

- ### (1) Simple oxides [Thorianite ( $\text{Th}_2\text{O}_3$ )].

- (2) Simple silicate [Thorite ( $\text{ThSiO}_4$ )].  
 (3) Complex oxides containing one or more of the metals, namely, Y, Er, Ca, Nb, Ta, Fe, Ti, Ce, Zr, Pb, and Sn.  
 (4) Complex phosphates and silicates containing varying proportions of the aforementioned elements.

Monazite, the most important ore of thorium, belongs to the last category and is generally represented as  $(\text{Ce}, \text{La}, \text{Y}, \text{Th})\text{PO}_4$ . The thorium content of monazite ranges between 2 per cent and 26 per cent. India possesses the richest and the most extensive resources of thorium in the form of monazite deposits along the southern coastline. It has been estimated that these deposits exceed 5 million tons. Other economic deposits of monazite are located in Brazil, Australia, Sri Lanka, Indonesia, Malaysia, Madagascar, South Africa, and the U.S.A. The ore also occurs, to a lesser extent, in the U.S.S.R. Table 8.5 shows the typical compositions of monazite obtained in various countries.

Table 8.5 Composition of Various Monazite Deposits (Prakash *et al.*, 1962; Sundaram and Gupta, 1980)

Constituent	India	Brazil	U.S.A.	South Africa	Madagascar
$\text{ThO}_2$	8.88	6.5	3.1	5.9	8.75
$\text{U}_3\text{O}_8$	0.35	0.17	0.47	0.12	0.41
$(\text{Rare earth})_2\text{O}_3^*$	59.37	29.2	40.7	46.41	46.2
$\text{Ce}_2\text{O}_3$	28.46	26.8		24.9	23.2
$\text{P}_2\text{O}_5$	27.03	26.0	19.3	27.0	
$\text{Fe}_2\text{O}_3$	0.32	0.51	4.47	4.5	2.2
$\text{TiO}_2$	0.36	1.75		0.42	6.7
$\text{SiO}_2$	1.00	2.2	8.3	3.3	

\*Includes  $\text{Ce}_2\text{O}_3$ .

High-grade monazite is recovered from the raw ores by physical beneficiation procedures. Figure 8.7 shows the flowsheet followed at the Indian Rare Earths Limited (IREL).

#### TREATMENT OF MONAZITE

Both acid leaching and alkali leaching have been used in the case of monazite. The acid leaching widely followed in the U.S.A. and the U.S.S.R. has certain advantages, i.e., it can be employed for all types of monazite ores and very fine grinding is not necessary. However, acid leaching consumes all the valuable phosphate, and prevents its recovery.

We now describe the acid leaching process. In this process, the monazite sand is treated with

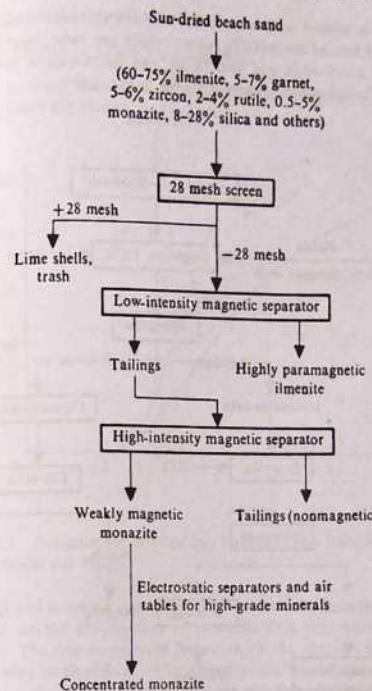


Fig. 8.7 Separation Process for Monazite (Prakash *et al.*, 1962; Sundaram and Gupta, 1980).

concentrated sulphuric acid at 150–200°C in cast iron pots fitted with heavy duty stirrers. The separation of thorium, the rare earths, and uranium is accomplished by the selective precipitation of the sulphate leach liquor with ammonia. To achieve better selectivity, thorium and the rare earths are precipitated from the solution as oxalate, free from phosphate, sulphate, and uranium. The oxalate is then converted to the nitrate and thorium and the rare earths are separated by liquid extraction.

The alkali process—first developed in France and U.S.S.R. and now followed in India and Brazil—yields sodium phosphate as a byproduct (which is a valuable fertilizer). This process, however, requires a finely ground ore. Moreover, because of difficulties encountered during filtration, the process is not adaptable to low-grade ores or ores containing silicates.

In India nearly 2500 tons of monazite are processed every year at Alwaye (Kerala). Here,

finely ground monazite is treated with hot concentrated caustic soda solution, when the gangue goes into solution leaving behind the metallic values, which are later recovered as a hydroxide cake. This cake is later dissolved in acid, and U, Th, and the rare-earth metals are precipitated at different pH values. The relevant flowsheet is shown in Fig. 8.8.

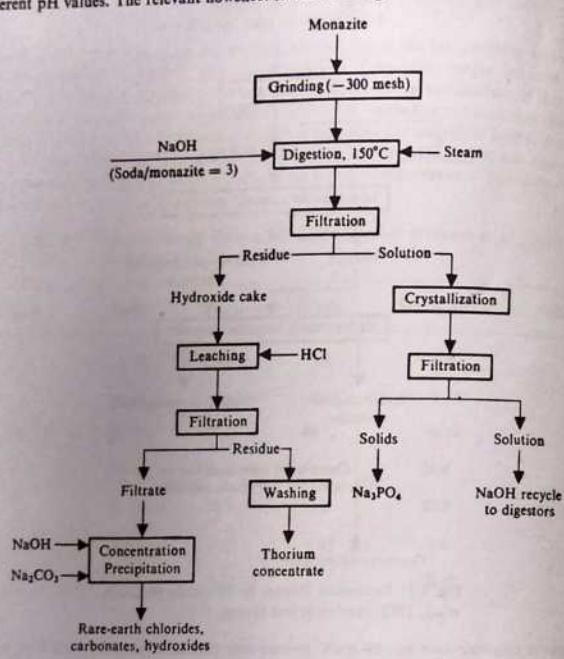
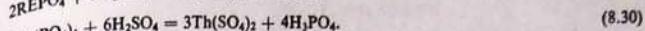
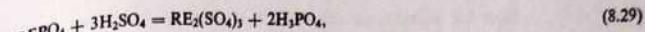
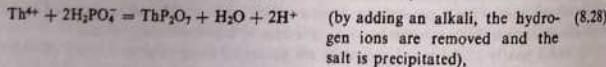


Fig. 8.8 Treatment of Monazite.

The hydroxide is dissolved in HCl and then NaOH added in order to adjust the pH to around 1.05, when most of the thorium is precipitated out. Subsequently, at a slightly higher pH, i.e., 2.3, the rare-earth phosphates are mainly precipitated. Uranium is completely precipitated at a pH of 6. The basis for the selective precipitation of thorium, uranium, and the rare-earth metals is indicated in Fig. 8.9. The precipitation reactions may be written as



It should, however, be noted that at no time is the separation of U, Th, and the rare earths complete; the precipitates are always contaminated.

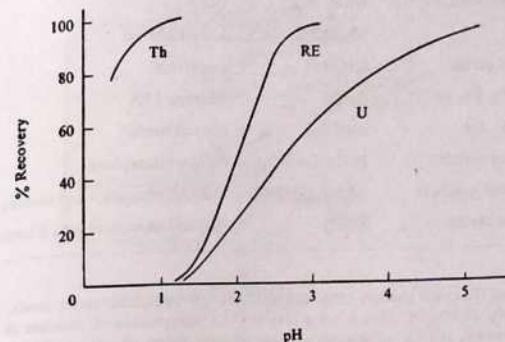


Fig. 8.9 Precipitation of Thorium, Uranium, and Rare-Earth Metals at Different pH Values.

A recently developed process for the separation of monazite from the rare earths that appears promising is based on the chlorination of monazite at a temperature of 700–1000°C in the presence of carbon. The free energies of formation of the thorium chlorides and those of the rare earths are not very much different. Consequently, selective chlorination does not seem to be promising. However, the vapour pressures of the chlorides differ appreciably, and fractional distillation could provide a feasible mode of carrying out the separation. The advantages would be as follows:

- (1) The phosphates are volatilized as oxychlorides in a single operation, rendering the resulting chlorides phosphate-free.
- (2) The impurities present in the ore are eliminated to a large extent as volatile chlorides.
- (3) The anhydrous rare-earth chlorides and thorium chlorides produced can be extracted either with water or with nonaqueous solvents or else recovered in the molten state.

There are five major processes for purifying thorium concentrates, namely, solvent extraction, fractional crystallization, ion exchange, selective precipitation, and selective leaching. Fractional crystallization and selective precipitation (just discussed) are among the most common methods of purification, but for the continuous, large-scale production of high-purity thorium, the intermediate solvent extraction process is better suited. (Table 8.6 lists some solvent extraction systems for thorium purification.) Ion-exchange methods do not find industrial application.

Table 8.6 Solvent Extraction Systems for Thorium Production  
(Prakash *et al.*, 1962)

Separation of thorium from	Aqueous phase	Solvent and added agents
Rare earths, Fe, Al	HNO <sub>3</sub> -NO <sub>3</sub> <sup>-</sup>	Ether
Nd	NH <sub>4</sub> SCN	n-amyl alcohol
Rare earths	NH <sub>4</sub> SCN	1-pentenol
B, Te, Pb, Ac	Acidic	Benzene-TTA
Ti, U, Ce	Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	Mesityl oxide
Many metals	HNO <sub>3</sub> -Ca(NO <sub>3</sub> ) <sub>2</sub>	Tributyl phosphate
Fission products	Al(NO <sub>3</sub> ) <sub>3</sub> -H <sub>3</sub> PO <sub>4</sub>	Tributyl phosphate in kerosene
Rare earths	HNO <sub>3</sub>	Tributyl phosphate plus diluent

For purifying the crude thorium cake obtained from the Indian monazite sands, a modified process has been developed. This process involves the precipitation of thorium as oxalate, its conversion to nitrate, and the subsequent extraction with tributyl phosphate. The various steps are schematically shown in Fig. 8.10.

Some of the other compounds of thorium may be produced from the nitrate obtained by the scheme shown in Fig. 8.10. For instance, thorium oxide may be produced by converting the nitrate to oxalate and the subsequent calcination of the oxalate. The oxide may further be chlorinated to yield the chloride.

### 8.8 METHODS FOR PRODUCING THORIUM METAL

All the general methods for the production of reactive metals have been tried in the case of thorium. Table 8.7 gives the free energy values calculated for some reduction reactions. This table indicates that Ca and Na are the strongest reducing agents in the case of thorium compounds.

We now discuss some of the methods that have been used in recent years to produce thorium from its compounds.

(1) Reduction of the tetrachloride with sodium at 525°C (initial temperature). Here,



The excess sodium and the sodium chloride (byproduct) can be removed from the charge and the thorium sponge separated by heating in a vacuum at 900°C for 16 hours. The sponge is then pressed into bars which are subsequently arc melted to give solid ingots.

(2) Reduction of the tetrachloride with sodium in dilute sodium amalgam. In this case, thorium is produced as a Th-Hg compound (~1 per cent thorium) which is subsequently heated to remove mercury. Most of the liquid mercury is pressed out from the mass to separate the

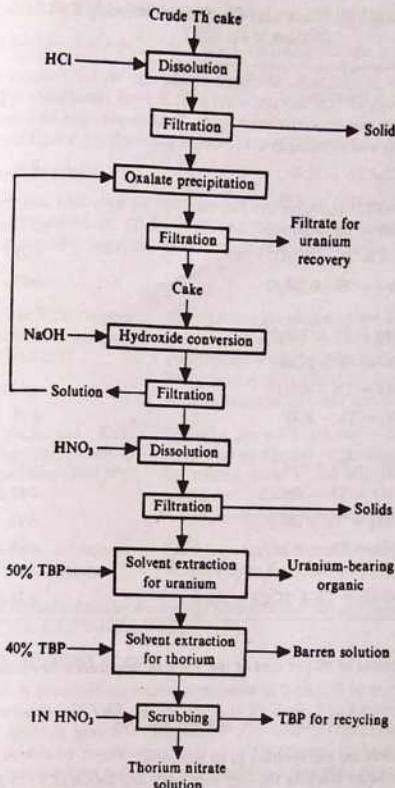


Fig. 8.10 Production of Reactor Grade Thorium Nitrate.

compound ThHg. This method suffers from the disadvantage that large quantities of a toxic substance such as mercury have to be handled.

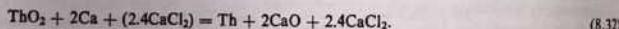
(3) Thorium can be produced by the electrolysis of its salts in the fused state.

(4) Bomb reduction of ThO<sub>2</sub> or ThF<sub>4</sub> with calcium. The reduction of ThO<sub>2</sub> with Ca is carried out with 25 per cent excess of calcium around 1000-1100°C. Calcium chloride is added

Table 8.7 Free Energy Changes for Reduction Reactions  
(Prakash *et al.*, 1962)

Reaction	$\Delta G^\circ$ (kcal/mole at 2500 K)
$\text{ThO}_2 + 2\text{H}_2 = \text{Th} + 2\text{H}_2\text{O}$	+136
$\text{ThO}_2 + 2\text{C} = \text{Th} + 2\text{CO}$	+30
$\text{ThO}_2 + 3\text{C} = \text{ThC} + 2\text{CO}$	-7.6
$\text{ThO}_2 + 4\text{Na} = \text{Th} + 2\text{Na}_2\text{O}$	+237
$\text{ThO}_2 + 2\text{Ca} = \text{Th} + 2\text{CaO}$	+28
$\text{ThO}_2 + 2\text{Mg} = \text{Th} + 2\text{MgO}$	+77
$\text{ThF}_4 + 2\text{Mg} = \text{Th} + 2\text{MgF}_2$	+41
$\text{ThF}_4 + 2\text{Ca} = \text{Th} + 2\text{CaF}_2$	-41
$\text{ThF}_4 + 4\text{Na} = \text{Th} + 4\text{NaF}$	+45
$\text{ThF}_4 + 2\text{H}_2 = \text{Th} + 4\text{HF}$	+69
$\text{ThCl}_4 + 2\text{H}_2 = \text{Th} + 4\text{HCl}$	+87
$\text{ThCl}_4 + 4\text{Na} = \text{Th} + 4\text{NaCl}$	+42.6
$\text{ThCl}_4 + 2\text{Mg} = \text{Th} + 2\text{MgCl}_2$	+52
$\text{ThCl}_4 + 2\text{Ca} = \text{Th} + 2\text{CaCl}_2$	-39
$\text{ThO}_2 + 2\text{CaH}_2 = \text{Th} + 2\text{CaO} + 2\text{H}_2$	+28.0

to the charge to the extent of 40 per cent of the  $\text{ThO}_2$  to help form a low melting slag with  $\text{CaO}$ . The reaction is

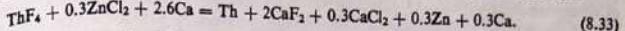


About an hour is allowed for the reaction to be completed.

Thorium is separated by leaching the slag with water and then with 1 : 10 nitric acid, followed by washing with water, alcohol, and then ether. The resulting metal powder is dried in vacuum to give a purity of 99.7–99.8 per cent.

Calculations based on thermodynamic data show that—under adiabatic conditions—assuming a 15 per cent excess of calcium and the initiation temperature of reaction (8.32) as 800°C, the exothermicity of this reaction will provide enough heat to raise the temperature of the products to above the melting point of thorium. In reality, however, since adiabatic conditions do not prevail,  $\text{ZnCl}_2$  is incorporated as booster. Apart from the previously discussed advantages of booster reactions, there is added exothermicity and fluxing potential of the secondary slag product

in this case.  $\text{ZnCl}_2$  also aids in the formation of a low melting Th-Zn alloy. The reaction is



The alloy normally contains 5–7 per cent zinc and melts at about 1200°C; the metal yield is more than 90 per cent. To obtain pure thorium from the alloy, zinc may be distilled off in a graphite crucible by applying a vacuum less than 10  $\mu\text{m}$  and heating to a temperature of about 1000°C. Thorium remains behind as a sponge which is subsequently consolidated.

#### FUSED SALT ELECTROLYSIS

The electrolytes that have been tried for the fused salt electrolysis of thorium compounds so far may be classified as (1) chlorides, (2) fluorides, and (3) oxides. We now list some of the baths employed along with the advantages and disadvantages associated with them:

Electrolyte	Remark
$\text{ThCl}_3$ in $\text{NaCl}$ or $\text{KCl}$ ; graphite anode and molybdenum cathode; temperature 750–850°C	The hygroscopic nature of the chloride creates problems; these may be overcome by preparing the chloride <i>in situ</i> by chlorinating a mixture of $\text{ThO}_2$ and starch at 850°C A more or less continuous operation is possible
$\text{KThF}_5$ in $\text{NaCl}$ and $\text{KCl}$ ; graphite anode and molybdenum cathode; temperature 750–770°C	Fluorides are not hygroscopic, but unlike chlorides, they accumulate in the electrolyte, raising the melting point of the bath and the electrical resistance A continuous operation is difficult
$\text{ThO}_2$ in $\text{KF-ThF}_4$ mixture or in $\text{NaCl-KCl-ThCl}_4$ mixture	Laboratory investigations have reported successful electrolytic dissociation of $\text{ThO}_2$

Thorium may be further refined by electrolytic processes that are analogous to copper refining processes or by the Van Arkel iodide process.

#### PRODUCTION OF THORIUM IN INDIA

At present, thorium is produced on a pilot plant scale at BARC. The method adopted involves the calciothermic reduction of  $\text{ThO}_2$  pellets on a 10-kg scale. The powders obtained are pyrophoric and special methods have been adopted to overcome pyrophoricity. The sintered and machined pellets produced by powder metallurgy show 98 per cent of theoretical density and are ductile so that a 25-mm-diameter pellet can be rolled into a thin strip to an extent of 90 per cent reduction in thickness by cold rolling without intermediate annealing. Large-sized billets are to be produced by vacuum arc melting of consumable electrodes.

#### 8.9 EXTRACTION OF ZIRCONIUM

Before describing the extraction of zirconium, let us discuss some of its properties. The most important property of zirconium is the low value of absorption cross-section for thermal neutrons. This value is only 0.15 barn per atom as compared with 8.21 for aluminium and 2.4 for iron. The metal is therefore highly valued for application in a nuclear reactor as a cladding element.

The corrosion resistance of zirconium in water at elevated temperatures is even better than that of aluminium. In addition, at high temperatures the mechanical strength of zirconium surpasses that of its frequent rival aluminium. The thermal conductivity is low, but adequate for use in nuclear fuel elements. At high temperatures, zirconium has lower thermal stresses because of its lower coefficient of expansion.

On the basis of neutron economy, corrosion resistance, mechanical strength, and other properties, zirconium alloys have been the ideal choice for the cladding of fuel and other components in water-cooled nuclear power systems.

Zirconium also finds some nonnuclear applications, e.g., as getters in the form of fine powder, in photoflash and detonator applications, in flash bulbs in the form of thin foils, and in ceramics as an oxide. Significant quantities of zirconium are added (as Zr-Si-Fe alloy) to electric furnace steel for improving various properties. Light-weight alloys of Mg-Zr, Mg-Zn-Zr, Mg-Th-Zr, and Mg-rare earth-Zr have superior strengths at elevated temperatures and are, therefore, used in the aircraft industry.

Zirconium minerals are almost always associated with hafnium to the extent of 1-3 per cent of the zirconium content. Whereas zirconium has a low absorption cross-section for thermal neutrons, pure hafnium is a strong neutron absorber. Therefore, in the interest of strict neutron economy, zirconium must be rendered substantially free from natural hafnium contamination. It may be noted that the tolerance limit for hafnium in nuclear grade zirconium is specified at 200 ppm.

#### ROLE OF ZIRCONIUM ALLOYS AS CLADDING ELEMENT IN NUCLEAR REACTORS

Before considering the role of the cladding element, it is necessary to know the basic arrangement in a nuclear reactor. A typical reactor consists of fuel elements in the form of rods separated by the moderator material. The moderator material, often graphite, serves to slow down neutrons without absorbing them. Around the fuel elements are channels through which a cooling medium circulates to take away the heat produced by fission. Consequently, the fuel elements have to be protected from mechanical erosion and corrosion. They are, therefore, suitably cladded by an alloy which can stand corrosion and allow high heat transfer.

In a nuclear reactor, when a given mass of fuel material is undergoing fission, the fast-moving neutrons generated face the following possibilities:

- (1) They may encounter additional fissile mass, producing more neutrons.
- (2) They may encounter a fertile atom such as  $U_{238}$  and produce another fissile atom such as  $Pu_{239}$ .
- (3) They may encounter some other atom which absorbs them without any useful result.
- (4) They may escape from the mass altogether.

If possibility (1) predominates, then the number of fast-moving neutrons rapidly rises, causing the nuclear fission reaction to proceed at an accelerated pace. Accordingly, heat is also generated at a rapid rate and must be effectively removed by the coolant. This condition of accelerated chain reaction requires that the cladding element itself should not absorb the neutrons [possibility (3)]. Possibility (4) is minimized by using moderators which slow down the very fast-moving neutrons and by increasing the size and the mass of the fissile mass. For a given mixture of fissile and nonfissile atoms, there is a certain critical size beyond which the proportion of neutrons that escape is so reduced that the condition for a nuclear reaction to take place is attained. This critical size depends to a great extent on the proportion of fissile atoms and the

nature of the nonfissile atoms with which they are mixed. Zirconium alloys, which have a very low capacity for absorbing neutrons, allow the pile to be kept as small as possible.

For the foregoing purpose, zirconium is alloyed with tin and minor amounts of Cr, Fe, and Ni. In zircaloy-2, 1.2-1.7 per cent tin effectively counteracts the deleterious effects of nitrogen, enhancing the corrosion resistance and the mechanical strength of the alloy. Chromium, iron, and nickel, amounting to a total of 0.18-0.38 per cent, reduce the hydrogen pick-up, contributing to the stability of the oxide film and thus preventing further corrosion. In recent years, a new alloy of zirconium containing 2.5 per cent Nb has been developed. This niobium alloy, as compared with a Zr-Sn alloy, possesses a tensile strength that is 40 per cent more in the cold worked condition and almost double in the heat-treated condition. Further, this alloy has a very high creep strength and a good ductility, permitting the use of a thinner section for cladding.

The chemical compositions of some zirconium alloys are shown in Table 8.8.

#### SOURCES OF ZIRCONIUM

The chief source of zirconium is the mineral zircon ( $ZrSiO_4$ ). This mineral is often associated with beach sands along with other minerals (such as rutile, ilmenite, and monazite) and oxides of metals such as iron and magnesium.

#### TREATMENT OF ZIRCON

At the outset, the beach sands are mined and screened to get rid of oversized particles. The heavy sands are concentrated by means of jigs, tables, spirals, and riffles. Further processing involves the magnetic and electrostatic separation of magnetite titanium minerals. Quartz and silica are removed by gravity separation. The final product is clean zircon mineral.

We now describe some of the methods that have been employed for the treatment of zircon. The direct graphite reduction of zircon in an inert atmosphere has yielded 90 per cent of the metal as  $ZrC$ , most of silicon being eliminated as volatile  $SiO$  which is formed at the electric arc temperature used to heat the charge. However, the graphite reduction of zircon in the presence of air gives the carbonitride. Conventional methods include: the direct chlorination of zircon to produce  $ZrCl_4$ ; NaOH treatment to produce soluble sodium zirconate; and treatment with  $K_2SiF_6$  to produce the double salt  $K_2ZrF_6$ . It should be noted that all these methods require high temperatures. Since the chemical behaviour of hafnium is similar to that of zirconium, all the hafnium present in the original ore finds its way into the zirconium compounds.

#### METHODS FOR SEPARATING HAFNIUM FROM ZIRCONIUM

A large number of methods have been tried for the separation of hafnium from zirconium. We now discuss some of the more important methods.

##### Fractional Crystallization of Double Compounds $K_2ZrF_6$ and $K_2HfF_6$

The double salts, namely,  $K_2ZrF_6$  and  $K_2HfF_6$ , have widely different solubilities in dilute (1 per cent) hydrochloric acid solution, the solubility of the hafnium compound being much higher. Sixteen to twenty crystallization steps are necessary to reduce the Hf content to the specified levels.

##### Solvent Extraction

Several solvent extraction systems have been used for Zr-Hf separation. In general, this is the most widely used method.

Table 8.8 Chemical Composition of Some Zirconium Alloys\*

Alloy type	Sn	Fe	Cr	Ni	Nb	Cu	Oxygen	Total (Fe+Cr+Ni)	Zirconium plus permitted impurities
Zircaloy-1	2.5								Balance
Zircaloy-2	1.20-1.70	0.07-0.20	0.05-0.15	0.03-0.08			1000-1400 ppm	0.18-0.38	Balance
Zircaloy-3	0.2-0.3	0.2-0.3	500 ppm	500 ppm					Balance
Ni-free									
Zircaloy-2	1.2-1.7	0.12-0.18	0.05-0.15	70 ppm					Balance
Zircaloy-4	1.2-1.7	0.18-0.24	0.07-0.13	70 ppm					Balance
Zr-Nb	100 ppm	1500 ppm	200 ppm	70 ppm	2.40-2.8		900-1300 ppm	0.28 minimum	Balance
Zr-Nb-Cu					2.4-2.8	0.5			Balance

\*Figures are in per cent except where otherwise stated.

**Fractional Distillation of Volatile Compounds**

A mixture of  $ZrO_2$  and  $HfO_2$  may be differentially chlorinated. Thus, some separation is made possible due to the difference in the vapour pressures of  $ZrCl_4$  and  $HfCl_4$ .

**Anion Exchange Methods**

Some anion exchange resins have been satisfactorily used for the separation of hafnium from zirconium.

**Pyrometallurgical Methods**

By and large, pyrometallurgical methods have not been very successful in view of the similarities in the properties of zirconium and hafnium. Some methods which claim partial success are based on the following processes:

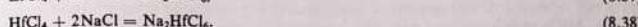
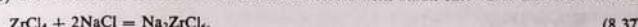
- (1) The differential oxidation of tetrachlorides. The reactions are



- (2) The formation of the lower chloride of zirconium. The reaction is



- (3) The differential reaction of the double chlorides with alkali chlorides. The reactions are

**REDUCTION OF ZIRCONIUM COMPOUND TO METAL**

Metallic zirconium can be conveniently produced by the metallothermic reduction of zirconium tetrachloride. Kroll's process of magnesium reduction is the most popular method. Recently, zirconium has been successfully produced also by the fused salt electrolysis of double salts such as  $Cs_2ZrCl_6$  dissolved in alkali chlorides. (Details of the various aspects of zirconium extraction are given in Section 8.10.)

**8.10 ZIRCONIUM PRODUCTION IN INDIA**

The first three power stations under the Indian nuclear power programme are located at Tarapur (Maharashtra), Kota (Rajasthan), and Kalpakkam (Tamil Nadu). The respective capacities are  $190 \times 2$  MW,  $200 \times 2$  MW, and 400 MW. These stations are designed to use zirconium alloys for the fuel tubes and other structural components. The initial inventory requirement of the alloys for the Tarapur reactors alone has been around 38 tons and the annual replacement 5-10 tons. The requirements of the Kota reactor as inventory and annual replacement are around 22 tons and 3 tons, respectively. To meet the zirconium requirements of aforesaid reactors, a plant was set up at Moula Ali, near Hyderabad (Andhra Pradesh), with an initial capacity of 50 tons of zircaloy-2 mill products, mainly in the form of tubing. The process flow-sheet selected has been based on the extensive development work carried out at BARC, Bombay (see Sundaram and Saratchandran, 1972; Sundaram and Sharma, 1972).

The economics of zirconium extraction—from the treatment of the ore to the production of

the final alloys—is governed by the following basic considerations:

- (1) The close similarity in the chemical behaviour of zirconium and hafnium requires the application of complex and expensive techniques for their separation.
- (2) Zirconium is highly reactive towards oxygen and nitrogen. Yet, the tolerance limits are specified at, respectively, 1400 ppm and 500 ppm, beyond which there is a serious loss of ductility which renders fabrication processes difficult. Thus, a strict control has to be exercised over the atmosphere at different stages of the production of zirconium.
- (3) Since molten zirconium is highly reactive, unconventional techniques are often needed for melting and casting the metal.

The process for the conversion of zircon sand into the alloy products would comprise three stages, namely,

- (1) the production of hafnium-free zirconium oxide from zircon,
- (2) the conversion of pure  $ZrO_2$  into ductile nuclear grade zirconium sponge, and
- (3) the production of mill products (alloy tubes) from the sponge metal.

#### STAGE 1: PRODUCTION OF PURE ZIRCONIUM OXIDE

The beach sands of South India contain about 5–9 per cent zircon associated with other minerals. The zircon concentrate, after beneficiation, has the following typical analysis (in weight per cent):

$$(ZrO_2 + HfO_2) = 65.5-66.5,$$

$$SiO_2 = 31-32,$$

$$Al_2O_3 = 0.7,$$

$$Fe_2O_3 = 0.1,$$

$$TiO_2 = 0.3-2.5,$$

$$ThO_2 = 0.02,$$

$$U_3O_8 = 0.035,$$

$$P_2O_5 = 0.1.$$

(The hafnium content, expressed as per cent  $HfO_2$ , is about 2.5 per cent.)

Two processes have been examined at BARC for the separation of hafnium from zirconium. In the first process, which is based on the fractional crystallization of double fluorides, zircon is fused with  $K_2SiF_6$  around 650–700°C, whereby the zirconium and hafnium values are converted into water-soluble  $K_2ZrF_6$  and  $K_2HfF_6$ . A 12-stage fractional crystallization of the double fluorides simultaneously removes the hafnium and other impurities, yielding pure  $K_2ZrF_6$  which can be converted to zirconia by ammonia precipitation.

The second process, based on solvent extraction, involves the fusion of zircon with excess caustic soda at about 600°C to form a sodium zirconate cake. This cake is dissolved in nitric acid to give a nitrate feed solution from which zirconium is extracted by tributyl phosphate diluted with kerosene. The loaded organic is then scrubbed with nitric acid for the removal of any associated hafnium. It is finally treated with sulphuric acid in order to strip off zirconium. The pure

zirconium solution is then precipitated with ammonia, filtered, dried, and calcined to yield pure zirconium oxide. Hafnium is left behind in the raffinate after zirconium extraction and is processed to give pure  $HfO_2$  by similar techniques.

The second process has been finally chosen after a comparison of the two processes with reference to capital cost, production cost, ease of separation, recovery of zirconium and hafnium, and availability of chemicals. Figure 8.11 shows the flowsheet for the solvent extraction process.

#### STAGE 2: PRODUCTION OF DUCTILE ZIRCONIUM

For the production of ductile zirconium, Kroll's process is employed, where anhydrous zirconium tetrachloride vapours are reduced by magnesium in an argon atmosphere. Subsequently, excess magnesium and  $MgCl_2$  are removed by high-vacuum treatment. Zirconium is obtained as a partially sintered sponge-like product. The process flowsheet is shown in Fig. 8.12.

The zirconium tetrachloride required as the initial raw material is produced by the chlorination of zirconia-carbon briquettes at 750°C in a silica brick-lined furnace. The briquettes are heated by graphite electrodes embedded in the charge itself. The chloride vapours from the furnace are condensed in a double-walled inconel condenser at 150–200°C to yield dense crystals.

Magnesium reduction is carried out in a specially designed stainless steel retort under slight positive pressure of argon. The tetrachloride and the metal are initially loaded into separate containers inside the retort. Some of the volatile impurities are then removed by flushing the reactor with argon at 150–200°C. Subsequently, the temperature is raised and the tetrachloride is distilled in a controlled fashion, i.e., it is made to react at the surface of the molten magnesium. Adequate provisions are made to control any excessive rise in temperature or pressure. There are also provisions for the automatic and manual bleeding of chloride vapours whenever necessary. At the end of the reduction reaction, the reactor contains zirconium sponge that is covered by magnesium chloride.

The separation of magnesium chloride and excess magnesium is carried out in another heavy-walled inconel retort under a vacuum of 1 micron Hg at 900°C. The resulting sponge is pyrophoric, and proper precautions need to be taken during its collection.

It has been found that the addition of a small quantity of sodium to the magnesium during the initial stages of reduction not only improves the purity of the sponges but also increases its crushability, facilitating collection. The effectiveness of the sodium addition is attributed to the gettering action of sodium in the initial stages and the scavenging action of sodium chloride during magnesium reduction.

#### STAGE 3: PRODUCTION OF MILL PRODUCTS FROM SPONGE METAL

Conventional induction melting of zirconium alloys in graphite crucibles is unsuitable due to the prohibitive carbon pick-up. At present, consumable electrode arc melting with water-cooled copper moulds is the only process successfully employed for the tonnage melting of alloys. Procedures have been evolved for (1) the compaction of sponge briquettes with alloying additions, (2) the fabrication of consumable electrodes by argon arc welding in an inert atmosphere, and (3) controlled vacuum arc melting. For homogenizing the alloy composition and for removing the volatile impurities, a double vacuum arc-melting sequence is employed. The shaping of the alloy and extrusion of tubes are achieved through a series of steps, each of which need special precautions. (These precautions are, however, not discussed here.) A flowsheet for the fabrication of zircaloy-2 tubes is shown in Fig. 8.13.

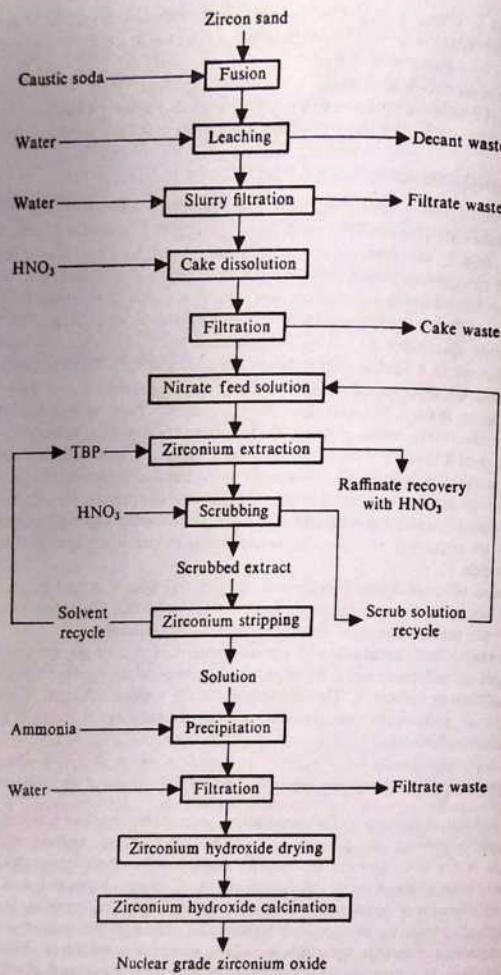


Fig. 8.11 Production of Pure Zirconium Oxide.

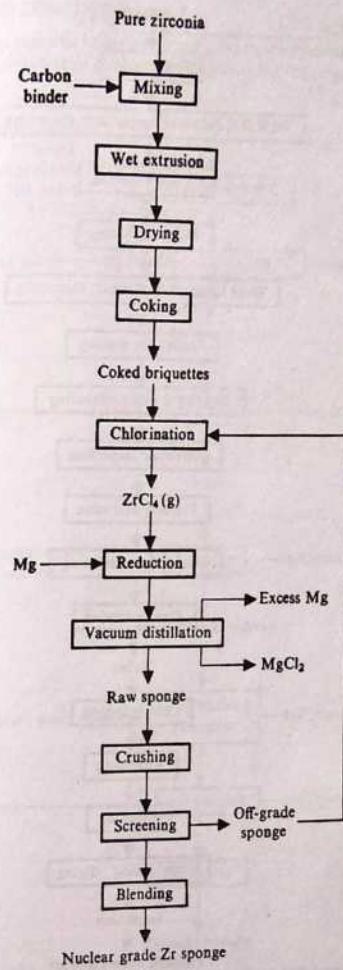


Fig. 8.12 Production of Zirconium Sponge.

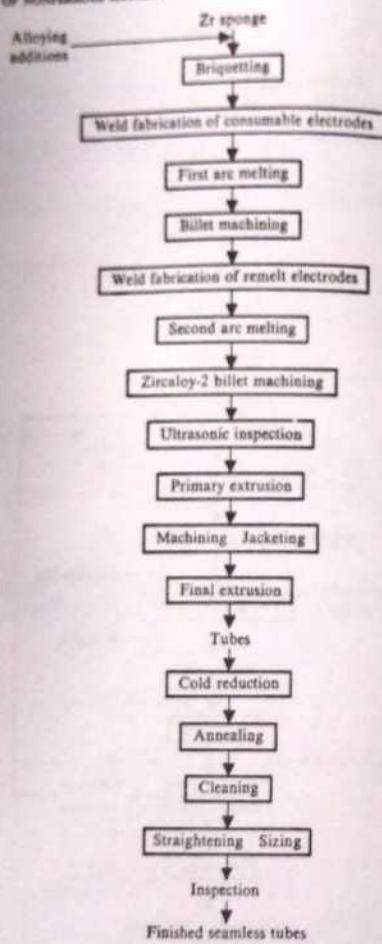


Fig. 8.13 Production of Zircaloy-2 Tubing.

## PRODUCTION OF ZIRCONIUM POWDER

Zirconium is sometimes required in the powdered form for nonnuclear uses. This powder is produced by the calcium reduction of the oxide. A flowsheet for the process is shown in Fig. 8.14.

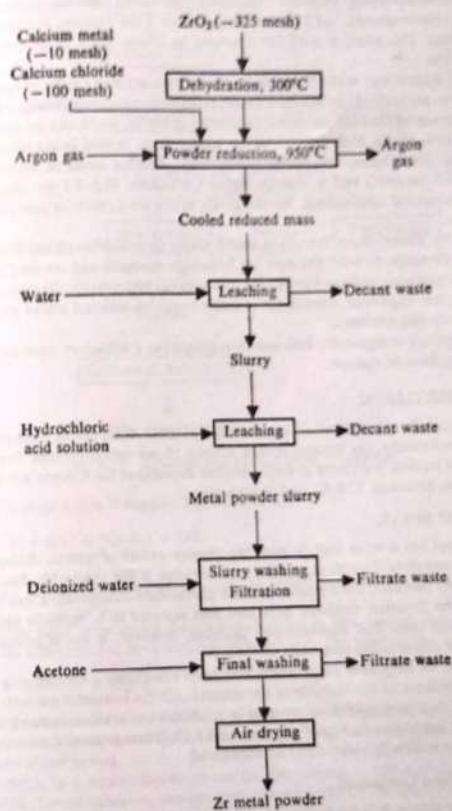


Fig. 8.14 Production of Zirconium Metal Powder.

### 8.11 BERYLLIUM EXTRACTION

Although beryllium has several nonnuclear uses, its applications in nuclear reactors have made the metal more important. In nuclear reactors, use is made of the metal's low atomic number and high neutron-absorbing capacity. Therefore, the metal can be used as a moderator. Under certain circumstances, such as under radiation from radium, beryllium by itself can produce neutrons. The metal is used for windows in X-ray tubes as it absorbs a minimum fraction of X-rays.

Among the nonnuclear uses of beryllium, the various series of Cu-Be alloys are noteworthy. For instance, one particular high-strength, heat-treated series of alloys contains 1.8–2.2 per cent Be and a slight amount of Co ( $\approx$  2 per cent). This series of alloys, which can be cast into complicated shapes because of the high fluidity in the molten state, is used in the manufacture of items such as springs, diaphragms, and pump components. Another series of alloys has a lower Be content (0.25–0.7 per cent) and a slightly higher Co content (1.5–2.5 per cent). This series is mostly used in electrical applications. All the Be-Cu alloys are capable of precipitation hardening to a high degree.

Besides Cu-Be alloys, there are other useful alloys in which beryllium forms an important constituent. Ni-Be alloys (1.7–2.5 per cent Be) have high strengths and are used in the fabrication of items such as precision springs for watches and surgical instruments. Beryllium finds application as a minor, but important, constituent in many corrosion-resistant alloys which are used in the watch industry and dentistry.

Amongst beryllium compounds, BeO can be employed as a refractory material up to 2200°C in an inert atmosphere or vacuum.

#### SOURCES OF BERYLLIUM

Beryl, a crystalline form of beryllium aluminium silicate ( $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) is the principal mineral of beryllium. Theoretically, the mineral should contain 14 per cent beryllium. Brazil, Argentina, and India are the leading producers of beryl. Smaller deposits of the mineral are found in South Africa, Zimbabwe, Morocco, U.S.A., and Madagascar.

#### TREATMENT OF BERYL

The density of beryl has a value that is near the density values of quartz, feldspar, and other common gangue materials. Therefore, gravity concentration is not applicable. Since beryl is often found as crystalline particles, during mining, some preliminary concentration can be achieved by hand-picking. Some flotation methods have also been reported to be partially successful in concentrating low-grade ores. The concentration problem, however, is not of primary importance because high-grade deposits are common.

The production of beryllium compounds from beryl constitutes a difficult step in the extraction of beryllium because of the stability of the mineral. All the successful methods of ore breakdown make use of an initial solid-state reaction to produce a leachable compound. The flowsheets for three processes are shown in Figs. 8.15, 8.16, and 8.17. These processes essentially yield the oxide, which can be indirectly chlorinated or fluorinated.

#### Reduction of Beryllium Compounds

It is not possible to reduce BeO by carbon at ordinary temperatures because of the high stability of the compound. However, it is possible to reduce BeO in an electric furnace at about 1800°C in

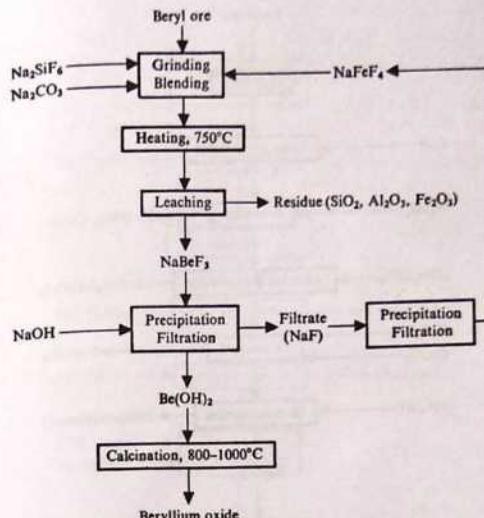
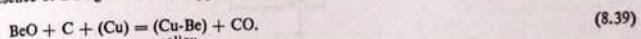


Fig. 8.15 Fluoride Process for Beryl Treatment.

the presence of a large excess of copper. The reaction is



By maintaining a low concentration of beryllium, carbide formation is avoided and the reduction is made easier.

Pure beryllium must be produced mainly from halides. In this context, the magnesium reduction of beryllium difluoride has been successfully employed. The reaction is



The MgF<sub>2</sub> produced contains a small amount of BeF<sub>2</sub>, which is separated by leaching with water. The beryllium metal finally produced contains 0.1 per cent BeO, metallic impurities such as magnesium, and chloride slag.

Although BeCl<sub>2</sub> is a nonconductor, it can be electrolyzed at 750–820°C after dissolution in sodium chloride. Lower operating temperatures (around 450°C) for electrolysis are attained by using eutectic mixtures of NaCl and KCl. BeCl<sub>2</sub> has also been reduced by Kroll's process. For this process, purified BeCl<sub>2</sub> vapour is made to react at a controlled rate with lithium, sodium, or

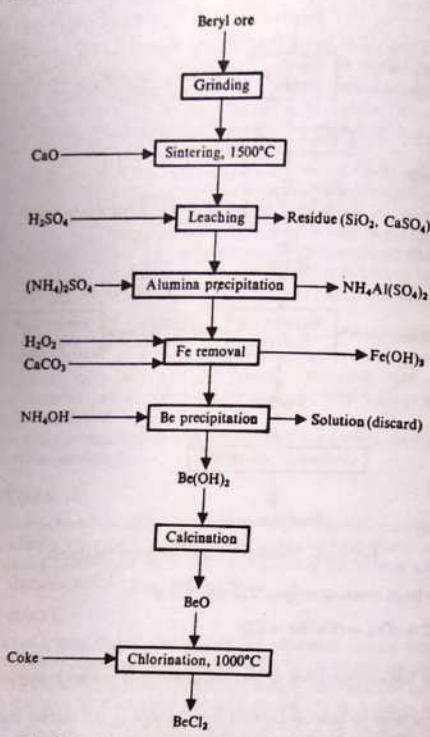


Fig. 8.16 Lime Sinter Process for Beryl Treatment.

magnesium in an inert atmosphere. The excess metal reductant and the byproduct salt are subsequently volatilized from the metallic sponge by vacuum heating.

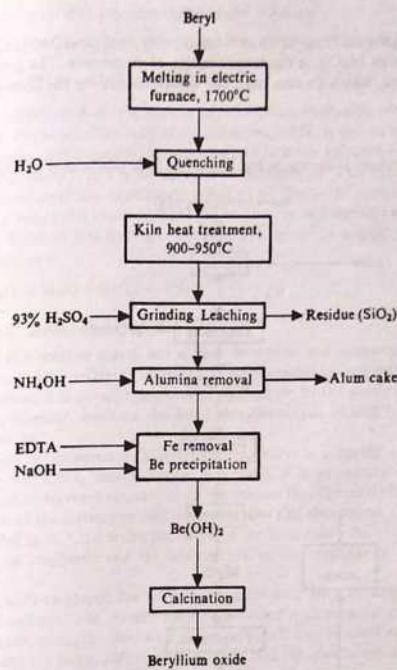


Fig. 8.17 Sulphate Process for Beryl Treatment.

## PART II

### 8.12 EXTRATION OF OTHER METALS FROM CHLORIDES

In addition to the nuclear reactor metals, other metals such as alkali and alkaline earth metals, rare-earth metals, and titanium are extracted from the halides. In general, they have a high affinity for both oxygen and the halogens and are extracted by the electrolytic decomposition of the chloride because, in most instances, the carbothermic or hydrogen or metallocerhetic reductions are not feasible or economically viable.

In this part, the extraction of magnesium (from sea-water), alkali and alkaline earth metals, rare-earth metals, and titanium is described.

### 8.13 MAGNESIUM

The production of magnesium from oxide ores has already been described in Chapter 6. However, sea-water, which contains  $MgCl_2$ , is the largest source of magnesium. The process for magnesium recovery from sea-water, which we now describe, was developed by the Dow Chemical Company (U.S.A.).

#### DOW PROCESS

The Dow process flowsheet is shown in Fig. 8.18. The bulk production of magnesium from sea-

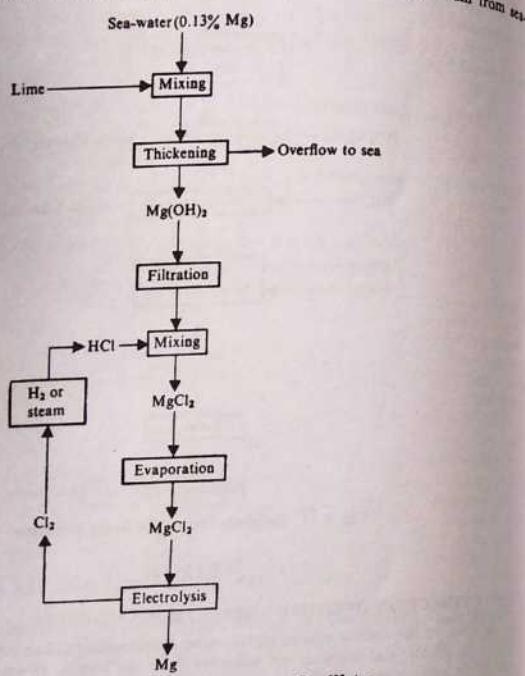
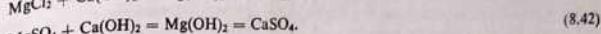
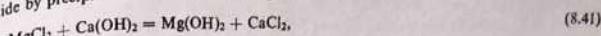


Fig. 8.18 Production of Magnesium from Sea-Water.

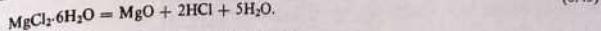
water constitutes an operation that is somewhat extraordinary, considering the immense volume of water that has to be handled.

The first step of the Dow process involves the collection of magnesium as the insoluble

hydroxide by precipitation with lime according to the reactions



The suspension is distributed to thickeners, in which the hydroxide settles; the clear overflow being pumped back to the sea. The milk of magnesia underflow is picked up by slurry pumps and delivered to filter tanks. Subsequently, magnesium hydroxide is agitated with 10 per cent hydrochloric acid, which converts it to a weak solution of the chloride. This dilute solution is concentrated and filtered to recover the crystallized solids. The filtrate is subjected to evaporation in order to recover the remaining chloride. Care has to be exercised during evaporation because the hydrochloric acid is liable to lose hydrogen chloride and result in a final product contaminated with oxide. The reaction is



#### ELECTROLYSIS OF MAGNESIUM CHLORIDE

Magnesium, which is a reactive metal, has a high decomposition potential. Therefore, aqueous electrolysis would not be feasible as hydrogen evolution would occur before the decomposition of  $MgCl_2$ . Nevertheless, it is possible to produce magnesium by the sodium reduction of  $MgCl_2$ . The usual process, however, involves the fused salt electrolysis of  $MgCl_2$  or mixtures of  $MgCl_2$  and other stable halides.

In the electrolysis of magnesium chloride, the electrolyte is normally composed of 25–30 per cent  $MgCl_2$ , 15 per cent  $CaCl_2$ , and 50–60 per cent  $NaCl$ . A large amount of flux is necessary to maintain fluidity and to increase the density of the bath so that the metal liberated at the cathode floats on the surface of the electrolyte and does not sink. The theoretical decomposition voltage of the dissolved  $MgCl_2$  is 3.3, but the resistance of the bath raises the voltage to 6.6. A current of 30,000–50,000 A is employed and the temperature of the electrolytic cell is maintained at 670–730°C.

The electrolytic cells employed for magnesium extraction may be divided into two classes: namely, lined and unlined. The former must be provided with separate cathodes, usually made of steel, whereas in the latter, the steel wall of the cell itself may be used as the cathode. In both cases, graphite anodes are employed. It may be noted that the anodes are inert and are, therefore, not consumed. The cells operate in an inert atmosphere.

It is necessary to prevent the chlorination of the metallic product by the gaseous chlorine evolved at the anode. Thus, the metal must be diverted away from the anode zone and recombination prevented by special design features. Chlorine gas is collected in a special hood and the collection of the metal is facilitated by diverting it to a pool. The chlorine set free at the anode is used to dry the incoming  $MgCl_2$  and also to chlorinate  $Mg(OH)_2$ . For perfect operation, the chloride feed must be completely anhydrous. However, complete drying is both expensive and difficult. Therefore, processes for electrolyzing a chloride that has between one and two moles of combined water have been evolved.

A simple sketch of an electrolytic cell for magnesium production is shown in Fig. 8.19.

#### 8.14 ALKALI AND ALKALINE EARTH METALS

Amongst the alkali metals, sodium is the most commonly used. Metallic sodium can be prepared

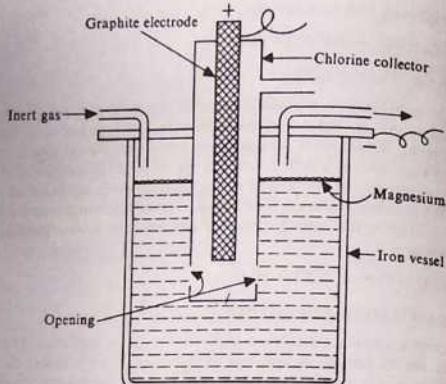


Fig. 8.19 Electrolytic Cell for Magnesium Production.

at a low cost and, therefore, it finds extensive technical application. The metal is used in vapour lamps, as a reducing agent in the laboratory and in the chemical industry (mostly as an amalgam), and as the starting material for the synthesis of a large number of compounds.

Potassium and caesium find occasional use in the laboratory and in the chemical industry. These metals have been used in photoelectric cells and as reducing agents. Lithium has found considerable technical application as an alloying element. A small addition of lithium is known to improve the mechanical properties of some alloys. For example, the addition of a few thousandths of a per cent to aluminium imparts a degree of hardness which cannot be equalled by other means. Lithium proves useful in the fabrication of heat-resistant glassware because it has a low thermal expansion coefficient. The metal is also used as a deoxidant for copper. High-energy secondary batteries that employ a combination of sodium and lithium are in the developmental stage. If commercially successful, the demand for sodium and lithium is likely to increase.

Amongst the alkaline earth metals, calcium finds wide application. Metallic calcium is used in the production of certain lead alloys, e.g., an alloy containing 0.7 per cent Ca, 0.6 per cent Na, and 0.04 per cent Li has been extensively used as a bearing metal. Calcium is also extensively used as a reducing agent in the reduction of compounds of several reactive metals. The uses of beryllium and methods of its production have been discussed elsewhere in this chapter.

#### PREPARATION OF ALKALI AND ALKALINE EARTH METALS

Since the alkali and alkaline earth metals themselves form stable halides, they are not produced by the metallocermic reduction of their halides. Because of the difference in the stabilities of various halides, it is theoretically possible to reduce NaCl by, say, potassium, which forms a more stable chloride. However, such a reduction is not considered commercially sound or attractive from technical point of view because of the rather small difference in the free energies of

formation of the chlorides. Hydrogen reduces a number of chlorides, particularly if a high H<sub>2</sub>/HCl ratio is maintained at elevated temperatures. However, such a reduction is not commercially attractive and not possible in the case of alkali and alkaline earth metal chlorides. These metals are, therefore, produced by the electrolytic decomposition of their fused salts. Halides generally have low melting points, especially in the form of binary or ternary mixtures. In most cases, they are mutually soluble, thus making available a wide variety of compositions for electrolysis.

Many halides have low boiling points and high vapour pressures. These liquids may, therefore, be purified by distillation or fractional distillation. Of the halides to be considered for fused salt electrolysis, the fluorides and the chlorides are preferred. Chlorides are normally hygroscopic and, therefore, they present handling problems. On the other hand, fluorides have the disadvantage of producing on electrolysis, fluorine, which is more corrosive than chlorine.

A typical electrolytic cell used for the production of alkali and alkaline earth metals would involve (1) a suitable low melting mixture of electrolytes and (2) a proper electrolytic cell design in order to eliminate chances of back reaction.

We now describe the extraction of individual alkali and alkaline earth metals using the electrolytic route.

#### Production of Sodium

Sodium was first produced on a commercial scale towards the end of the nineteenth century. The process employed was the electrolytic decomposition of fused sodium hydroxide (Castner's process). This process was eventually superseded in the 1920's by the Downs process, which involved the electrolysis of fused sodium chloride. The Downs process, which is still in use, accounts for an annual world production of nearly 200,000 tons.

The electrolytic process is entirely dependent on the availability of cheap electric power. Where power is not easily available or is prohibitively expensive, other methods have been attempted. Some of which are now mentioned.

Carbon reduction, at high temperature, of various sodium compounds, e.g., chloride, sulphate, carbonate, or hydroxide. In this case, the reduction is aided by applying reduced pressures or by employing an inert atmosphere. The metal is recovered by the distillation and condensation. The recovery can be enhanced by employing a continuously flowing inert carrier gas. After reduction, rapid cooling of sodium vapours is sometimes achieved using molten sodium lead alloys or molten tin as quenching liquids.

Sodium is also produced when sodium chloride is made to react with calcium carbide by applying reduced pressures or by passing a stream of inert gas at temperatures above 800°C.

Still other methods include the reduction of sodium chloride by silicon in the presence of lime and the reduction of sodium ferrite and sodium silicate with iron. However, none of these methods has ever found wide application.

Although it is theoretically possible to produce a sodium amalgam that contains a small percentage of sodium by the electrolysis of brine using a flowing mercury cathode, the weight of the mercury to be subsequently evaporated in order to obtain pure sodium is very large. This process, therefore, will not become commercially attractive unless a cheap method for the separation of mercury is developed.

#### Downs' Process

The most well-established process for the production of sodium, the Downs process, involves the electrolytic decomposition of sodium chloride. Since the principal and, indeed, the almost sole

source of sodium in nature is common salt, it has a number of advantages over sodium hydroxide as the raw material. For example, common salt is considerably cheaper than sodium hydroxide and is also more readily purified and the electrolysis of the chloride produces a valuable byproduct, namely, chlorine. Consequently, earlier processes, such as Castner's process and Gilbert's process, which employed the electrolysis of the hydroxide, became obsolete. It should, however, be noted that the sodium chloride electrolysis suffers from certain drawbacks. For instance, the melting point of sodium chloride is high ( $804^{\circ}\text{C}$ ). Chloride electrolysis, therefore, requires much higher operating temperatures compared with hydroxide electrolysis which can be carried out at  $310\text{--}320^{\circ}\text{C}$ . The boiling point of sodium is also high ( $880^{\circ}\text{C}$ ). Consequently, the vapour pressure of sodium is quite high in the Downs cell, which operates at around  $850^{\circ}\text{C}$ . The vapours may readily burn in air (unless the cell design is suitably amended), leading to serious corrosion problems at high temperatures. Some of these drawbacks can be overcome as follows:

- (1) The liberated sodium may be dissolved in a molten cathode to form an alloy from which the metal may be recovered later by distillation or other methods.
- (2) The operating temperature may be lowered by using low melting eutectic mixtures (obtained by adding other more stable salts to sodium chloride).

A very large number of cells have been designed and operated. The Downs cell, shown schematically in Fig. 8.20, is amongst the most successful ones. This cell employs a hydrostatic

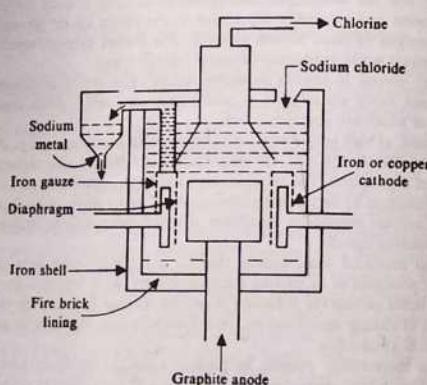


Fig. 8.20 Downs' Cell for Electrolytic Production of Sodium.

head of the electrolyte to ensure the continuous removal of the sodium automatically produced. The most distinguishing feature of this cell is that the anode is located inside the cathode. The cathode is a cylindrical ring of cast steel. The anode is constituted by a composite cylindrical graphite assembly which gives a projection through the cell bottom. A conical brick-lined bell dome, submerged in the electrolyte and situated directly above the anode, serves to collect the

chlorine. The contact of sodium with chlorine is prevented inside the cell by a diaphragm made of 16 mesh steel gauze. The dome carries an inverted trough located over the cathode which collects the metal. The electrolyte is a mixture of sodium chloride about 42 per cent and calcium chloride. The melting point of the mixture is sufficiently low to allow cell operation at around  $590^{\circ}\text{C}$ . The sodium automatically produced rises in the submerged collector because its density is less than that of the electrolyte. The metal goes through a riser pipe and then overflows into an external receiver.

The process is made continuous by continuously feeding dry sodium chloride during electrolysis.

#### Production of Other Alkali Metals

Various methods have been proposed for the reduction of lithium compounds to the metal. The classical electrolytic method, however, remains the most satisfactory. In this method, an eutectic mixture of lithium chloride and potassium chloride is electrolyzed at  $400\text{--}420^{\circ}\text{C}$  at 8–9 V. The recommended current density for the electrodes is around  $9\text{--}12 \text{ A/m}^2$ . In this case, 85–90 per cent current efficiency is achieved.

The annual demand for metallic lithium is small enough for the metal to be produced in cells with small unit capacities, say, 40–50 kg of metal per day.

Potassium is another metal that is produced by the electrolysis of halides. Potassium chloride can be dissociated in the same manner as sodium chloride or lithium chloride. The decomposition of the oxyacid salts of potassium dissolved in fused potassium halides is a chlorine-free operation as only  $\text{CO}_2$  is set free at the graphite anode. Apart from electrolytic processes, purely chemical processes also possess considerable importance in the preparation of potassium. The metal can be produced either by making  $\text{CaC}_2$  react with KF at high temperatures or  $\text{KCl}$  with Na also at high temperatures. In the latter case, a K-Na alloy is produced which can be directly used in heat exchangers.

#### 8.15 THE ALKALINE EARTH METALS

Group IIA of the periodic table contains the metals Be, Mg, Ca, Sr, Ba, and Ra. The extractive metallurgy of beryllium and magnesium has already been discussed in Sections 8.11 and 8.13, respectively. In this section, the production of the alkaline earth metals, calcium, strontium, and barium is discussed. Radium is used primarily in the form of its salts and has few applications as metal. Of the alkaline earth group metals, calcium follows magnesium as far as usage is concerned. Calcium is also abundant in the earth's crust, ranking fifth in the order of abundance.

The alkaline earth metals are less reactive than sodium and potassium and have higher melting points and boiling points. The common ores are sulphates, carbonates, oxides, and chlorides.

Calcium is the least expensive of the three alkaline earth metals, but is more expensive than sodium, which has a tonnage production that is almost 100 times higher. Yet, in metallurgical operations, calcium is often preferred to sodium. This is because the low melting point and the high vapour pressure of sodium are the disadvantages in deoxidizing, reducing, degassing, and alloying. Consequently, the less volatile calcium is often more suitable in such operations.

The metallurgical applications of the alkaline earth metals depend on their reactivity at high temperatures leading to the formation of stable nitrides, silicides, and carbides. At lower temperatures, stable hydrides are formed. Since the alkaline earth metals have the ability to fix residual

gases as oxides, nitrides, and hydrides, these metals have an important function, i.e., as getters, in the manufacture of electronic tubes.

#### PRODUCTION OF CALCIUM, BARIUM, AND STRONTIUM

Calcium can be produced by the electrolysis of pure molten calcium chloride or by the reduction of lime by aluminium under vacuum. The former process is carried out at about 800°C with a current efficiency of about 50 per cent. The latter, which is a retort process, is similar to the Pidgeon process for magnesium in the sense that the reaction proceeds under vacuum at 1150–1200°C with the vapour pressure of calcium being only 1–1.3 mm Hg. Calcium can also be produced by the sodium reduction of calcium chloride. The Downs cell, which is used for the electrolysis of fused NaCl, produces molten sludges that contain calcium. The calcium crystallizes out of the solution and is recovered from it by filtration. In fact, several processes have been developed which aim at the recovery of calcium from the Downs cell sludges which contain both sodium and calcium.

Attempts have been made at the Central Electrochemical Research Institute at Karaikudi (Tamil Nadu) to produce calcium through the electrolysis of  $\text{CaCl}_2$  by employing the sodium cell set-up, with bottom graphite arrangement having an interelectrode distance of about 5 cm. The hood arrangement has been eliminated. The possibility of obtaining Ca-Mg alloys has also been established using  $\text{CaCl}_2\text{-MgCl}_2$  mixtures.

In the case of barium, it should be noted that the electrolysis of the chloride does not yield any metal but only a subchloride. Therefore, it is convenient to prepare barium by the reduction of barium oxide at temperatures above 1000°C using aluminium as the reducing agent. Alloys of barium and zinc can be produced by the electrolysis of a mixture of the chlorides of both metals employing a zinc cathode. Also, other heavy metal cathodes may be employed to produce other alloys. Barium-calcium alloys can be produced by the reduction of barium chloride by calcium.

Strontium may be produced by the electrolysis of the fused chloride mixed with potassium chloride. The aluminium reduction of strontium oxide is also comparatively easy.

#### 8.16 RARE-EARTH METALS

The rare-earth metals consist of fifteen Group III elements of the periodic table with atomic numbers from 57 to 71. These metals, which are present in a variety of minerals, are chemically very similar and their properties are, therefore, often discussed as a group. Monazite contains an appreciable amount of rare-earth metals. To a lesser extent, these metals are also present in the fission products of uranium and plutonium.

Rare earths are used to the largest extent (about one-fourth of total production) in the form of misch metal, which has an approximate composition: 45–50 per cent Ce, 18 per cent Nd, 5 per cent Pr, 20–25 per cent La, and small amounts of other metals. Misch metal is used in desulphurizing ferrous alloys, in improving mechanical properties of ferrous alloys, and in making nodular cast irons. It is also used as the flint material in lighters. Misch metal has also found several alloying applications in nonferrous metallurgy. For instance, it reduces the porosity in magnesium alloys, imparts strength to aluminium alloys without impairing their conductivity, and improves hot workability of brass.

Next to misch metal, several thousand kg of cerium, lanthanum, and didymium ( $\text{Nd} + \text{Pr}$ ) are produced annually for special use in chemical and metallurgical industries. Various compounds of rare earths are used in the ceramic and glass industries and in carbon arc lighting. Some particular uses of rare-earth compounds are as follows:

Compound	Use
Rare-earth chlorides	Glass polishing, as catalysts for petrochemical industries, in special ferrous casting, and as electronic components in colour television
Rare-earth fluorides	In carbon electrode manufacture, in the production of nodular cast iron, special steels, and rare-earth alloys
Cerium oxide	In the manufacture of special glass and refractory, electronic and solid-state devices, and television industry
Cerium nitrate	In gas mantle manufacture, in fertilizer and petrochemical catalysis
Rare-earth oxides	In the arc carbon industry, glass polishing, in optical glass production, and in refractory applications

#### PRODUCTION OF RARE EARTHS

The rare earths are obtained from monazite during the extraction of thorium and are recovered from the monazite leach liquors by precipitation. Cerium may be separated by oxidizing it to the tetravalent state, when it acquires properties that are quite different from those of the trivalent rare earths. The separation is carried out on the basis of chemical precipitation and the crystallization of suitable salts. The other rare earths are subsequently separated as compounds by ion-exchange methods.

Several methods have been used for the production of rare-earth metals from their compounds. Some of these methods are as follows:

- (1) The electrolysis of fused chlorides in alkali chlorides such as  $\text{NaCl}$  and  $\text{KCl}$ . (This method is mainly used for the commercial preparation of misch metal.)
- (2) The electrolysis of anhydrous chlorides in alcohol with a mercury cathode.
- (3) The metal reduction of anhydrous halides using Mg, Ca, Na, K, and Al.
- (4) The thermit process of reduction of the oxides and nitrates by metals such as Al and Zr with a chlorate booster.
- (5) The electrolysis of fused chlorides with an Mg-Cd cathode. (Mg and Cd can be subsequently distilled off from the alloy produced.)
- (6) The electrolysis of aqueous chloride solutions and acetate solutions using sodium amalgam cathodes.
- (7) The reduction of oxides by molten magnesium at around 1000°C.
- (8) The reduction of fluorides by molten magnesium at around 800°C.

The foregoing methods have their own advantages and disadvantages. The large-scale commercial production of rare earths, i.e., in the form of misch metal has been limited to the electrolysis of fused anhydrous chlorides because special procedures must be adopted for the

dehydration of the compounds. Usually, the chlorides are melted in cast iron or steel pots or in ceramic vessels and dehydrated by prolonged vacuum treatment.

#### PRODUCTION OF RARE EARTHS IN INDIA

The Indian Rare Earths Limited (IREL) has set up a plant in Alwaye (Kerala) which has a capacity to treat about 4500 tons of monazite per year. IREL, which is export-oriented, meets about a third of the total world requirement of rare-earth products such as rare-earth fluorides, rare-earth oxides, pure cerium oxide and pure rare-earth metals.

#### COMMERCIAL PRODUCTION OF MISCH METAL

Misch metal is produced on a commercial scale by the fused salt electrolysis of rare-earth chlorides obtained mainly from monazite. A flowsheet for obtaining rare-earth chlorides from monazite is shown in Fig. 8.21.

The rare-earth chloride from which the metal is to be extracted is dehydrated by vacuum heating. A vacuum of 700 mm Hg at 350°C produces a product with only about 1.5 per cent oxychloride. Sometimes, the hydrolysis of the chloride is retarded by adding, during heating, sodium chloride and calcium chloride. However, the addition of ammonium chloride is known to counter hydrolysis.

The mixed rare-earth chlorides are electrolyzed in a bath of  $\text{CaCl}_2\text{-NaCl}$  in a firebrick-lined cell at 850°C using a carbon anode and an iron cathode. The power requirement is around 15–16 kWh/kg of metal and the current efficiency around 45 per cent. The power requirement is rather high because nearly 14 V are applied across the electrodes. Although the reduction potential of the rare-earth metals ranges from –2.4 V for lanthanum to –2.1 V for lutetium, a high voltage is needed to overcome the ohmic resistance.

During electrolysis, the rare-earth metal collects at the bottom of the chloride bath and, therefore, strict atmosphere control in the cell is unnecessary.

A typical composition of the electrolytic misch metal is given in Table 8.9.

Table 8.9 Composition of Electrolytically Produced Misch Metal

Element	Chloride in the initial mixture (per cent)	Metal in misch metal (per cent)
Ce	46.9	53.0
La	24.5	23.0
Nd	19.5	16.0
Pr	6.0	5.0
Gd	0.5	2.0
Other rare earths Si, Fe, and Mg	≈ 2.6 to traces	≈ 1.0 to traces

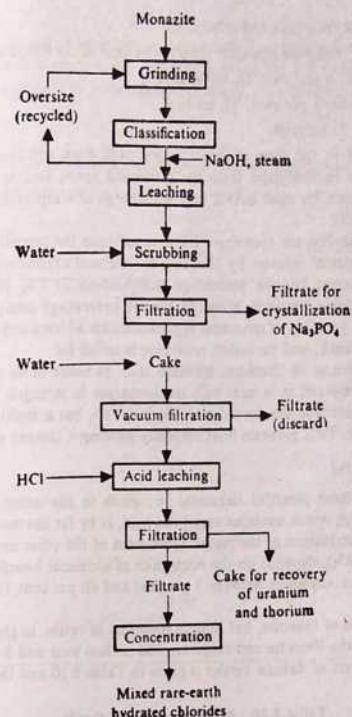


Fig. 8.21 Production of Rare-Earth Chlorides.

#### 8.17 TITANIUM

Titanium is playing an increasingly important role in this age of special alloys. The strength-to-weight ratio of titanium is very high, almost twice that of steel, and its corrosion resistance is better than even 18-8 stainless steel. Titanium alloys retain their strength even at higher temperatures and show less creep. Many titanium alloys can be age-hardened to enhance their strength properties. The current percentage breakdown of the usage of titanium on a world-wide basis is broadly as follows:

- (1) Jet engine components, 45.
- (2) Air frames, 25.
- (3) Missiles and spacecraft, 20.

(4) Chemical process industries and others, 10.

In the aerospace industry, titanium is mainly used in the form of the following alloy compositions:

- (1) Al, 6 per cent; V, 4 per cent; Ti, balance.
- (2) Al, 4 per cent; Mn, 4 per cent; Ti, balance.
- (3) Mn, 8 per cent; Ti balance.

Pure titanium is used in the form of sheets, tubes, rods, bars, and forgings. In the chemical industry, the bulk of the consumption is in the unalloyed form, i.e., as sheets and tubes. In general, Al-V-Ti alloys can be used over a very wide range of temperature, i.e., from 250°C to about 600°C.

Minor additions of titanium are sometimes made to enhance the corrosion resistance of stainless steels and reduce thermal stresses by lowering the thermal expansion. One particular alloy used in electrolytic processes has the percentage composition Ti 2.4, Ni 42, Cr 5.4, and Fe remainder. Various Weldable titanium alloys (a typical percentage composition V 13, Cr 11, Al 3, Ti rest) are used in a variety of structural applications for which a combination of properties such as light weight, strength, and corrosion resistance is called for.

Among other applications of titanium, mention may be made of its use as a deoxidizer for ferrous alloys. As a deoxidizer, it is next only to aluminium in strength. Yet, titanium may be preferable to aluminium because the deoxidation product  $TiO_2$  has a melting point much lower than that of  $Al_2O_3$ ; hence,  $TiO_2$  globules float up easily yielding a cleaner steel.

#### SOURCES OF TITANIUM

Titanium is among the most plentiful elements, i.e., ninth in the order of abundance in the earth's crust. Rutile ( $TiO_2$ ), which contains very little iron, is by far the more commonly accepted source material for the production of the metal. Utilization of the other more abundant mineral, namely, ilmenite ( $FeO \cdot TiO_2$ ), depends on the economics of chemical beneficiation. The common titanium ores can contain anywhere between 1 per cent and 60 per cent  $TiO_2$ , depending on the grade of the mineral.

India has vast deposits of ilmenite, but limited resources of rutile. In the Kerala beach sands, the estimated reserves of the ilmenite and rutile are 100 million tons and 3 million tons, respectively. The typical analysis of Indian rutiles is given in Table 8.10 and that of Indian ilmenites

Table 8.10 Analysis of Indian Rutiles

Constituents	Chavara grade (per cent)	Manavalakurichi grade (per cent)
$TiO_2$	91.8	96.2
$SiO_2$	1.9	1.2
$Fe_2O_3$	0.6	0.6
$Al_2O_3$	2.9	
$ZrO_2$	2.4	1.4

is given in Table 8.11.

The ilmenite ores can be magnetically concentrated to produce almost pure mineral (90-95 per cent ilmenite). The left-overs yield valuable raw material for the extraction of zirconium, thorium, and the rare earths. The beneficiation procedure for beach sands has been given earlier in this chapter.

Table 8.11 Analysis of Indian Ilmenites

Constituents	Chavara grade (per cent)	Manavalakurichi grade (per cent)
$TiO_2$	60.60	54.20
$Fe_2O_3$	24.18	14.20
FeO	9.25	26.60
$Al_2O_3$	0.96	1.25
MnO	0.39	0.40
$Cr_2O_3$	0.12	0.07
$V_2O_5$	0.15	0.16
MgO	0.89	1.03
$P_2O_5$	0.21	0.12
$ZrO_2$	0.90	0.80
Rare earths	Traces	0.12

#### 8.18 TREATMENT OF ILMENITE FOR UPGRADATION

To obtain titanium from ilmenite, the ores must be upgraded to a titania-rich product containing over 90 per cent  $TiO_2$ . Sometimes, this upgraded ilmenite is known as synthetic rutile. Apart from being the desired raw material for indigenous titanium production, this upgraded concentrate is used for pigment grade  $TiO_2$  production and has a good export market.

Ilmenite contains titania and iron oxide in (bound) spinel form and, therefore, cannot be upgraded by physical methods. Most beneficiation methods aim at the removal of the iron oxide by preferential chemical reaction with suitable reagents. The methods used are as follows:

- (1) The reduction smelting of ilmenite with carbon (and a suitable flux) resulting in a titania-rich slag and pig iron.
- (2) The direct leaching of ilmenite with acids under atmospheric pressure or high pressure resulting in the preferential dissolution of iron.
- (3) The selective halogenation of iron oxide to produce volatile iron halides.

**ELECTRIC SMELTING OF ILMENITE**

$TiO_2$  is a stable oxide and cannot be easily reduced. Carbon smelting in an electric furnace, therefore, produces pig iron and a high-titania slag. Ilmenite may thus serve as a source of iron as well. The titaniferous slag may be subsequently subjected to acid treatment for titania extraction.

**ACID LEACHING OF ILMENITE**

It is possible to selectively leach the iron oxides present in ilmenite by hot concentrated acids. Obviously, these oxides can be leached faster using finer particle size, high temperatures, and high pressures. Since ferrous oxide is more leachable, sometimes it is advantageous to subject ilmenite to an initial pre reduction. The partially reduced ilmenite, essentially containing ferrous oxide and titania, is then leached to remove iron. In another variation of this method, ilmenite is reduced in the solid state using reducing agents such as C, Co, H<sub>2</sub>, and CH<sub>4</sub>, to give metallic iron and unaffected  $TiO_2$ . Subsequently, iron is removed either magnetically or by chemical treatment, such as leaching with acids.

**HALOGENATION OF ILMENITE**

The halogenation of ilmenite aims at forming a volatile iron halide using reagents such as chlorine, bromine, hydrochloric acid, and ammonium chloride. Chlorination reactions have drawn the maximum attention, and several investigations have been carried out to determine the optimum conditions for the selective chlorination of ilmenite. Several Indian ore samples have also been thoroughly tested in this regard.

The removal of volatile iron halides leaves a  $TiO_2$ -rich residue. This residue itself may be chlorinated at 800–850°C in the presence of carbon to produce  $TiCl_4$ . The process is conducted either in a static bed chlorinator using hard porous briquettes or in a fluid bed chlorinator employing a granulated (rutile-carbon) charge. Titanium tetrachloride vapours invariably contain some ferric chloride. The efficient separation of ferric chloride and a high collection efficiency for the product are achieved by using a series of condensers and cyclone separators maintained at different temperatures.

The actual method to be used for the upgradation of any particular ilmenite ore would depend on the nature of the ore. Detailed laboratory tests and economic analysis have to be conducted before the final choice can be made. In all the foregoing processes, the aim is to finally produce titanium tetrachloride, from which the metal is produced by a metallothermic reaction. The main steps involved in the production of the tetrachloride are indicated in the flowsheet shown in Fig. 8.22.

**UPGRADATION PROCESSES**

It is not possible to discuss here in detail all the upgradation processes that have been reported in the literature. However, the essential features of some of the processes are summarized to bring out the variety of reactions that have been studied.

**Smelting of Ilmenite: Sorel Process**

Thermodynamic considerations indicate that iron can be selectively reduced from ilmenite by carbon. Although CaO and Na<sub>2</sub>O are suitable fluxes, they are not used in commercial practice as the objective is to obtain a high-titania slag with a minimum of other oxides. The reaction is

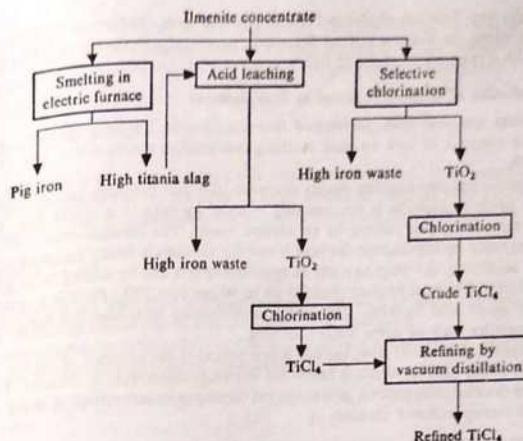
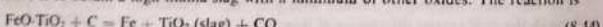


Fig. 8.22 Production of Titanium Tetrachloride from Ilmenite.

It should be noted that the presence of excess carbon produces pig iron. The slag contains 70–90 per cent  $TiO_2$ , 5–10 per cent Fe, and oxides of MgO and CaO from the gangue present in ilmenite. If the ore contains oxides of metals such as chromium and vanadium, then these oxides are also reduced to a large extent. The pre reduction of ilmenite often helps the smelting operation. The electrothermic smelting process has found commercial application in many countries, e.g., Canada, the U.S.A., Norway, Japan, and the U.S.S.R.

**Direct Acid Leaching of Ilmenite**

As already indicated, the leaching process may have many variations. For example, digestion with concentrated hydrochloric acid is essentially selective whereas that with concentrated sulphuric acid is not. In the latter case, both the oxides are taken into solution. However, subsequent processing of the leach liquor yields titania.

**Hydrochloric Acid Digestion of Ilmenite**

The hydrochloric acid digestion process has many variations with respect to factors such as temperature, pressure, acid concentration, and pre reduction of ferric oxide in the ore. In India, a plant at Tuticorin (Tamil Nadu) has adopted a leaching process for the treatment of about 60,000 tons of ilmenite per year to produce about half as much of synthetic rutile. Here, the ilmenite is pre reduced and the reduced iron is leached with dilute HCl, leaving behind high-grade  $TiO_2$  as a residue.

**Sulphuric Acid Digestion of Ilmenite**

The dissolution of ilmenite in hot concentrated sulphuric acid produces a solution that contains

$\text{FeSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{Ti}(\text{SO}_4)_2$ . Hydrous  $\text{TiO}_2$ , in a coarse form, is obtained from the solution by preferential hydrolysis. In India, a unit at Kerala is presently manufacturing  $\text{TiO}_2$  pigment by this process, with a capacity of about 25,000 tons per year.

## Solid-State Reduction of Ilmenite Followed by Iron Removal

Iron is sometimes removed from prereduced ilmenite by acid leaching, rusting, or magnetic separation. The removal of iron by acid leaching can produce a concentrate that contains 97 per cent  $TiO_2$ .

A slightly acidic aqueous solution simply corrodes iron and produces ferrous hydroxide. In one particular process, ilmenite is continuously reduced by coke in a rotary kiln, and iron is subsequently removed by this rusting in an aerated vessel. The ilmenite-water slurry (weight ratio 1 : 6) is agitated by blowing air through it and the solution is finally decanted off. Rusting is assisted by acidifying the pulp to a pH of approximately 4 and by adding small quantities of ammonium chloride. The final product contains up to 90 per cent TiO<sub>2</sub>. Further upgrading may be achieved by direct acid leaching. This reduction-oxidation technique has been tried out in India on a laboratory scale on some indigenous ores.

For the magnetic removal of iron, the ore is first heated in the presence of carbon and NaCl (or  $\text{Na}_2\text{CO}_3$ ) to about  $1200^\circ\text{C}$ , which is below the smelting temperature of ilmenite. The reduced ilmenite is then crushed, wet-ground, and subjected to magnetic separation in order to remove the slurries containing iron and titania.

## Preferential Chlorination of Ilmenite

Iron oxides in ilmenite are easily chlorinated in the presence of carbon by a variety of chlorinating agents. For chlorination, the mineral, taken in a powdery form, is briquetted with charcoal and a binder, for example, asphalt, tar, starch, molasses, or ferric chloride. The use of ferric chloride is said to have several advantages. For instance, it is produced by the chlorination reaction itself. In addition, it has a pronounced catalytic action on the chlorination of iron oxides. The rate of chlorination of iron oxides depends on several variables. The best results have been obtained by using ferric chloride as a binder, a fine particle size, smaller carbon content in the briquettes, and higher temperature. Better selectivity in chlorination is achieved by using higher temperatures. The chlorinating agents that have been used are chlorine, hydrogen chloride and various gas mixtures such as chlorine-hydrogen chloride, and carbon monoxide-chlorine.

The chlorination of ilmenite at 500–600°C in the presence of carbon (as about 6 per cent charcoal) and a  $\text{FeCl}_3$  binder yields a product that contains about 90 per cent  $\text{TiO}_2$ . The reaction may be accelerated by catalysts such as  $\text{CuO}$ ,  $\text{PbO}$ ,  $\text{MnO}_2$ ,  $\text{CaO}$ ,  $\text{CeO}$ , and  $\text{Ca}_3(\text{PO}_4)_2$ . By increasing the temperature to 900–1000°C, we can obtain a residue richer in  $\text{TiO}_2$  (95–98 per cent).

As already indicated earlier,  $TiO_2$  itself is subsequently chlorinated to give crude  $TiCl_4$ . This crude  $TiCl_4$  is purified by several techniques. For instance, dissolved gases may be removed by using inert gases and more volatile impurities such as  $SiCl_4$  are removed by fractional distillation.

### 8.19 CHLORINATION OF TiO<sub>2</sub>

The  $TiO_2$  from natural rutile or upgraded ilmenite has to be chlorinated to produce  $TiCl_4$  that is suitable for metal production. Chlorination is carried out in the presence of carbon. If there is no carbon in the system, then the reaction is



The free energies of formation of the oxide and the chloride at 1000°C are, respectively, -162 kcal per mole of the compound and -132 kcal per mole of the compound. Accordingly, the standard free energy change  $\Delta G^\circ$  of the chlorination reaction is 30 kcal. Now,  $\Delta G = \Delta G^\circ$  in K, that is,

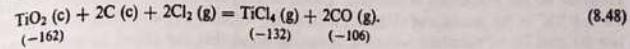
$$\Delta G = 30,000 + R1273 \ln \frac{P_{O_2} \cdot P_{TiCl_4}}{\sigma_{TiO_2} \cdot P_{Cl_2}}. \quad (8.46)$$

The activity of  $TiO_2$  is unity because the oxide stays as a pure solid. Also, according to reaction (8.45) the partial pressure of oxygen must be equal to that of titanium tetrachloride gas. For the reaction to proceed  $\Delta G < 0$ , we obtain the necessary condition for the reaction to occur as

$$\frac{P_{TiCl_3}}{P_{Cl_2}} = 1.25. \quad (8.47)$$

If the total pressure is 1 atm, then it is easy to show that  $p_{\text{TiC}_4}$  is about 0.3 atm. It is obvious that in the absence of carbon, there would be very little conversion.

The conditions change drastically when carbon is present in the system. Assuming that only CO is formed, the reaction for indirect chlorination is



The figures within parentheses give the free energies of formation of the respective compounds at 1000°C. From these values, the standard free energy change for indirect chlorination is obtained as -76 kcal. Therefore,

$$\Delta G = -76,000 + R1273 \ln \frac{P_{CO}^2 \cdot P_{TiCl_4}}{P_{Cl_2}^2 \cdot \sigma_{TiO_2} \cdot \sigma_C^2}. \quad (8.49)$$

The activity of  $TiO_2$  and that of carbon may be taken as unity. Again, it is obvious that, in the products, the partial pressure of carbon monoxide must be twice that of titanium tetrachloride. Using these data, we obtain

$$\frac{P_{\text{THCH}}}{n^2} \approx 1.2 \times 10^{13}. \quad (8.50)$$

Since

$$p_{\text{Cl}_2} + p_{\text{HgCl}_4} + p_{\text{CO}} = 1 \text{ atm}, \quad (8.51)$$

$$p_{\text{CO}} = 2p_{\text{TiCH}_4} \quad (8.52)$$

we get

$$P_{\text{TiCl}_4} = \frac{1 - P_{\text{CH}_4}}{3}$$

From eq. (8.50),

$$\frac{(1 - p_{Cl_0})^3}{p_{Cl_0}^2} \approx 3 \times 10^{14},$$

that is, for equilibrium,

$$1 - 3p_{\text{Cl}_4} + 3p_{\text{Cl}_4}^2 - p_{\text{Cl}_4}^3 = 3 \times 10^{14} p_{\text{Cl}_4}^2 \quad (8.53)$$

Since  $p_{\text{Cl}_4} \ll 1$ , we can ignore  $3p_{\text{Cl}_4}^2$  and  $p_{\text{Cl}_4}^3$  for an approximate calculation. Consequently,  $p_{\text{Cl}_4}$  is given by

$$1 - 3p_{\text{Cl}_4} - 3 \times 10^{14} p_{\text{Cl}_4}^2 \approx 0,$$

which gives the value of  $p_{\text{Cl}_4}$  as  $5.7 \times 10^{-8}$  atm. It is evident that we can expect a very high (99.9 per cent or higher) extent of conversion of chlorine to tetrachloride during the indirect chlorination of  $\text{TiO}_2$  at 1000°C. Chlorination may also be done using HCl.

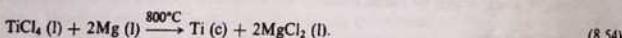
### 8.20 PRODUCTION OF METALLIC TITANIUM BY REDUCTION OF TITANIUM TETRACHLORIDE

Thermodynamic calculations indicate that  $\text{TiO}_2$  can be reduced either by carbon or other metals. Carbon reduction, however, is likely to produce the brittle carbide and magnesium reduction leads to a product that is contaminated with  $\text{TiN}$  and  $\text{TiH}_x$ . The alkali reduction of  $\text{TiO}_2$  is possible only at very high temperatures. Consequently, the halide route has always been more attractive for the production of titanium. The oxide  $\text{TiO}_2$  can be easily chlorinated by chlorine at about 600°C in the presence of carbon. The resulting chloride, namely,  $\text{TiCl}_4$ , serves as the main raw material for all reduction reactions. It may be noted that the efforts to produce the metal through the electrolytic reduction of  $\text{TiO}_2$  have largely been unsuccessful. Attempts have also been made to dissolve  $\text{TiO}_2$  in cryolite and to electrolyze the solution in order to produce titanium along the lines of the Hall-Héroult process for aluminium. Although  $\text{TiO}_2$  is slightly soluble in a cryolite-sodium chloride bath, the deposit obtained is usually powdery and heavily contaminated with impurities. Nevertheless, the electrolysis of halides such as titanium fluoride is said to produce a lumpy, ductile metal.

The successful commercial production of titanium was initiated by Hunter's process which used sodium vapours for the reduction of the tetrachloride gas. Sodium was later discarded in favour of a cheaper reducing metal, namely, magnesium. Magnesium reduction (Kroll's process), however, produces a spongy, brittle metal, and special treatment becomes necessary in order to produce a ductile metal from this sponge. The brittle nature of the metal is essentially due to residual impurities.

#### KROLL'S PROCESS

The reduction reaction in Kroll's process is written as



This reaction is carried out in a stainless steel container which has a provision for external heating by gas or electricity. The exothermicity of the reaction helps in maintaining the temperature once it has been attained and the reaction initiated. After the reaction is over, the titanium sponge is recovered either by dissolving  $\text{MgCl}_2$  and the excess magnesium by leaching with cold dilute hydrochloric acid or by distilling off  $\text{MgCl}_2$  and the excess magnesium by vacuum heating. The residue is a pure titanium sponge.

Several precautions have to be taken during reduction. For example, the reduction chamber has to be first heated to a high temperature of about 900°C and flushed with hydrogen to eliminate

all oxygen in order to avoid the oxidation of magnesium. All possible  $\text{MgO}$  coating is thus removed and the temperature lowered to 800–850°C. The chamber is then evacuated and kept under an inert atmosphere.  $\text{TiCl}_4$  is introduced into the chamber in the form of a stream of drops. A flowsheet for the production of titanium sponge from  $\text{TiO}_2$  is shown in Fig. 8.23.

The magnesium reduction of  $\text{TiCl}_4$  has been extensively studied at BARC, Bombay. The chlorination of  $\text{TiO}_2$  has been carried out using a temperature of 820–860°C in an argon atmo-

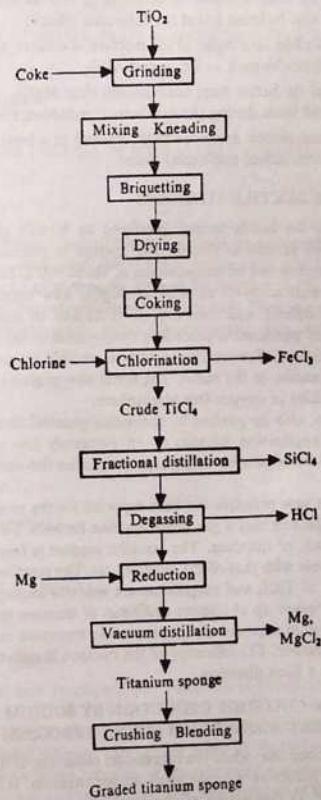


Fig. 8.23 Production of Titanium Sponge.

sphere, the reduction time being 5 hours. A maximum yield of about 85 per cent has been obtained using about 40 per cent excess magnesium. Any additional amount of magnesium is not beneficial. The average iron content at 860°C, due to the iron pick-up from the reaction chamber, is about 0.2 per cent. Bimetal reduction—using a mixture of magnesium and about 15 per cent sodium as the reducing agent—is said to markedly improve the yield of titanium sponge to about 96 per cent. Also, the sponge has a relatively lower iron content. As already mentioned, similar advantages have been noted also in the case of reduction of  $ZrCl_4$  by Mg-Na mixtures. The introduction of sodium into the system is said to bring about the following effects:

- (1)  $NaCl$ , which is formed as a result of the reaction of sodium, acts as an efficient scavenger with respect to impurity chlorides such as  $FeCl_3$  and  $AlCl_3$ .
- (2)  $NaCl$ , because of its better heat conductivity than  $MgCl_2$ , prevents, to a large extent, local overheating at isolated spots during the exothermic reduction reaction.
- (3)  $NaCl$ - $MgCl_2$  compositions are more fluid, leading to a better separation of metal from slag, a purer metal after distillation, and excess metal.

### 8.21 PRODUCTION OF DUCTILE TITANIUM

As stated in Section 8.20, the brittle sponge produced by Kroll's process can be converted to ductile titanium by various processes. Firstly, the sponge is purified. Vacuum distillation at pressures less than 100 microns and at temperatures of about 900°C for a period of 30–40 hours effectively removes the small amounts of residual  $MgCl_2$  and magnesium. The products are cooled in an argon atmosphere and then dry air is flushed to remove the traces of volatile chlorides. This complicated purification procedure nearly doubles the price of the metal.

Next, the sponge is melted. For melting, a carbon crucible is used which leads to about 0.5 per cent carbon contamination in the metal. The metal also contains small amounts of  $Mg$ ,  $Fe$ , and  $Si$ . Melting must be done in oxygen-free atmosphere.

The metal sponge can also be purified by the iodide process. However, this process has not found wide commercial application because of an extremely low rate of production. Better success has been obtained using powder metallurgy techniques for consolidating and briquetting the sponge.

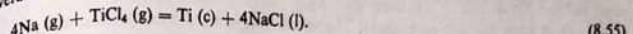
A process based on a new principle has been reported for the production of ductile titanium directly from  $TiCl_4$ . This method uses a gas phase reaction between  $TiCl_4$  and magnesium vapours to produce massive crystals of titanium. The metallic product is free of  $MgCl_2$  and magnesium and has purity comparable with that of the iodide metal. The reaction is a sort of wall reaction in which mixed vapours of  $TiCl_4$  and magnesium are made to impinge, and react at 900–950°C on the hot wall surfaces made up of ribbons or fillings of titanium metal. The  $MgCl_2$  produced and any unreacted magnesium vapours are spontaneously separated out of the reaction zone and condensed in a cooling chamber. The efficiency of the reaction is enhanced by causing the vapour mixture to flow rapidly in a fixed direction.

#### THEORY OF TITANIUM CHLORIDE REDUCTION BY SODIUM (HUNTER'S PROCESS) AND MAGNESIUM (KROLL'S PROCESS)

It has already been mentioned that while the magnesium reduction of  $TiCl_4$  (l) normally produces sponge titanium, sodium reduction directly gives ductile titanium. It is important to discuss the reasons for the difference in the nature of the metallic products of two apparently similar reactions.

#### Sodium Reaction

The overall reaction for the sodium reduction of  $TiCl_4$  is



This reaction is highly exothermic, and when carried out by simultaneously adding stoichiometric quantities of sodium and titanium tetrachloride to a reactor, local temperatures of about 1000°C are obtained.

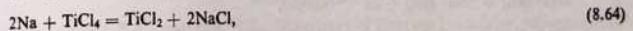
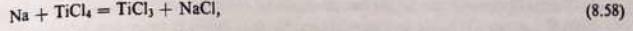
The free energy change of reaction (8.55) at 1000°C is  $-135.4$  kcal which amounts to the following  $K_p$  value:

$$K_p = \frac{a_{Ti} \cdot a_{NaCl}^4}{p_{Na} \cdot p_{TiCl_4}} \approx 10^{23}. \quad (8.56)$$

Since the activities of  $Ti$  and  $NaCl$  can be taken as unity, at least in the initial stages, we may write

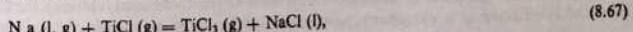
$$p_{Na}^4 \cdot p_{TiCl_4} \approx 10^{-23}. \quad (8.57)$$

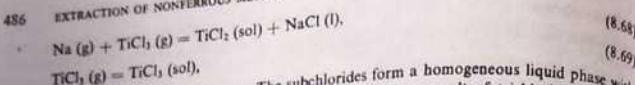
It is obvious that the equilibrium concentrations of sodium and titanium tetrachloride must be very small. It has been suggested that this is not possible if the reaction mechanism involves a reaction among five molecules at a time as implied by reaction (8.55). Obviously, a reaction is more likely if a smaller number of molecules are involved. Thus, we may postulate a series of steady-state elementary reactions taking place simultaneously. For instance, let us consider the reactions



Of these reactions, the first four reactions, i.e., reactions (8.58)–(8.61), should predominate because they are bimolecular.

The sublimation points of  $TiCl_3$  and  $TiCl_2$  at the atmospheric pressure are approximately 820°C and 1280°C, respectively, whereas the boiling point of  $NaCl$  is 1465°C. Since the subchlorides are soluble in fused sodium chloride at the operating temperatures, several equilibria are established between the liquid and the vapour. The most important reactions are





where sol denotes the solvated phase. The subchlorides form a homogeneous liquid phase with sodium chloride, and any excess sodium that is left over as a result of trichloride formation reacts with this condensed phase to produce titanium metal.

It has been shown that the mechanism of the reaction of sodium with titanium subchlorides in fused sodium chloride is of an electrochemical nature. The model is the same as that proposed for the galvanic corrosion of iron in an acidic solution containing oxygen (see Fig. 8.24). The

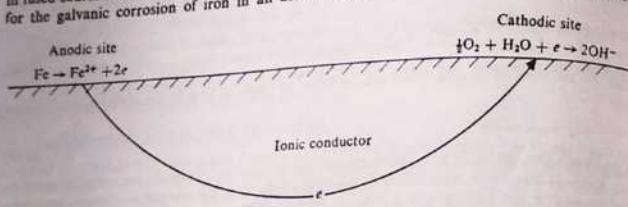


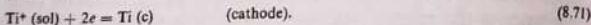
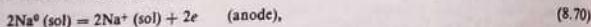
Fig. 8.24 Galvanic Corrosion of Iron.

requirements for an electrolytic reaction of this type are:

- (1) An active metal site for the anodic reaction.
- (2) A metallic conductor to transport the electrons from the anodic site to the cathodic site.
- (3) An electrolyte that is capable of ionic transport.
- (4) An ionic molecule.

The aforementioned requirements are met by the Na-TiCl<sub>4</sub> system contained in a metallic chamber.

For the condensed phase reaction between sodium metal and titanium subchlorides in solution, the reactions that have been proposed are



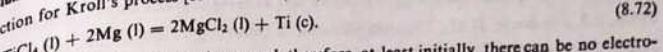
The anode reaction takes place at a metal surface (reactor walls or growing titanium crystals), where sodium metal, fused sodium chloride, and chloride ions are available for the solvation of the sodium ions produced. The cathodic reaction also takes place at a metal site where soluble titanium in the fused salt is available and chloride ions are released to complete the anodic reaction.

A great deal of evidence has been put forward to support the aforementioned postulates. The most interesting observations are as follows. Titanium always grows from metallic surfaces and the reaction is inhibited if the reactor wall is made of a material which does not conduct electricity, e.g., a ceramic coating on a steel reactor. In reactions, where complete reduction is forced to take place in the gas phase (a molecular rather than an electrochemical reaction), the titanium produced is obtained in a pyrophoric powder form rather than as crystals. An ionic reaction

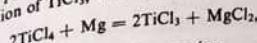
deposits the metal ion on an existing particle of titanium. Then the ion discharges itself and positions itself favourably with respect to the substrate, the continuing phenomenon giving a crystalline material. In a molecular reaction, individual particles of the metal seldom come together to form coherent masses of bigger particles.

#### Magnesium Reduction

The reaction for Kroll's process [see reaction (8.54)] is



Titanium tetrachloride is a nonconductor and, therefore, at least initially, there can be no electrochemical mechanism for the reaction. The reaction as written implies a termolecular reaction. It is not possible to write step-by-step bimolecular reactions in this case. For example, for the formation of TiCl<sub>3</sub>, we may write



which is also a termolecular reaction.

From the foregoing discussion, we observe that the magnesium reaction in Kroll's process is perhaps molecular in nature which leads to a metallic sponge only. However, it has already been noted that a crystalline product may appear if the reduction is a complete gas phase reaction in the presence of prearranged titanium ribbons. It is likely that the existing surfaces of titanium help in the nucleation and the growth of the metal. The exact mechanism, however, is not clear.

#### PROBLEMS

1. Ductile titanium cannot be produced by the direct reduction of titania by a chemical reducing agent. Discuss this statement in terms of the thermodynamics of the Ti-O system. Explain how this problem has been overcome in the commercial production of titanium.
2. Give an account of the use of chlorine in the extractive metallurgy of reactive metals and refractory metals. Describe the preparation of vanadium from ferrovanadium.
3. Discuss the significant contributions of Kroll's process to extraction metallurgy.
4. Review the methods that have been used to consolidate and fabricate zirconium sponge.

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## 9 Precious Metals

### 9.0 INTRODUCTION

The precious metals include silver, gold, and the platinum group metals. These metals have a low affinity for oxygen and, hence, are found in nature either in the native form or in the form of easily reducible compounds. However, this does not mean that the winning of the metals is simple. The precious metals and their easily reducible compounds are invariably associated with large quantities of gangue materials. Winning, therefore, necessarily requires an elaborate method for the separation of the values from the gangue. Such separation is often achieved by leaching the metal or its compound, followed by reduction.

Gold is one of those precious metals whose worth is not judged merely in terms of practical applications. Since time immemorial, the metal has been valued for its outstanding ability to retain its shine against the ravages of time. Other useful properties of gold include formability and ductility which are truly remarkable. In fact, a piece of gold of the size of a one rupee coin can be drawn into a wire 1.5 km long. The metal can also be beaten into very thin foils which are sometimes used to decorate expensive sweets.

Silver, like gold, also does not get tarnished when exposed to air. This property has enabled silver to be extensively used in jewellery-making and as a coinage metal. Over the ages, the use of silver for ornamental and practical purposes has been very similar to that of gold. Silver surpasses gold as far as electrical conductivity is concerned. In fact, of all the metals, silver has the highest electrical conductivity.

The platinum metals constitute a group of six, namely, platinum, palladium, iridium, rhodium, ruthenium, and osmium. Although these metals have some properties in common, i.e., they offer an excellent resistance to corrosion and high melting points, they differ in structure and other properties.

### 9.1 OCCURRENCE AND PRODUCTION

The relative abundance (in per cent) of the precious metals is indicated in Fig. 9.1, which compares the cosmic occurrence of the metals. The relative abundance (in per cent) of copper and zinc is also shown for comparison. The price of the precious metals is high because of their rarity.

The total annual world production of gold is about 1000 tons. South Africa accounts for almost 40 per cent, the U.S.S.R. for 20 per cent, and Canada for 11 per cent. Silver is obtained mainly as a byproduct during the refining of lead and copper.

The annual world production of silver is approximately 6000 tons, of which Mexico contributes about 20 per cent, the U.S.A. about 15 per cent, and Canada and South America about 10 per cent each. South Africa is also the largest producer of the platinum group metals, followed by Canada and Russia, where these metals are recovered as byproducts during the extraction of nickel from nickel sulphide ores.

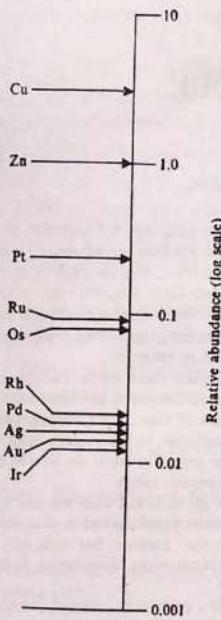


Fig. 9.1 Relative Abundance of Precious Metals (with reference to Zn as 1.0).

#### PROPERTIES AND USES OF PRECIOUS METALS

Gold is chiefly used for making jewellery, dental alloys, gold-coated base metal and parts of scientific instruments. The fact that gold can be hammered into a foil only 0.000002 cm thick is exploited when the metal is employed for decorative purposes. The metal has also found application in the manufacture of containers and pipes for the preparation of special chemicals where a high resistance to oxidation is called for. In India, gold is used in the preparation of certain Ayurvedic medicines.

Gold, and also silver, are usually used in the form of alloys because they are too soft in the pure state. Silver and copper additions harden gold and also impart a wide variety of colours that range from red through yellow to green. These colours are highly valued in jewellery. Gold is also alloyed with palladium, platinum, or nickel for a number of special applications.

Silver has found a large number of industrial applications, besides its ornamental value,

because of its comparatively low cost *vis-à-vis* the other precious metals. The metal is used in electroplating, in photography (as a silver halide deposit), and in the manufacture of surgical instruments, cutlery, dental alloys, and reflectors (made of electroplated silver or silver deposited on glass). Silver solders prove handy in industry for joining metals.

The criteria for the specific use of a platinum group metal are based on one or more of the following characteristics, namely, catalytic activity, resistance to corrosion, resistance to oxidation at elevated temperatures coupled with resistance to attack by molten salts and slags, a high melting point, a low vapour pressure, a high strength at elevated temperatures, high ductility, a low coefficient of thermal expansion (nearly equal to that of glass), stable thermoelectric behaviour, a high temperature coefficient of electrical resistivity, a high reflectivity, and a pleasing

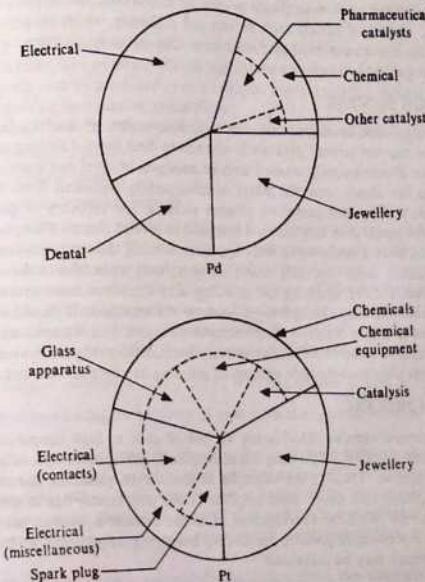


Fig. 9.2 Uses of Palladium and Platinum.

colour. The relative extents of application of platinum and palladium for different purposes are shown in Fig. 9.2.

## 9.2 EXTRACTION OF GOLD

Gold is widely distributed in nature in both the native and combined forms. The native metal occurs in the form of grains or particles that are disseminated through veins of quartz and other rocks or are intermixed with river-bed sands. The metal is invariably alloyed with silver. Small quantities of gold are often associated with ores of lead, copper, and zinc.

Gold is generally extracted by any one of the following processes:

- (1) The amalgamation process.
- (2) The cyanidation process.
- (3) The chlorination process.

Each of these processes is preceded by a preliminary concentration step. The metal may be liberated from the quartzite rock matrix itself by crushing and grinding. Recently, some advances have been made with regard to the separation of a substantial fraction of silica from the quartz rock by flotation. Oxides of metals such as iron and antimony, which are sometimes present in the quartz rock, can also be removed by this process. Gravity concentration methods also seem promising because gold is a very heavy metal (sp. gr. 19).

### AMALGAMATION PROCESS

The amalgamation process, developed centuries ago, is now almost obsolete. In this process, a slurry made up of the wet ground gold ore is allowed to flow down a sloping surface lined with copper. The surface is continuously washed with an amalgam of silver and mercury. The amalgam takes up gold from the slurry, and the metal is subsequently recovered from the amalgam by distilling off mercury. The amalgamation process yields a low recovery of gold, i.e., only 40–60 per cent. The substantial gold loss can be attributed to several factors. First, very fine fractions of the rock particles have a tendency to float up, thus allowing the accompanying gold to escape amalgamation. Second, metal particles which are completely embedded in the rock fractions do not get amalgamated. Finally, crushing and grinding may introduce some grease and oil which would also interfere with the absorption of gold by the amalgam. It should be noted that the amalgamation process is very sensitive to the nature of the ore. For example, an ore containing a sulphide would lead to a particularly low recovery because the gold particles remain surrounded by the sulphide even after considerable amount of grinding has been carried out.

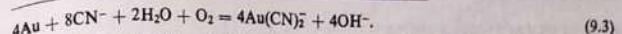
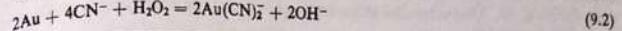
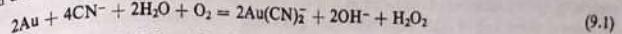
### CHLORINATION PROCESS

The chlorination process aims at chlorinating an ore of gold at high temperatures to produce soluble gold chloride ( $AuCl_3$ ). Gold may be subsequently precipitated as a sulphide by passing  $H_2S$  through the solution. Finally, the sulphide is smelted to yield the metal. Although the process seems simple, it had never been popular in the past mainly due to the problems faced while handling chlorine. With the development of better corrosion-resistant materials in recent years, chlorination reactions, in general, are finding increasing application, and the feasibility of this particular approach may be reassessed.

### CYANIDATION PROCESS

By far the most widely used method, the cyanidation process, aims at dissolving the gold present in the ore in a  $NaCN$  solution. The kinetic aspects of the cyanidation process have been discussed in Section 4.13. It has been shown that cyanide leaching takes place more readily when oxygen is bubbled through the  $NaCN$  solution so as to cause intense aeration and when an ad-

tional oxidizing agent such as  $H_2O_2$  is present. A higher rate of leaching is obtained by passing oxygen under pressure. The reactions may be written as



It should be noted that  $NaCN$  is a highly poisonous chemical. An even more poisonous chemical, namely,  $HCN$  gas, is produced if any acid such as  $H_2SO_4$  is present in the system. The reaction is



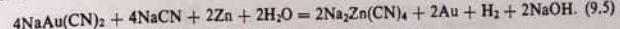
This reaction also implies the loss of the leaching agent. To guard against such a loss, an alkali is added during the reaction.

The efficiency of the cyanidation process is affected by impurities such as iron, copper, tellurium, and graphite. The presence of tellurium can be counteracted by the addition of  $Ba(CN)_2$  and oxidizing agents such as perchlorates and nitrates. These oxidizing agents enhance the dissolution by maintaining an oxidizing atmosphere.

Gold is recovered from the cyanide solution by any one of the following methods:

- (1) The cementation process.
- (2) The electrolytic process.
- (3) The selective absorption process.

In the cementation process, gold is precipitated from the cyanide solution by adding zinc dust (or wires) or aluminium powder. The use of zinc is by far more common because, subsequently, it can be easily separated from the impure gold. Despite this advantage, a certain amount of zinc (20–40 per cent) is trapped in the gold during cementation. This cemented gold is purified by heating, when zinc volatilizes. Some zinc is also dissolved by the cyanide and is lost. This loss is greater if the atmosphere is oxidizing. The deaeration of the cyanide solution is known to reduce the zinc loss. The overall cementation reaction may be written as



The electrolytic process for the recovery of gold from the cyanide solution has been described in Section 4.15.

In the selective absorption process, the complex gold cyanide ion is absorbed, at the room temperature, on a specially prepared carbon powder surface. (This carbon can be subsequently separated by filtration.) When the carbon powder is heated in the presence of water, the complex is released into the aqueous phase. The metal is thus preferentially separated from various other impurities. Subsequently, the metal can be recovered in the elemental form either by cementation or electrolysis.

In addition to the zinc which is trapped during cementation, the common impurities in gold are silver, copper, and the platinum group metals. For purification purposes, this impure gold can be melted along with a flux (borax, silica, or sodium carbonate) and then fire-refined. The metal can also be partially purified by the parting process, i.e., by leaching with hot sulphuric acid which dissolves only silver and the base metals and not gold and the platinum group metals. The platinum group metals can be recovered by electrolyzing an aqueous solution of  $AuCl_4^-$  using

impure gold bullion as the anode and a pure gold sheet as the cathode. If the major impurity in gold is silver, then it is purified by the parting process just described. Silver can also be separated by chlorination. If chlorine is bubbled through a molten gold-silver alloy, then the chlorides of silver and of other impurities such as Fe and Sb are preferentially formed and some are volatilized out. After controlled chlorination and cooling, very pure gold is obtained under a crust of silver chloride.

#### GOLD EXTRACTION IN INDIA

In India, gold mining activity is confined to the Kolar and Huttis gold fields of Karnataka. The Nundydurga mine, Kolar is currently the primary source of gold. The gold in the ore is present as native gold in the veins and in disseminated particles in the siliceous gangue and as fine locked up particles ( $\approx 4$  microns) in arsenopyrite. Silver is associated with the gold in the ratio of about 1 : 13. The mineralogical analysis of the Kolar gold ore is given in Table 9.1. In addition to the constituents listed in Table 9.1, the ore contains small amounts of graphite and tellurides.

Table 9.1 Mineralogical Analysis of Kolar Gold Ore

Mineral	Quantity (per cent)*
Siliceous minerals	91.0
Arsenopyrite	2.5
Pyrrhotite	5.0
Pyrite	1.1
Chalcopyrite	0.2
Marcosite	Traces
Magnetite	0.2

\*Unless otherwise stated.

During extraction, the ore is subjected to three stages of crushing with screen classification and two stages of grinding, the first in a pebble mill and the second in tube mill with cone classification to yield 80 per cent – 200 mesh product. This product is subjected to gravity concentration in tables provided with blankets. Here, 60–70 per cent of the gold is collected in the concentrate. This concentrate is next cyanided with a concentrated NaCN solution in cone agitators. The resultant pulp is filtered and the gold solution treated in zinc extractor boxes for gold cementation. The cement obtained after cementation is first acid leached to extract base metals and then roasted and smelted to produce a bullion. The furnace treatment is similar to that described in Section 7.3 for treating the copper anode slimes.

The tailings from the gravity concentrator contain 30–40 per cent of the gold. These together

with the tailings from the cyanidation of the concentrate are subjected to cyanidation in air-agitated pachuca tanks. The cyanided solution containing the gold is treated as before for gold precipitation, and the gold is recovered by smelting. The residue obtained after leaching is discarded. The flowsheet for the Kolar operation is given in Fig. 9.3.

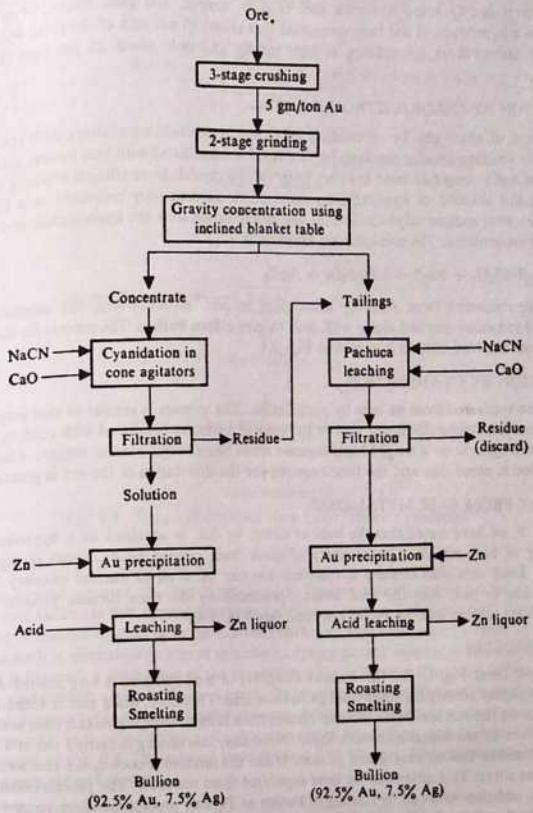


Fig. 9.3 Gold Extraction at Kolar Gold Fields.

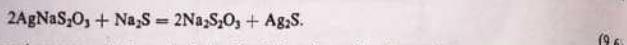
### 9.3 EXTRATION OF SILVER

The common ores of silver are argenteite ( $\text{Ag}_2\text{S}$ ) and cerargyrite ( $\text{AgCl}$ ). Virtually all naturally occurring gold deposits contain some silver; the amount usually being sufficient to meet the cost of refining the impure gold bullion.

Argenteite is closely associated with ores of lead, copper, and zinc. Hence, silver is largely produced as a byproduct. It has been computed that about 75 per cent of the total world output of silver is derived from the refining of base metals and only about 25 per cent from silver ore proper.

#### EXTRATION BY CHLORIDIZING ROASTING

Sulphide ores of silver can be successfully subjected to chloridizing roasting with common salt. A solid-state roasting usually produces impure  $\text{AgCl}$  contaminated with base metals, and attempts to leach out  $\text{AgCl}$  using hot brine have not been very successful. More efficient leaching is achieved by using a hot solution of hyposulphite, silver being subsequently recovered as a sulphide by precipitation with sodium sulphide. During the precipitation step, the hyposulphite is regenerated and can be recirculated. The precipitation reaction is



Silver can be recovered from  $\text{Ag}_2\text{S}$  by dissolution in acid. Alternatively, the sulphide can be roasted and reduction smelted along with lead to give a lead bullion. The process for the recovery of silver from the lead bullion is shown in Fig. 9.4.

#### EXTRATION BY CYANIDATION

Silver can be recovered from its ores by cyanidation. The process is similar to that employed for gold. It should, however, be noted that in the case of silver, as compared with gold, cyanidation requires more cyanide on a weight basis because silver has a lower atomic weight. Also, cementation consumes more zinc and the time required for the dissolution of the ore is greater.

#### RECOVERY FROM BASE METAL ORES

In Chapter 7, we have stated that the bulk of silver, by far, is obtained as a byproduct during the refining of base metals. The recovery of silver from copper anode slimes is described in Chapter 7. Lead ores also contain a sufficient amount of silver to warrant recovery. Here, the silver is made to pass into the lead bullion produced by the blast furnace process. Silver is recovered from molten lead by Parke's process (see Fig. 9.4).

#### PARKE'S PROCESS

As is evident from Fig. 5.14a, the mutual solubility of lead and zinc is very limited. Also, zinc has a much higher affinity for silver (and gold) than lead. Therefore, when zinc is added to molten lead it floats on the surface. After the two phases have been thoroughly mixed, then nearly all the silver dissolves in the supernatant zinc layer. Normally, this mixing is carried out at 470°C, i.e., about 50°C above the melting point of zinc. When the mixture is cooled, the zinc forms a crust that contains silver. This silver can be later separated from the crust. The process of desilverizing lead by zinc addition followed by cooling is known as Parke's process for silver recovery. Figure 9.4 gives the flowsheet for this process together with the treatment of the zinc-silver crust for silver recovery. (The details of drossing, softening, and cupellation have been given in Section 7.9.)

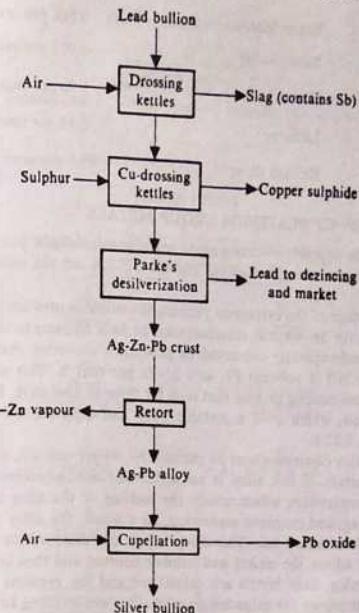


Fig. 9.4 Recovery of Silver from Lead (Parke's process).

#### SILVER PRODUCTION IN INDIA

In India, a limited amount of silver is produced at Tundoo (Bihar) during the refining of lead. The crude lead bullion is first treated for the separation of copper and antimony. Subsequently, desilverizing is effected by adding to the hot lead bath zinc and low-zinc crust from the previous charge. The bath is mechanically stirred in order to ensure proper mixing. When the temperature of the bath is lowered, a thick crust of the zinc-silver alloy is formed. The crust is taken out and pressed by compressed air in a Howard press. On pressing, most of the mechanically entrained lead is freed, leaving behind a crust (called the press crust) with a high content of silver and zinc. This crust is sent to a silver refinery for the recovery of zinc, silver, and lead according to the process outlined in Fig. 9.4. The refining process takes 7 to 8 hours. The concentrations of silver at various stages are as follows:

Low-zinc crust	0.42 per cent
Press crust	2.0 per cent

Retort zinc	0.006 per cent
Blue powder	0.072 per cent
Retort lead	3.90 per cent
Litharge	0.12 per cent
Refined silver	99.8 per cent

#### 9.4 EXTRACTION OF PLATINUM GROUP METALS

At present, the lode deposits occurring along with the sulphides in South Africa and the copper-nickel sulphide ores occurring in Canada and the U.S.S.R. are the main sources of the platinum-group metals.

At the initial stage of the extraction process, the sulphide ores are concentrated by flotation and then smelted (in an electric, reverberatory, or flash furnace) so as to produce a matte. The furnace matte is subsequently converted to produce a converter matte which contains about 75 per cent ( $Cu + Ni$ ), 1 per cent Fe, and 21–23 per cent S. This matte is subjected to matte separation by a slow cooling process that lasts for three to four days, followed by grinding and magnetic separation, which yield a metallic alloy and copper-nickel sulphides. (For a typical flowsheet, see Fig. 7.32.)

The metallic alloy contains about 64 per cent Ni, 16 per cent Cu, and 10 per cent S and most of the precious metals. If this alloy is not sufficiently rich in precious metals, it is subjected to secondary matte separation, which entails the melting of the alloy along with sulphides, subsequent slow-cooling, and magnetic separation. As a result, the alloy gets enriched in precious metals by a factor of about ten. This alloy is cast into anodes with unrefined nickel addition, which is made to adjust the nickel and sulphur content and then subjected to electrorefining. During electrorefining, base metals are solubilized and the precious metals are present in the anode slimes. These slimes are subjected to sulphation and leaching to remove any residual base metals present and to produce a concentrate of precious metals that contains 80 per cent of the platinum group metals along with gold and silver. This concentrate is roasted to eliminate the sulphates and the sulphur present in it. During the final stages of roasting, osmium volatilizes as  $O_3O_4$ , which is scrubbed and recovered. The flowsheet for the typical processing of the platinum concentrate by INCO is shown in Fig. 9.5.

In the initial aqua regia leach, a separation occurs between Au, Pt, and Pd (which enter the solution) and Rh, Ru, Ir, Os, and Ag (which remain in the residue). The separation of Au from Pt and Pd is carried out by solvent extraction and the separation of Pt from Pd is effected in the form of an insoluble ammonium chloroplatinate.

The residue, which contains Rh, Ru, Ir, Os, Ag, and any unleached Pt or Pd together with insolubles such as silica, is subjected to lead smelting along with coke and  $PbO$ . Smelting eliminates the gangue and produces a lead grain containing the precious metals. When this lead grain is leached with  $HNO_3$ , a solution containing Ag and the Pt and Pd which had escaped the first aqua regia leaching is obtained. The Ag is precipitated as  $AgCl$  and the Pt-Pd solution sent for processing in the same manner as described. The residue containing the Rh, Ru, Ir, and Os is first subjected to sulphation to dissolve Rh and then to alkali hydroxide fusion to render Ru and Os soluble. The final residue, which contains Ir, is treated for Ir recovery.

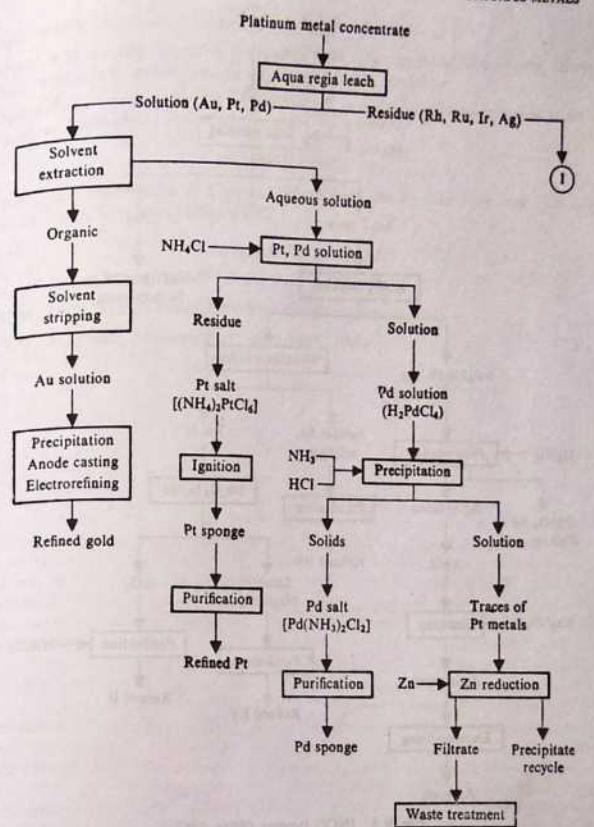


Fig. 9.5 INCO Process (Wise, 1968) (cont.).

The major problems encountered during the recovery of precious metals are the incomplete separation due to the incomplete dissolution and the large recycling loads. Further, the presence of impurities such as Sn, Te, Sb, and As affect the separation by tending to remain in the extraction circuit, and care has to be exercised while bleeding out the refinery from time to time.

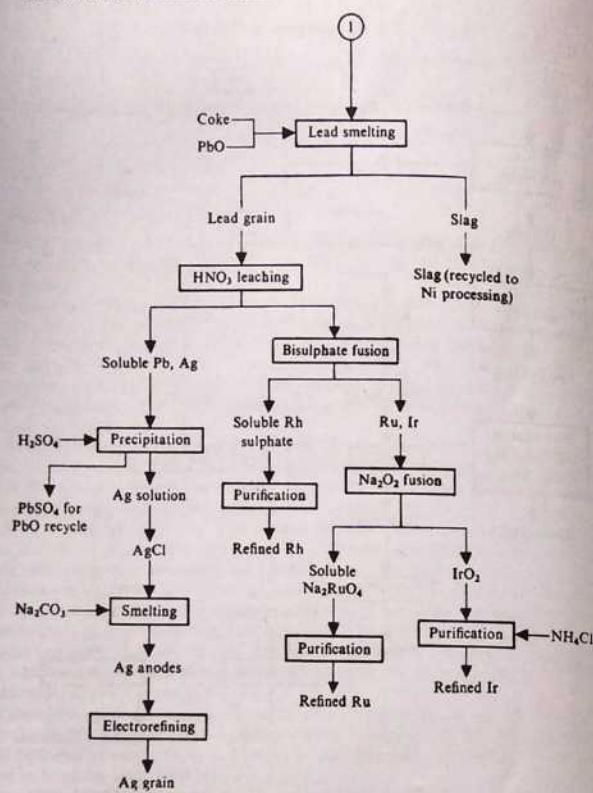


Fig. 9.5 INCO Process (Wise, 1968).

## PROBLEMS

1. Describe from a physicochemical point of view, the processes used for the recovery of silver and gold from lead bullion, up to the parting of silver and gold from each other.
2. Describe how bullion can be recovered from a gold-bearing quartz ore, assuming gold to be present in both coarse and fine particles. How would you modify the process if the ore contains arsenopyrite with which gold is intimately associated?
3. Oxygen is an essential reagent in the cyanide process for the dissolution of gold. Discuss this statement in relation to its influence on the technology of the process.
4. Explain Parke's process for the recovery of silver from argentiferous lead in terms of the ternary system involved.

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## 10 Secondary Metals and Utilization of Metallurgical Wastes

### 10.0 INTRODUCTION

Secondary metals are those that are recovered from scrap. As is evident from Table 4.10, the recovery of metals from scrap requires far less energy than that required for production from the primary ore. The rapid depletion of primary ore reserves and the energy scarcity are bound to create more interest in the recovery of metals from secondary sources. At present, although large quantities of major nonferrous metals such as copper, lead, aluminium, and zinc are being recovered from scrap, there is still ample scope for increasing the tonnage.

Examples of byproduct metals are selenium, tellurium, bismuth, and cadmium. These are so named because they are essentially obtained as byproducts in the extraction of other metals such as copper, lead, and zinc. The recovery of some of these metals has already been described in Chapter 7 and byproduct metals are not considered in this chapter, however, a brief description of the utilization of metallurgical waste like slags is included.

### 10.1 SECONDARY COPPER

Secondary copper is a major source of copper in the developed countries. The copper scrap originates from foundries, fabricators, and user industries. The breakdown is as follows: dross, spillages, and skimmings from foundries; swarf, punchings, turnings, and borings from fabricators; scrap cable, wire, and radiators from cars and trucks; brass and bronze (salvaged from machinery and demolitions) from the user industries.

The scrap dealers sort out the scrap according to the grade and composition, and wherever possible, clean scrap is sent to brass and bronze foundries. Also, the wire and cable manufacturers have their own facility for remelting reverts. Normally, a rotary type furnace that is 5-7 m in length and 3 m in diameter is used to melt and cast the copper for rerolling to wire rods. The contaminated scrap containing iron such as copper-clad steel, machine parts carrying brass and bronze is subjected to electromagnetic separation in order to separate iron and steel to the extent possible. This leaves behind a composite scrap which has to be smelted and refined to recover copper and associated metals.

The flowsheet followed for the recovery of low-grade scrap copper is shown in Fig. 10.1. The compacted scrap is smelted in a blast furnace along with a return converter slag, a flux, and a reductant so as to produce molten black copper and a discard slag which typically analyzes 1 per cent Cu, 0.8 per cent Sn, 10 per cent ZnO, 15 per cent CaO, 35 per cent FeO, and 37 per cent ( $\text{SiO}_2 + \text{Al}_2\text{O}_3$ ). The furnace gases, which contain zinc, tin, and lead, are sent to bag houses or Cottrell dust collectors in order to recover the valuable oxide fumes. The smelting campaigns of high zinc and high tin and lead are carried out separately so that high-grade zinc oxide suitable

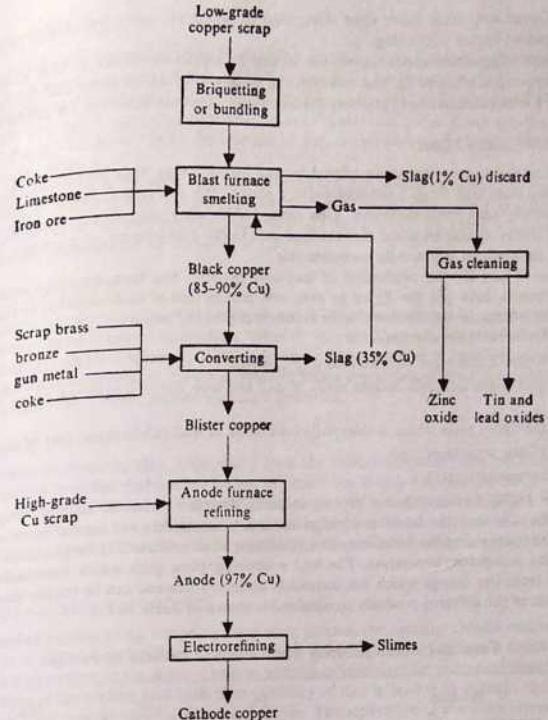


Fig. 10.1 Recovery of Copper from Scrap.

for sale and a tin-lead oxide suitable for soldering purposes or for the production of a white metal alloy can be produced.

The molten black copper is sent to a converter where high-grade brass or high-grade bronze or gun metal scrap is added to it. Unlike in the case of sulphide matte conversion, there is no sulphur available for oxidation, and external fuel has to be provided. Therefore, coke is fed into the converters as fuel. The slags produced contain 30-35 per cent copper and 20 per cent zinc when zinc scraps are processed or 15 per cent tin when tin scraps are treated. These slags are sent to the blast furnace. The converter gases, which contain oxides of Zn, Sn, and Pb, and are sent to gas-cleaning equipment. It should be noted that the refractories of secondary copper

converters wear out much faster than those used in primary copper production because of the highly corrosive nature of the slag.

The blister copper and anode copper are treated in a manner similar to that employed for primary copper (see Chapter 7). The recovery and treatment of anode slimes and the recovery of nickel and cobalt sulphates as byproducts are also similar to those described for primary copper.

## 10.2 SECONDARY LEAD

The excellent resistance to corrosion offered by lead allows a very high portion of the metal to be recovered from lead scrap. Lead-acid battery plates form the largest source of scrap. Other sources include hard cable sheathing, type casts, babbitt alloy, solder scrap, and soft lead from pipes and sheets. It may be noted that the lead used in the manufacture of pigments, tetrachethyl lead, and ammunition is generally unrecoverable.

The use of lead for the production of lead-acid batteries has been steadily increasing, and recent estimates have put the figure at over one million tons of lead annually. In the Western countries, the batteries are discarded after about three years of use.

Lead batteries essentially consist of

- (1) a plastic container with an iron grip or handles,
- (2) grid plates and pole bridges made of lead and lead alloys containing up to 9 per cent antimony,
- (3) the filling mass which is essentially lead oxide or lead sulphate and free of antimony,
- (4) plastic separators, and
- (5) accumulator acid.

Fischer (1970) has described a process specially designed to handle battery scrap. In this process, the acid and the lead-free components such as containers and separators are separated from the lead containing the metallic grids and fillings, after mechanically breaking the batteries, by screening and gravity separation. The lead containing these grids which have antimony are separated from the fillings which are essentially antimony-free and can be readily slurried. The composition of the different products so obtained is shown in Table 10.1.

Table 10.1 Lead Recovery from Lead Acid Batteries (per cent)

Product	Pb	Sb	H <sub>2</sub> O
Grid metal (25 per cent)	93	6.8	1.5
Middlings (35 per cent)	75	1.5	12.0
Slurry (19 per cent)	65	0.7	18.0
Plastics (21 per cent)	0.5		

The grid metal is sent to a lead refinery where softening kettles are used for lead and antimony recovery (see Chapter 7). The middlings are charged into a lead blast furnace, while the slurry is subjected to lead sulphide roasting to eliminate sulphur. The plastic materials are rejected.

## 10.3 SECONDARY ZINC

In addition to the zinc present in scrap brass (whose recovery has been described in Section 10.1), the other main secondary source is zinc dross. The zinc dross has been identified as a compound, FeZn<sub>13</sub>, with about 6.2 per cent iron. In reality, the iron content is less because the dross contains a substantial amount of entrapped zinc. This dross is formed due to the direct reaction between molten zinc and steel as well as by the reaction of molten zinc with the iron salts formed during the galvanizing of steel.

The zinc entrapped in the dross may be recovered through simple techniques such as melting and decantation. However, the recovery of zinc from the compound, FeZn<sub>13</sub>, is more difficult, although a number of recovery processes have been widely reported. We now discuss some of the more important processes for the recovery of zinc.

### DISTILLATION PROCESS

The distillation process is based on the relative instability of the intermetallic compound, FeZn<sub>13</sub>. When this compound is heated in a retort, the zinc vapours liberated are distilled off and are condensed in a suitable condenser. Recoveries up to 95 per cent have been reported for this process. The distillation process, however, requires rather sophisticated equipment, skilled operation, and general facilities for high-temperature operation.

### ALUMINIUM PROCESS

In the aluminium process, zinc is displaced from the FeZn<sub>13</sub> compound by aluminium to form FeAl<sub>3</sub>. It should be noted that a small weight of aluminium is able to liberate a large weight of zinc. For instance, in the case of a dross containing 4 per cent iron, the addition of 1 kg of aluminium would release 19 kg of zinc from about 30 kg of dross. Moreover, since the melting point of FeAl<sub>3</sub> is higher (1160°C) and the density is nearly half that of zinc, the separation of zinc is greatly facilitated.

### MODIFIED ALUMINIUM PROCESS

In the modified version of the foregoing aluminium process, the zinc dross mixed with aluminium is added to a bath of molten lead at about 700°C. The weight of aluminium is about 1.5 times that of the iron present in the dross. The iron-aluminium intermetallic compound easily floats up to the surface of the molten lead bath. The solubility of zinc in lead is 14 per cent at 720°C, but only about 2 per cent at the freezing point of zinc. The separation of the three layers, namely, FeAl<sub>3</sub>, Zn, and Pb is, therefore, almost complete. First, the FeAl<sub>3</sub> is skimmed off and then the zinc recovered by cooling the lead to a temperature below the freezing point of zinc.

## 10.4 SECONDARY ALUMINIUM

The use of aluminium for structural applications and in the manufacture of containers is constantly increasing. The secondary aluminium contained in scrap material such as turnings, borings, trimmings, foils, and cans can be recovered. The process involves the melting of the scrap in either a reverberatory or a rotary furnace using fluoride fluxes. These fluxes prevent the loss of aluminium due to oxidation.

For recovering aluminium from impure and mixed scrap, a short-shaft furnace is employed. This furnace has a sloping hearth on which the scrap is melted and a forehearth in which the

molten aluminium is collected. The unmelted iron and steel are raked out of the hearth. The aluminium thus obtained is used to make aluminium-copper or aluminium-silicon alloys or used as a deoxidant in steel.

The impure aluminium can be refined by the Beck process. In this process, 25–30 per cent of magnesium is added to the impure aluminium and the mixture cooled to a temperature that is about 130°C above the freezing point of aluminium. The metal is next filtered on a perforated iron plate filter with crushed basalt as the filtering medium. The resulting liquid aluminium is vacuum refined at 900–950°C in a vacuum induction furnace. This results in aluminium that is suitable for the commercial production of light alloys. The Beck process is based on the principle that the addition of magnesium causes the formation of insoluble intermetallics with the impurities in the scrap such as Fe, Si, Mn, and Ti and are separated during filtration. During vacuum refining, magnesium together with zinc, cadmium, and calcium are distilled off, leaving behind aluminium and copper.

The foregoing scheme is rather tedious, and often impure aluminium is refined by chlorination. Chlorination efficiently removes magnesium which is the major contaminant.

## 10.5 ALUMINIUM FROM NONSCRAP SOURCES

### ALUMINIUM FROM RED MUD

Red mud, which is the leached residue left behind after the treatment of bauxite by the Bayer process, may contain up to about 22 per cent  $\text{Al}_2\text{O}_3$ , 50 per cent  $\text{SiO}_2$ , 20 per cent  $\text{Fe}_2\text{O}_3$ , and 30 per cent  $\text{TiO}_2$ . It is, therefore, a potential source of aluminium and titanium.

Red mud is roasted with  $\text{Na}_2\text{O}$  to extract  $\text{Al}_2\text{O}_3$ . Nearly 90 per cent aluminium may be recovered using a  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio of about 4 (the  $\text{Na}_2\text{O}/\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{O}/\text{TiO}_2$  ratios each being about 1). The recovery is, of course, facilitated by high temperatures and long roasting periods.

The alumina content of red mud would be particularly high when the silica content of the bauxite ore is high. The alumina values are recovered by the lime sintering of red mud in the presence of sufficient  $\text{Na}_2\text{O}$  to first form a soluble sodium aluminate and an insoluble dicalcium silicate. Subsequent leaching and precipitation regenerate alumina. If red mud contains vanadium, as is often the case, the metal remains in the leach liquor and can be recovered after a sufficient amount is accumulated. The titanium-rich residues left behind after aluminium recovery may be used in the production of ferrotitanium.

In a slightly different procedure, red mud is roasted at 1300–1350°C along with a specified quantity of limestone that is required to convert all the alumina into calcium aluminate, silica into dicalcium silicate, and the minor constituents, such as  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  into ferrites and titanates. Calcium aluminate is leached with a dilute sodium carbonate solution to convert it into sodium aluminate from which alumina is subsequently recovered.

Some workers recommend the smelting of red mud along with titaniferous ores in order to get a quality pig iron and a slag that is rich in titania and alumina, from which  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  can be recovered by chemical methods. The chlorination of red mud appears to be another possible method for the recovery of the metallic values, especially vanadium which can be easily recovered by the low-temperature chlorination of red mud with  $\text{HCl}$  or chlorine gas. It is also possible to preferentially chlorinate the iron oxide and then the titanium oxide to yield a  $\text{Al}_2\text{O}_3$ -rich residue.

In spite of the reported success of the foregoing processes for the recovery of aluminium from red mud, they have not yet been applied on a commercial scale to any appreciable extent.

## 10.6 SECONDARY TIN

Nearly 50 per cent of the tin produced is used for the production of tin plates. The metal is also used as a constituent in soldering alloys (containing about 65 per cent tin) and in bronze and babbitt alloys of various compositions. Tin is added to some plastics to ensure transparency. The metal is also a constituent of paints, industrial fungicides, and disinfectants.

From the recovery point of view, tin can scrap is the only worthwhile source. The recovery of tin also renders the steel can suitable for use as a valuable scrap addition during the electric furnace melting of steel. Tin-coated steel cannot be charged in an electric furnace because tin is an unwanted alloying addition and  $\text{SnO}_2$  would enter the slag phase, creating operational problems.

The normal thickness of the tin coating is about  $1.5 \times 10^{-4}$  cm and the weight of tin amounts to about 1 per cent of the total. It is thus obvious that a large amount of tin can be recovered from tin cans provided a suitable detinning process is available. From the middle of the nineteenth century onward, several detinning processes involving melting, volatilization, chemical attack, amalgamation, and electrolytic stripping have been patented. Commercial installations, however, have been limited entirely to three methods, namely, the alkaline chemical process, the chlorine process, and the alkaline electrolytic process. We now briefly discuss these three processes.

### ALKALINE CHEMICAL PROCESS

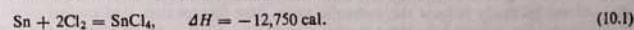
In the alkaline chemical process, a caustic solution containing an oxidizing agent is used to remove both tin and the underlying iron-tin alloy from the steel. After washing, the steel becomes virtually free of tin. The solution obtained after washing can be processed in several ways to yield either pig tin or tin chemicals. The alkali normally used is, sodium hydroxide. Sodium nitrate, sodium nitrite, litharge, manganese dioxide, various mixtures of these oxidizing agents, or plain air agitation have been used for aiding oxidation.

After detinning has been carried out, the solution contains sodium stannate, from which tin can be recovered by several methods, some of which are now discussed. Sodium stannate can be crystallized (by cooling and evaporation) or directly electrolyzed to yield tin.

### CHLORINE PROCESS

In the chlorine process, tin is recovered in the form of a liquid chloride by being made to react with chlorine gas. Precautions must be taken to exclude all traces of moisture from the process in order to avoid the corrosion of iron. Moreover, it is also necessary to ensure that the materials be free from all organic substances such as paper and straw.

Chlorination of tin is an exothermic reaction and may be written as



The exothermic heat produces liquid  $\text{SnCl}_4$ . When the chlorination is complete, water is cautiously added to cool the liquid, and at this stage  $\text{SnCl}_4$  crystallizes out.

### ALKALINE ELECTROLYTIC PROCESS

In the alkaline electrolytic process, tin plate scrap is used as the anode and an iron plate as the cathode in a warm electrolyte of caustic soda solution containing stannate. Tin is recovered at the cathode in the form of a spongy or a finely granulated precipitate which is removed and melted.

### 10.7 RECOVERY OF VANADIUM FROM BAYER PLANT LIQUORS AND RED MUD

Vanadium occurs as a trace impurity in bauxite and constitutes about 0.05 per cent by weight in the bauxite ores found in Bihar. During alkali digestion in the Bayer process, nearly one-third of vanadium also dissolves in the process liquor.

The concentration of vanadium in the Bayer process liquor amounts to 0.1–0.2 per cent by weight. This vanadium can be separated out as an insoluble calcium residue by boiling the liquor with an appropriate quantity of milk of lime.

The recovery of the trace impurity vanadium not only yields a valuable byproduct but also avoids the contamination of aluminium with vanadium, resulting in impaired electrical properties.

Red mud, which roughly contains as much as 22 per cent alumina, holds most of the vanadium initially present in the ore and remains insoluble in the Bayer leaching process. The mud residues from the Indian plants generally contain about 0.1 per cent vanadium, which represents about 70 per cent of the vanadium present in the bauxite ore. Assuming that about 200,000 tons of red mud are produced in India per annum, the total vanadium content of red mud is about 200 tons. If recovered, this can meet a substantial part of the domestic annual demand for vanadium which is about 1000 tons. Unfortunately, the presence of comparatively large amounts of the compounds of iron, titanium, and silicon in red mud renders the extraction of the vanadium from this source somewhat complicated, and, as yet, no viable recovery process has been reported.

### 10.8 UTILIZATION OF METALLURGICAL WASTES

Slags constitute the major waste product obtained from pyrometallurgical smelting processes. However, slags are not strictly waste products. In fact, certain slags are so rich in metallic values that they could become potential metal sources, especially as high-grade ores are getting rapidly depleted. Let us consider a case in point. During tin smelting, large amounts of  $\text{SnO}_2$  enter the slag phase as  $\text{SnO}_2\text{-SiO}_2$ , and the slag itself is smelted during the later stages for tin recovery.

#### BYPRODUCTS FROM SLAGS

At present, several valuable byproducts are being manufactured from slags—mostly from blast furnace slags because of their wide availability. The principles underlying the processes for the manufacture of byproducts from slags are very often quite general.

#### CEMENT FROM SLAGS

All slags are not suitable for making hydraulic binding agents. The hardening properties of a granulated slag depend on the temperature at which it is produced and on its chemical composition. Basic slags with an  $\text{Al}_2\text{O}_3$  content are the best suited for making cement. An increasing silica content gradually reduces the hydraulic value. Blast furnace slags that are best suited for cement production usually have the following composition:  $(\text{CaO} + \text{MgO})$  40–42 per cent;  $\text{SiO}_2$  27–73 per cent; and  $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$  10–25 per cent. The basicity ratio, i.e.,  $(\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3)/\text{SiO}_2$ , should be greater than unity. This condition is fulfilled by most Indian slags; the typical composition of an Indian slag being  $\text{SiO}_2$  31 per cent,  $\text{Al}_2\text{O}_3$  26.5 per cent,  $\text{Fe}_2\text{O}_3$  0.7 per cent,  $\text{MnO}$  1 per cent,  $\text{CaO}$  36 per cent, and  $\text{MgO}$  3.8 per cent. The actual cement production method involves a combination of three operations, namely, grinding, sieving, and roasting. It should be noted that the slags encountered in nonferrous metallurgy have not yet been used for cement production.

#### INSULATION MATERIAL FROM SLAGS

A light-weight or foamed slag, which is a good insulating material, is produced by treating a slag with a limited amount of water in the hot condition. A large quantity of water at a high pressure usually leads to granulation, whereas limited water addition gives a lumpy product with a dry cellular structure. Foamed slag can also be used as a constituent of a lighter variety of cement to be used in prefabricated houses as heat- and sound-resisting bricks and as a filler in building construction.

#### SLAG WOOL FROM SLAGS

Many slags may be used for the production of slag wool. The process is as follows. The slag is melted and drawn through a tapping hole, the stream of slag being made to pass in front of a jet of air or dry steam. The fluid slag is dispersed into globules which are drawn out into long fibres by air resistance to their flight. These fibres are sucked into a chamber for further processing.

Slag wool finds application as insulating and packaging material.

#### SLAG-CERAM FROM SLAGS

*Slag-ceram* is the name given to the material produced by the controlled crystallization of a slag which is a vitreous substance. The material thus produced has ceramic properties.

Traditional ceramics are produced by the sintering of refractory crystalline particles. In the ceramic product, the grains or crystallites fuse at the grain boundaries. In slag-ceram, the same condition is approached from the opposite direction, i.e., the vitreous phase is carefully crystallized to produce a large number of crystallites in the matrix.

To produce the ceramic product, suitable nucleating agents are added to the molten slag which is then poured into a mould, and the casting that results is cooled and annealed. This product is then heated to a temperature called the nucleation temperature (where the nucleation rate is very high). This produces a very large number of nuclei in the solid bulk. Subsequently, the product is heated to a different temperature to attain the rapid growth of the nuclei, which leads to a dense product with increased hardness and better strength properties.

Of late, remarkable progress has been made in the production of slag-ceram from blast furnace slags. Slags encountered in nonferrous metallurgy have, however, not yet been investigated for slag-ceram production.

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National Metallurgical Laboratory, Proceedings of Symposium on Utilization of Metallurgical Wastes, Jamshedpur (1964).

## APPENDIX I

## Some Minerals and their Formulae

Name	Formula	Percentage metal	Name	Formula	Percentage metal
Anglesite	PbSO <sub>4</sub>	Pb (68.3)	Chrysocolla	CuO·SiO <sub>2</sub> ·2H <sub>2</sub> O	Cu (36.2)
Apatite	Ca <sub>4</sub> (CaF)(PO <sub>4</sub> ) <sub>3</sub>	P <sub>2</sub> O <sub>5</sub> (42.3)	Cinnabar	HgS	Hg (86.2)
Argentite	Ag <sub>2</sub> S	Ag (87.1)	Corundum	Al <sub>2</sub> O <sub>3</sub>	Al (52.9)
Azurite	2CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	Cu (55.0)	Covellite	CuS	Cu (66.5)
Barite	BaSO <sub>4</sub>	BaO (65.7)	Cryolite	Na <sub>3</sub> AlF <sub>6</sub>	Al (13) F (54.4)
Bauxite	Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	Al (34.9)	Cuprite	Cu <sub>2</sub> O	Cu (88.8)
Beryl	Be <sub>3</sub> Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>6</sub>	Be (5) Al <sub>2</sub> O <sub>3</sub> (19)	Diaspore	Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub> (85)
Bismite	Bi <sub>2</sub> O <sub>3</sub>	No metal source	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	CaO (30.4) MgO (21.9)
Bismuthinite	Bi <sub>2</sub> S <sub>3</sub>	Bi (81.2)	Epsom	MgSO <sub>4</sub> ·7H <sub>2</sub> O	Mg (9.9)
Borax	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub> (36.6) Na <sub>2</sub> O (16.2)	Fluorite	CaF <sub>2</sub>	F (48.9)
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	Cu (63.3)	Galena	PbS	Pb (86.6)
Braunite	3Mn <sub>2</sub> O <sub>3</sub> ·MnSiO <sub>3</sub>	Mn (78.3)	Gibbsite	Al(OH) <sub>3</sub>	Al (34.6)
Brochantite	CuSO <sub>4</sub> ·3Cu(OH) <sub>2</sub>	Cu (56.2)	Greenockite	CdS	Cd (77.7)
Brucite	MgO·H <sub>2</sub> O	MgO (69)	Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	CaO (32.6)
Calamine	H <sub>2</sub> (Zn <sub>2</sub> O)·SiO <sub>4</sub>	ZnO (67.5)	Hematite	Fe <sub>2</sub> O <sub>3</sub>	Fe (70)
Calcite	CaCO <sub>3</sub>	CaO (56)	Ilmenite	Fe, Mg(TiO <sub>3</sub> )	Ti (31.6)
Carnallite	KMgCl <sub>3</sub> ·6H <sub>2</sub> O	K (14.1) Cl (38.3)	Kainite	MgSO <sub>4</sub> ·KCl·3H <sub>2</sub> O	KCl (30.0)
Cassiterite	SnO <sub>2</sub>	Sn (78.8)	Kieserite	MgSO <sub>4</sub> ·H <sub>2</sub> O	Mg (17.6)
Cerussite	PbCO <sub>3</sub>	Pb (77.5)	Limestone	CaCO <sub>3</sub>	Ca (40)
Chalcocite	Cu <sub>2</sub> S	Cu (79.8)	Limonite	2Fe <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	Fe (59.9)
Chalcopyrite	CuFeS <sub>2</sub>	Cu (34.6)	Magnesite	MgCO <sub>3</sub>	Mg (28.9)
Chromite	FeO·Cr <sub>2</sub> O <sub>3</sub>	Cr (46.2)	Magnetite	FeO·Fe <sub>2</sub> O <sub>3</sub>	Fe (72.4)
			Malachite	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	Cu (57.5)
			Manganite	Mn <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	Mn (62.5)
			Millerite	NiS	Ni (64.8)
			Molybdenite	MoS <sub>2</sub>	Mo (60)
			Molybdate	MoO <sub>3</sub>	Mo (66.67)

Name	Formula	Percentage metal
Monazite	(Ce, La, Y, Th)PO <sub>4</sub>	
Muscovite	H <sub>2</sub> KAl <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	Variable
Nitre	KNO <sub>3</sub>	K (38.6) N (13.9)
Olivine	(Mg, Fe) <sub>2</sub> SiO <sub>4</sub>	No metal source
Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>	Al <sub>2</sub> O <sub>3</sub> (18.4)
Pentlandite	(FeNi)S	Fe (42.0) Ni (22.0)
Psilomelane	MnO <sub>2</sub> ·H <sub>2</sub> O·K <sub>2</sub> BaO <sub>2</sub>	
Pyrite	FeS <sub>2</sub>	Fe (46.7)
Pyrolusite	MnO <sub>2</sub>	Mo (63.2)
Quartz	SiO <sub>2</sub>	Si (46.9)
Ruby	Al <sub>2</sub> O <sub>3</sub>	Al (52.9)
Rutile	TiO <sub>2</sub>	Ti (60)
Scheelite	CaWO <sub>4</sub>	W (63.9)
Senarmontite	Sb <sub>2</sub> O <sub>3</sub>	Sb (83.6)
Serpentine	H <sub>4</sub> Mg <sub>3</sub> Si <sub>2</sub> O <sub>9</sub>	Mg (43)
Siderite	FeCO <sub>3</sub>	Fe (48.3)
Smithsonite	ZnCO <sub>3</sub>	Zn (52)
Soda nitre	NaNO <sub>3</sub>	Na (27)
Sphalerite	ZnS	Zn (67.1)
Spinel	MgO·Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> (71.8) MgO (28.2)
Spodumene	LiAl(SiO <sub>3</sub> ) <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> (27.4) Li <sub>2</sub> O (8.4)
Stannite	Cu <sub>2</sub> S·FeS·SnS <sub>2</sub>	Sn (27.5) Cu (29.5)
Stibnite	Sb <sub>2</sub> S <sub>3</sub>	Sb (71.8)
Titanite	CaTiSiO <sub>5</sub>	TiO <sub>2</sub> (40.8)
Valentinite	Sb <sub>2</sub> O <sub>3</sub>	Sb (83.5)

Name	Formula	Percentage metal
Witherite	BaCO <sub>3</sub>	BaO (77.7)
Wolframite	(Fe, Mn)WO <sub>4</sub>	W (51.3)
Wulfenite	PbMoO <sub>4</sub>	Pb (56.4) Mo (26.2)
Zincite	ZnO	Zn (80.3)
Zircon	ZrSiO <sub>4</sub>	ZrO <sub>2</sub> (67.2)

## APPENDIX 2

## Selected Physical Properties of Metals

<i>Symbol</i>	<i>Atomic number</i>	<i>Atomic weight</i>	<i>Density</i> (gm/cm <sup>3</sup> )	<i>Melting point</i> (°C)
Al	13	26.98	2.7	660
Sb	51	121.76	6.68	630.5
As	33	74.91	5.727	814
Ba	56	137.36	3.5	710
Be	4	9.013	1.845	1284
Bi	83	209.0	9.8	271.3
B	5	10.82	2.34	2300
Cd	48	112.41	8.65	320.9
Ca	20	40.08	1.54	851
Ce	58	140.13	6.66	795
Cs	55	132.91	1.873	28.5
Cr	24	52.01	7.19	1875
Co	27	58.94	8.90	1493
Cb	41	92.91	9.57	2468
Cu	29	63.54	8.94	1083
Dy	66	162.51	8.536	1407
Er	68	167.21	9.051	1497
Eu	63	152.0	5.259	826
Gd	64	157.26	7.895	1312
Ga	31	69.72	5.907	29.75
Ge	32	72.60	5.32	936
Au	79	197.2	19.32	1063
Hf	72	178.50	13.29	2150
Ho	67	164.94	8.803	1461

<i>Symbol</i>	<i>Atomic number</i>	<i>Atomic weight</i>	<i>Density</i> (gm/cm <sup>3</sup> )	<i>Melting point</i> (°C)
	49	114.82	7.31	156.6
Ja	77	192.2	22.42	2410
Fr	26	55.85	7.87	1535
Fe	57	138.92	6.174	920
La	82	207.21	11.34	327.4
Pb	3	6.940	0.534	179
Li	71	174.99	9.842	1652
Lu	12	24.32	1.74	651
Mg	25	54.94	7.44	1244
Ma	80	200.61	13.55	-38.87
Hg	42	95.95	10.22	2610
Mo	60	144.27	7.004	1024
Nd	28	58.69	8.9	1452
Ni	76	190.2	22.5	3000
Os	46	106.4	12.02	1552
Pd	78	195.09	21.40	1769
Pt	94	239.11	19.84	639.5
Pu	19	39.10	0.87	63.7
K	59	140.92	6.782	935
Pr	61	145		1035
Pm	75	186.22	21.02	3180
Re	45	102.91	12.44	1960
Rh	44	101.1	12.4	2250
Ru	37	85.48	1.53	38.5
Rb	62	150.35	7.536	1072
Sc	21	44.96	2.99	1539
Se	34	78.96	4.79	217
Si	14	28.09	2.33	1410
Ag	47	107.873	10.49	960.5

<i>Symbol</i>	<i>Atomic number</i>	<i>Atomic weight</i>	<i>Density</i> (gm/cm <sup>3</sup> )	<i>Melting point</i> (°C)
Na	11	22.991	0.97	97.9
Sr	38	87.63	2.6	770
Ta	73	180.95	16.6	2996
Te	52	127.61	6.25	449.5
Tb	65	158.93	8.272	1356
Tl	81	204.39	11.85	303
Th	90	232.05	11.66	1750
Tm	69	168.94	9.332	1545
Sn	50	118.7	7.3	232
Ti	22	47.90	4.54	1668
W	74	183.92	19.3	3410
U	92	238.07	19.07	1132
Yb	70	173.04	6.977	824
Y	39	88.92	4.472	1509
Zn	30	65.38	7.133	419.5
Zr	40	91.22	6.45	1852

Source: Hampel, Clifford A., ed., *Rare Metals Handbook*, Chapman and Hall, London (1961).

### APPENDIX 3 physical Properties of Metals

<i>Symbol</i>	<i>Boiling point</i> (°C)	<i>Latent heat of fusion</i> (cal/gm)	<i>Latent heat of vaporization</i> (cal/gm)	<i>Specific heat</i> (cal/gm)
Al	2450	96	3050	0.214 (20°C)
Sb	1440	38.3	383	0.0504 (20°C)
As	615	88.5	102 (sublimation point)	0.078
Ba	1500	13.3	262	0.068 (20°C)
Be	2507	250–275	5917	0.425 (20°C)
Bi	1627	12.5	204.3	0.0294 (20°C)
B	2550	489	8300	0.307 (25°C)
Cd	767	13.2	286.4	0.055 (28°C)
Ca	1482	55.7	918	0.149 (20°C)
Ce	3468	15.7	679	0.049 (20°C)
Cs	705	313.766	146	0.052 (20°C)
Cr	2199	61.5	1474	0.1068 (20°C)
Co	3100	62	1500	0.1056 (20°C)
Cb	4927	69	1782	0.0642 (20°C)
Cu	2595	48.9	1150	0.092 (20°C)
Dy	2600	25.2	412	0.0413 (0°C)
Er	2900	24.5	401	0.0398 (0°C)
Eu	1439	15.15	276	0.0395 (0°C)
Gd	3000	23.6	459	0.0713 (0°C)
Ga	1983	19.16	1014	0.0977 (29°C)
Ge	2700	111.5	1200	0.086 (25°C)
Au	2966	14.96	415	0.0312 (18°C)

<i>Symbol</i>	<i>Boiling point (°C)</i>	<i>Latent heat of fusion (cal/gm)</i>	<i>Latent heat of vaporization (cal/gm)</i>	<i>Specific heat (cal/gm)</i>	<i>Symbol</i>
Hf	5400	29.1	885	0.0352 (20°C)	Se
Ho	2600	24.8	405	0.0391 (0°C)	Si
In	2075	6.8	484	0.058 (20°C)	As
Ir	5300	32.6	790	0.032 (20°C)	Na
Fe	300	66.2	1515	0.107 (20°C)	Sr
Pb	1737	5.89	204.6	0.031 (20°C)	Ta
Li	1317	158	4680	0.784 (0°C)	Te
Lu	3327	26.3	515	0.0368 (0°C)	Tb
Mg	1103	82.2	1337	0.25 (25°C)	Tl
Mn	2097	63.7	977.6	0.114 (20°C)	Th
Hg	357	2.8	69.7	0.03325 (20°C)	Tm
Mo	5560	69.8	1222	0.066 (0°C)	Sn
Nd	3027	18.0	479	0.0499 (0°C)	Ti
Ni	2900	73.8	1487	0.105 (20°C)	W
Os	5500	36.9	790	0.039 (20°C)	U
Pd	3980	37.8	88.3	0.0584 (20°C)	V
Pt	4530	24.1	625	0.0314 (20°C)	Yb
Pu	3235	3	336.6	0.034 (25°C)	Y
K	760	14.6	496	0.18 (14°C)	Zn
Pr	3127	17.0	560	0.0458 (0°C)	Zr
Pm	2730		415		
Re	5900	42.4	815	0.03262 (20°C)	
Rh	4500	50.5	1150	0.059 (20°C)	
Rb	688	6.1	212	0.080 (0°C)	
Ru	4900	60.3	1340	0.057 (20°C)	
Sm	1900	17.3	306	0.0431 (20°C)	
Sc	2727	85.3	1743	0.1332 (20°C)	

<i>Symbol</i>	<i>Boiling point (°C)</i>	<i>Latent heat of fusion (cal/gm)</i>	<i>Latent heat of vaporization (cal/gm)</i>	<i>Specific heat (cal/gm)</i>
Se	685	16.5	79.6	0.081 (20°C)
Si	2480	395	2530	0.1597 (0°C)
As	2212	25	556	0.056 (20°C)
Na	883	27.05	1005	0.295 (20°C)
Sr	1380	25	383	0.176 (20°C)
Ta	6100	41.5	995	0.034 (0°C)
Te	990	32	95	0.047 (20°C)
Tb	2800	24.5	440	0.041 (0°C)
Tl	1457	5.04	189.9	0.031 (20°C)
Th	4200	19.8	560	0.0282 (20°C)
Tm	1727	26.0	348	0.0381 (0°C)
Sn	2270	14.5	573	0.0542 (20°C)
Ti	3260	104.5	2350	0.125 (20°C)
W	5900	46	1038	0.032 (20°C)
U	3813	19.75	420	0.028 (20°C)
V	3000	82.5	2150	0.120 (0°C)
Yb	1427	12.71	220	0.0347 (0°C)
Y	3200	46.2	1045.8	0.074 (50°C)
Zn	910	24.4	419.5	0.0925 (20°C)
Zr	3580	60.2	1360	0.0659 (20°C)

## APPENDIX 4

### Thermal Conductivity of Metals

Metal	Thermal conductivity (cal/cm/cm <sup>2</sup> /sec/°C)
Aluminium	0.503 (25°C)
Antimony	0.045 (25°C)
Beryllium	0.35
Bismuth	0.020
Cadmium	0.222 (18°C)
Calcium	0.3
Cerium	0.026
Cesium	0.044 (28.5°C)
Chromium	0.15 (20°C)
Cobalt	0.165 (0–100°C)
Columbium	0.125 (0°C)
Copper	0.934 (20°C)
Dysporosium	0.024
Erbium	0.023
Gadolinium	0.021
Gallium	0.08 (30°C)
Gold	0.707 (25°C)
Hafnium	0.0533 (50°C)
Indium	0.06
Iridium	0.35
Iron	0.175
Lanthanum	0.033
Lead	0.0827 (18°C)
Lithium	0.17 (0°C)
Magnesium	0.376 (20°C)
Mercury	0.020 (0–100°C)
Molybdenum	0.298 (204°C)

## APPENDIX 5

### Electrical Resistivity of Metals

Metal	Thermal conductivity (cal/cm/cm <sup>2</sup> /sec/°C)	Metal	Resistivity (microhm-cm)	Metal	Resistivity (microhm-cm)
Neodymium	0.031	Palladium	2.66 (20°C)	Indium	8.8 (22°C)
Nickel	0.215 (25°C)	Platinum	41.7 (20°C)	Iridium	5.3 (0°C)
Palladium	0.17	Plutonium	33.3 (20°C)	Iron	10.7 (20°C)
Platinum	0.17	Potassium	4.2 (20°C)	Lanthanum	57 (25°C)
Plutonium	0.020 (25°C)	Praseodymium	106.8 (0°C)	Lead	22 (20°C)
Potassium	0.232 (21°C)	Rhenium	650 × 10 (27°C)	Lithium	8.55 (0°C)
Praseodymium	0.028	Rhodium	6.83 (0°C)	Lutetium	68 (25°C)
Rhenium	0.17	Rubidium	4.6 (20°C)	Magnesium	4.46 (20°C)
Rhodium	0.36	Selenium	75 (25°C)	Manganese	185 (20°C)
Rubidium	0.07 (39°C)	Silicon	36.6 (30°C)	Mercury	95.78 (20°C)
Selenium	0.0007–0.00183	Silver	12.8 (20°C)	Molybdenum	5.78 (27°C)
Silicon	0.20	Sodium	5.68 (0°C)	Neodymium	64 (25°C)
Silver	0.934 (100°C)	Tantalum	14.6 (20°C)	Nickel	7.8 (20°C)
Sodium	0.317 (21°C)	Tellurium	1.692 (20°C)	Osmium	9.5 (0°C)
Tantalum	0.13 (20°C)	Thallium	91 (25°C)	Palladium	10.3 (20°C)
Tellurium	0.014 (25°C)	Thorium	86 (25°C)	Platinum	10.58 (20°C)
Thallium	0.093	Tin	81.0 (25°C)	Plutonium	146.5 (0°C)
Thorium	0.09 (200°C)	Titanium	134.0 (25°C)	Potassium	6.1 (0°C)
Tin	0.1528 (0°C)	Tungsten	56.8 (20°C)	Praseodymium	68 (25°C)
Titanium	0.041	Uranium	60 × 10 <sup>6</sup> (25°C)	Rhenium	19.14 (0°C)
Tungsten	0.31 (20°C)	Vanadium	2.44 (20°C)	Rhodium	4.7 (0°C)
Uranium	0.0645	Yttrium	35.5 (20°C)	Rubidium	11.6 (0°C)
Vanadium	0.074 (100°C)	Zinc	94 (25°C)	Ruthenium	7.16–7.6 (0°C)
Yttrium	0.024	Zinc			
Zinc	0.2653 (18°C)	Zirconium			
Zirconium	0.04 (25°C)				

Metal	Resistivity (microhm-cm)	Metal	Resistivity (Microhm-cm)
Samarium	92 (25°C)	Thorium	18 (25°C)
Scandium	66 (25°C)	Thulium	90 (25°C)
Selenium	12 (0°C)	Tin	11.5 (20°C)
Silicon	$15 \times 10^6$ (300°C)	Titanium	42 (20°C)
Silver	1.59 (20°C)	Tungsten	5.5 (20°C)
Sodium	4.3 (0°C)	Uranium	30 (25°C)
Strontium	23 (20°C)	Vanadium	24.8 (20°C)
Tantalum	13.6 (25°C)	Ytterbium	28 (25°C)
Tellurium	52,700 (25°C)	Yttrium	65 (25°C)
Terbium	116 (25°C)	Zinc	5.75 (0°C)
Thallium	18 (0°C)	Zirconium	44 (20°C)

## APPENDIX 6

Thermal Neutron Absorption Cross-Sections of Possible Structural Materials in Ascending Order of Absorption Cross-Section  
(for 2200 m/sec neutron velocity)

Element	Absorption cross-section (barns/atom)	Element	Absorption cross-section (barns/atom)	Element	Absorption cross-section (barns/atom)
C	0.0034	Ni	4.8	Ag	63
Be	0.010	V	4.98	Ho	65
Bi	0.034	Sb	5.7	Re	86
Mg	0.063	Ti	5.8	Au	98.9
Si	0.16	Th <sup>232</sup>	7.56	Hf	105
Pb	0.170	U	7.68	Lu	112
Zr	0.180	Pd	8.0	Tm	127
Al	0.23	Pt	8.8	Rh	156
Sn	0.625	La	9.3	Np <sup>237</sup>	170
Ce	0.73	Pr	11.6	Er	173
Zn	1.10	Se	12.3	In	196
Cb	1.15	Mn	13.2	Pu <sup>240</sup>	295
Y	1.31	Os	15.3	Ir	440
Ge	2.45	W	19.2	B	755
Fe	2.53	Ta	21	Dy	950
Ru	2.56	Sc	24	Pu <sup>239</sup>	1026
Mo	2.7	Th <sup>230</sup>	27	Pu <sup>241</sup>	1400
Cr	3.1	Co	37	Cd	2450
Tl	3.4	Yb	37	Eu	4300
Cu	3.77	Nd	46	Sm	5600
Te	4.7	Tb	46	Gd	46,000

## APPENDIX 7

Vapour Pressures of Some Metals and Corresponding Temperatures  
(temperature in K for various partial pressures in atmosphere)

Metal	$10^{-6} \text{ atm}$	$10^{-5} \text{ atm}$	$10^{-4} \text{ atm}$	$10^{-3} \text{ atm}$	$10^{-2} \text{ atm}$	$1 \text{ atm}$
Ag	1200 (s)	1305	1442	1607	1816	2485
Al	1290 (l)	1405	1545	1725	1940	2600
Au	1570 (l)	1720	1896	2112	2388	3239
Be	1390 (s)	1505	1655 (l)	1830	2070	2780
Bi	873 (l)	960	1060	1190	1360	1900
Ca	790 (s)	867	961	1075	1231 (l)	1755
Cb	2820 (l)	3050	3340	3700	4120	5400
Cd	485 (s)	530	585 (l)	657	744	1038
Co	1750 (s)	1900 (l)	2100	2300	2600	3370
Cr	1350 (s)	1465	1600	1755	1960	2495 (l)
Cs	383 (l)	425	476	544	634	963
Cu	1400 (l)	1530	1685	1875	2117	2668
Fe	1550 (s)	1680	1837 (l)	2033	2277	3008
Hf	2850 (l)	3100	3350	3750	4150	5500
Hg	287 (l)	316	351	394	449	634
K	429 (l)	475	534	605	702	1052
Li	705 (l)	775	865	980	1130	1640
Mg	653 (s)	715	789	881	1000 (l)	1399
Mn	1140 (s)	1240	1360	1570 (l)	1750	2370
Mo	2530 (s)	2740	3000 (l)	3330	3750	5077
Na	510 (l)	558	623	705	813	1187
Ni	1630 (s)	1765 (l)	1930	2130	2380	3110
Pb	887 (l)	975	1088	1226	1408	2010

Source: Parker, L.S. and Gwory, R.W., Physical Chemistry of Metals, McGraw-Hill, New York (1953), Chapter 12.

# Index

The entries in parentheses represent the section numbers

- Activated complex, 45 (2.16)
- Activation energy, 45 (2.16)
- Activator, 125 (3.19)
- ALCAN process, 310 (6.13)
- ALCOA process, 308 (6.13)
- Alkali metals, extraction of, 491 (8.15)
- Alkaline earth metals, extraction of, 491 (8.15)
- Alumina
  - decomposition potential of, 294 (6.9)
  - production of, 291 (6.8)
- Aluminium
  - electrolysis of, 293 (6.9)
  - ores, 290 (6.6)
  - production in India, 303 (6.11)
  - refining, 301 (6.9)
  - uses of, 288 (6.6)
- Aluminothermic reduction, 329 (6.28)
- Amalgamation process, 492 (9.2)
- Anode slime, 352 (7.3)
- Antimony, extraction of, 412 (7.24)
- Arrhenius equation, 44 (2.15), 176 (4.15)
- Atomic bonding, 82 (3.3)
- Bayer process, 291 (6.8)
- Beryllium
  - extraction of, 462 (8.11)
  - sources of, 462 (8.11)
- Bipolar cell, 308 (6.13)
- Bismuth, extraction of, 413 (7.24)
- Blister formation, 349 (7.3)
- Boltzmann's relationship, 11 (2.3)
- Bond's law, 114 (3.12)
- Boundary layer, 48 (2.19)
  - effective, 48, 50 (2.19)
  - thickness of, 49 (2.19)
- Cadmium, extraction of, 412 (7.24)
- Calcination, 130 (4.2)
- Calcium, production of, 472 (8.15)
- Carbonyl process, 264 (5.3)
- Cell design, 221 (4.28)
- Cementation (contact reduction), 189 (4.19)
  - diffusion in, 193 (4.19)
  - kinetics of, 191 (4.19)
- Chalcolithic period, 1 (1.0)
- Change of standard state, 37 (2.13)
- Chemical
  - methods of refining, 256 (5.3)
  - potential, 30 (2.9)
  - precipitation, 257 (5.3)
- Chlorination, 157 (4.11), 341 (7.1), 424 (8.2), 478 (8.18)
- Chrome alum process, 317 (6.19)
- Chromium
  - electrolytic, 317 (6.19)
  - extraction of, 317 (6.19)
  - occurrence of, 317 (6.19)
  - uses of, 316 (6.19)
- Cladding element, 452 (8.9)
- Classifier, 120 (3.16)
- Closed system, 7 (2.2)
- Cobalt
  - ammine, 199 (4.20)
  - extraction of, 410 (7.24)
- Coefficient
  - activity, 32 (2.10)
  - extraction, 245 (5.2)
  - mass transfer, 50 (2.19)
  - partition, 53 (2.19)
- Collector, 125 (3.19)
- Collision theory, 44 (2.15)
- Comminution
  - efficiency in, 113 (3.12)
  - laws, 114 (3.12)
- Complex sulphides, 397 (7.19)
- Hydrometallurgy of, 398 (7.19)
- Concentrates, typical compositions of, 170 (4.13)
- Contact angle, 126 (3.19)
- Copper
  - continuous production of, 356 (7.4)
  - hydrometallurgy of, 367 (7.6)
  - production energetics of, 367 (7.5)
  - refining of, 257 (5.3), 367 (7.3)
  - secondary, 502 (10.1)
  - smelting, 345 (7.3), 372 (7.7)
  - uses of, 341 (7.2)
- Counter current contacting, 247 (5.2)
- Covalent bonds, 82 (3.3)
- Cryolite
  - role of, in electrolysis of aluminium, 298 (6.9)
  - synthesis of, 294 (6.9)
- Current efficiency, 300 (6.9)
- Cyanidation, 177 (4.15), 492 (9.2)
- Dead roast, 131 (4.3)
- Degassing, 163, 165 (4.12)
- Degree of liberation, 111 (3.11)
- Deoxidation, 166 (4.12)
- Depressor, 125 (3.19)
- Deville-Pechiney process, 302 (6.10)
- Diffusion
  - in liquid, 47 (2.19)
  - laws of, 47 (2.18)
- Distillation, 252 (5.3)
  - rate, 253 (5.3)
  - selective, 252 (5.3)
- Dow process, 466 (8.13)
- Downs' process, 470 (8.14)
- Drag force, 119 (3.15)
- Drossing, 377 (7.9)
- Dwight-Lloyd sintering machine, 143 (4.5)
- Electrochemical dissolution, 176 (4.15)
- Electrode kinetics, 67 (2.24)
- Electrode potential, 61 (2.21)
  - application of, 66 (2.23)
- Electrolysis
  - sign of, 65 (2.22)
  - standard, 65 (2.22)
- Electrolytic extraction (see Electrolysis)
- Electrometallurgy, 129 (4.0), 205 (4.23)
- Electromotive force, 62 (2.21)
  - cell, 62 (2.21)
- Electron beam melting, 277 (5.3)
- Electronegativity, 78 (3.1)
- Electroplating, 223 (4.29)
- Electrorefining, 257 (5.3)
- Electrostatic separation, 123 (3.18)
- Ellingham diagrams, 19 (2.7)
- Energy aspects
  - of copper smelting, 367 (7.5)
  - of metal production, 224 (4.30)
- Enthalpy, 7 (2.2)
- Entropy, 10 (2.2)
  - as criterion for spontaneity, 12 (2.4)
  - configurational, 11 (2.3)
  - statistical treatment of, 11 (2.3)
  - vibrational, 12 (2.3)
- Equilibrium constant, 15 (2.6)
- Excess thermodynamic quantities, 34 (2.11)
- Faraday, 60 (2.21)
- Faraday's laws, 60 (2.21)
- Ferroalloying elements
  - extraction of, 316 (6.19)
- Ferroalloys, 325 (6.26)
  - extraction of, 327 (6.29)
  - refining of, 331 (6.29)
  - uses of, 325 (6.26)
- Ferrochrome, production of, 333 (6.28)
- Ferromanganese, production of, 332 (6.28)
- Fick's laws, 47 (2.18)
- Flotation, 123 (3.19)
- Fluidized bed, 141 (4.5)
- Fluxes, 144 (4.6)
- Free energy, 13 (2.5)
  - data compilation for, 17 (2.7)
  - diagram, 19 (2.7)

of formation, 19 (3.1)  
standard change in, 15 (2.7)

Gaseous reduction, 194 (4.20)  
kinetics of, 201 (4.21)  
precipitation of Ni and Co by, 198 (4.21)

Gibbs-Duhem equation, 29 (2.9)

Gibbs' free energy, 13 (2.4)

Gibbs-Helmholtz equation, 14 (2.5)

Gold  
extraction of, 492 (9.2)  
hydrometallurgy of, 176 (4.14), 492 (9.3)

Grain size, 111 (3.11)

Grinding, ideal speed of, 114 (3.11)

Grizzly, 117 (3.14)

Halide metallurgy, 157 (4.11)  
reduction in, 156 (4.10)

Hall-Héroult process, 293 (6.9)

Halogenation, 157 (4.11), 421 (8.1)

Heat(s)  
capacity, 8 (2.2)  
content, 8 (2.2)  
of formation, 9 (2.2)

Henry's law, 33 (2.10)

Hess's law, 9 (2.2)

Hunter's process, 484 (8.21)

Hydrogen  
electrode, 65 (2.23)  
overvoltage, 70 (2.24)

Hydrometallurgy, 168 (4.13)

Ignition temperature, 142 (4.5)

Ilmenite, processing of, 477 (8.18)

Imperial Smelting process, 389 (7.16)

INCO process, 354 (7.4)

Interaction parameter, 40 (2.14)

Internal energy, 7 (2.2)

Iodide process, 265 (5.3)

Ion exchange, 206 (4.22), 238 (5.3)  
kinetics of, 240 (5.2)  
plants, 241 (5.2)

Ionic bonds, 82 (3.3)

Isolated system, 7 (2.2)

Isotope separation, 428 (8.4)

Jigging, 121 (3.16)

Kick's law, 114 (3.12)

Kinetic steps, 51 (2.19)

Kirchhoff's equation, 9 (2.2)

KIVCET process, 380 (7.10)

Kroll's process, 482 (8.20)

Laterite ore, 403 (7.22)  
reduction smelting of, 407 (7.22)

Leaching, 170 (4.13), 171 (4.14)  
acid, 173 (4.15), 387 (7.15), 422 (8.2), 431 (8.4),  
479 (8.18)

agitation, 172 (4.14)

alkali, 173 (4.15), 182 (4.16), 408 (7.22),  
423 (8.2)

bacterial, 186 (4.18)

dump, 172 (4.14)

electrochemical mechanism of, 180 (4.15)

heap, 172 (4.14)

*in situ*, 172 (4.14)

kinetics in, 174 (4.15)

microbial, 186 (4.18)

percolation, 172 (4.14)

pressure, 182 (4.17)

role of oxygen in, 181 (4.16)

temperature dependence of, 176 (4.15)

theory of, 173 (4.15)

Lead, 374 (7.9)  
extraction of, 374 (7.9), 381 (7.11)

refining of, 377 (7.9)

uses of, 373 (7.8)

Liberation, 111 (3.11)

Lime sinter process, 302 (6.10)

Liquation, 254 (5.3)

Liquid-liquid extraction (see Solvent extraction)

MacDougall roaster, 138 (4.5)

Magnesium  
electrolysis of, 466 (8.13)

extraction of, 284 (6.3)

ores, 284 (6.2)

uses of, 283 (6.1)

Magnetic  
attractability, 121 (3.17)

separation, 121 (3.17)

Magnetherm process, 287 (6.4)

Manganese  
electrolytic, 318 (6.20)

nodules, 89 (3.7)

uses of, 318 (6.20)

Matte, 156 (4.9), 339 (7.1)  
grade of, 346 (7.3)

smelting, 156 (4.9), 339 (7.1)

size of particles, 116 (3.13)

Mean size, 115 (3.13)

Mesh size, 115 (3.13)

Metals  
reactivities of, 76 (3.1)

secondary, 86 (3.5), 502 (10.1)

sources of, 85 (3.5)

Metallic behaviour, 74 (3.0)

Metallothermic reduction, 146 (4.7), 164 (4.12)

Metallurgical wastes, 508 (10.8)

Metal solubility in molten salt, 217 (4.26)

Mineral(s), 82 (3.4)  
dressing, 109 (3.10)

exploration, 82 (3.4)

Indian reserves of, 101 (3.9)

world occurrences of, 90 (3.8)

Misch metal, 472 (8.16)

Mitsubishi process, 364 (7.4)

Modes of occurrence of metals, 80 (3.2)

Molybdenum, extraction of, 325 (6.25), 414 (7.24)

Monazite, treatment of, 444 (8.7)

Monodisperse mass, 115 (3.13)

Multicomponent solutions, 40 (2.14)

Multistage contacting, 246 (5.2)

Newton's equation, 120 (3.15)

Nickel, 399 (7.21), 403 (7.22)  
ammine, 199 (4.20)

extraction of, 403 (7.22)

hydrometallurgy of, 409 (7.22), 410 (7.23)

uses of, 399 (7.20)

Noranda process, 362 (7.4)

Nuclear  
fission, 428 (8.4)

reactor metals, 419 (8.1)

Ocean-floor nodules, 89 (3.7)

Ore(s)  
beneficiation, 109 (3.10)

crushing of, 111 (3.11)

definition of, 82 (3.3)

prospecting, 82 (3.4)

Outokumpu flash smelter, 354 (7.4), 380 (7.10)

Oxygen pressure, in equilibrium with metal-oxide system, 21 (2.7)

Oxygen scale, 22 (2.7)

Parke's process, 378 (7.9)

Partial molar property, 28 (2.8)

Particle size, 111 (3.11)  
typical values of, 117 (3.13)

Periodic table of elements, 74 (3.0)

Pidgeon process, 285 (6.4)

Pierce-Smith converter, 347 (7.3), 402 (7.21)

Platinum metals, extraction of, 498 (9.4)

Plutonium  
extraction of, 439 (8.6)

uses and properties of, 438 (8.6)

Polarization  
activation, 69 (2.24)

concentration, 70 (2.24)

Porosity factor, 57 (2.20)

Precious metals, uses of, 490 (9.1)

Predominance area diagram, 133 (4.4), 379 (7.10)

Process fuel equivalent, 367 (7.5)

Pulp, 125 (3.19)

Purification, 251 (5.3)  
chemical methods of, 237 (5.2), 256 (5.3)

Pyrometallurgy, advantages of, 129 (4.1)

Raoultian scale, 37 (2.13)

Raoult's law, 31 (2.10)

Rare-earth metals  
extraction of, 473 (8.16)

uses of, 472 (8.16)

Reaction(s)  
booster, 442 (8.6), 450 (8.8)

disproportionation, 263 (5.3)

first-order, 42 (2.15)

gas-solid, 54 (2.20)

heterogeneous, 47 (2.17)

homogeneous, 47 (2.17)  
order of, 42 (2.15)  
second-order, 42 (2.15)  
topochemical, 54 (2.20)

**Reaction rate**, 42 (2.15)  
absolute, 45 (2.16)  
effect of temperature on, 44 (2.15)  
overall, 58 (2.19)  
theory, 45 (2.16)

**Rectification**, 253 (5.3)

**Red mud**, 291 (6.8), 508 (10.7)

**Refining** 231 (5.0), 232 (5.1)  
electroslag, 278 (5.3)  
fire, 256 (5.3)  
general methods of, 230 (5.0)

**Reynold's number**, 119 (3.15)

**Riffler table**, 121 (3.16)

**Rittinger's law**, 114 (3.12)

**Roasting**, 131 (4.3)  
autogenous, 142 (4.5)  
blast, 132 (4.3), 143 (4.6)  
chemistry of, 132 (4.3)  
chloridizing, 132 (4.3)  
flash, 139 (4.5)  
fluosolid, 139 (4.5)  
multiple hearth, 138 (4.5)  
of sulphides, 338 (7.1), 343 (7.3)

**oxidizing**, 131 (4.3)

**sinter**, 143 (4.6)

**sulphating**, 132 (4.3)

**volatilizing**, 132 (4.3)

**Screen capacity**, 118 (3.14)

**Sea**, dissolved elements in, 87 (3.6)

**Serpel process**, 302 (6.10)

**Settling**  
free, 118 (3.15)  
hindered, 118 (3.15)

**Sieving**, 115 (3.13)

**Silicate degree**, 149 (4.7)

**Silicon**  
extraction of, 319 (6.21)  
occurrence of, 319 (6.21)  
uses of, 319 (6.21)

**Silver**, extraction of, 496 (9.3)

**Sizing**, 117 (3.14)

**scale**, 116 (3.13)

**Slag(s)**, 144 (4.6)  
acid, 149 (4.7)  
basic, 149 (4.7)  
formation of, 147 (4.7)  
fuming of, 393 (7.17)  
neutral, 149 (4.7)  
structure of, 147 (4.7)  
uses of, 508 (10.8)

**Smelting**, 144 (4.6)  
flash, 150 (4.8), 340 (7.1), 354 (7.4), 380 (7.10)  
furnaces, 150 (4.8)  
reduction, 145 (4.6)  
reverberatory, 150 (4.8), 345 (7.3)

**Sodium**, extraction of, 469 (8.14)

**Solution(s)**, 27 (2.8)  
dilute, 37 (2.13)  
ideal, 32 (2.10)  
nonideal, 32 (2.10)  
regular, 36 (2.12)  
thermodynamics of, 27 (2.8)

**Solvent extraction**, 205 (4.22), 243 (5.2)

**Sorel process**, 478 (8.18)

**Spontaneous processes**, 14 (2.5)  
criteria for, 14 (2.5)

**Stability diagram**, 133 (4.4)

**Stoke's equation**, 120 (3.15)

**Structure**, of solvent media, 207 (4.24)

**Sublimation**, 233 (5.2)

**Tafel equation**, 69 (2.24)

**Tantalum**, extraction of, 323 (6.24)

**Temkin's model**, 209 (4.24)

**Thermodynamics**  
equilibrium in, 15 (2.6)  
first law of, 7 (2.2)  
second law of, 10 (2.3)

**Thorium**, extraction of, 442 (8.7)

**Three-layer process**, 260 (5.3), 301 (6.9)

**Tin**  
refining of, 314 (6.17)  
smelting of, 312 (6.16)  
uses of, 310 (6.14)

**Titanium**, 475 (8.17), 482 (8.20)  
extraction of, 482 (8.20)

**Tungsten**  
extraction of, 320 (6.22)  
occurrence of, 320 (6.22)  
uses of, 320 (6.22)

**Tyler series**, 115 (3.13)

**Uranium**  
extraction of, 428 (8.4)  
hydrometallurgy of, 431 (8.4)  
production in India, 435 (8.5)

**Van Arkel process**, 265 (5.3)

**Vant Hoff equation**, 44 (2.15)

**Vapour transport processes**, 263 (5.3)

**Volatility, relative**, 235 (5.2)

**Wettability**, 125 (3.19)

**WORCRA process**, 358 (7.4)

**Zinc**  
extraction of, 383 (7.13)  
hydrometallurgy of, 387 (7.15)  
production in India, 394 (7.18)  
retort process for, 386 (7.13)  
uses of, 382 (7.12)

**Zircon**, treatment of, 453 (8.9)

**Zirconium**  
extraction of, 451 (8.9)  
production in India, 455 (8.10)  
refining of, 453 (8.9)  
separation of hafnium from, 453 (8.9)  
sponge, 457 (8.10)

### *the book*

Here is a comprehensive text that competently and elegantly combines the theoretical and practical aspects of extraction of nonferrous metals.

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This book, which presupposes only a knowledge of elementary undergraduate mathematics and basic thermodynamics, is primarily intended as a text for the undergraduate in nonferrous extraction metallurgy. It would also be of value to the postgraduate in process metallurgy and to the practising metallurgist, in addition to the teacher.

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