

CHAPTER 1

INTRODUCTION

Extractive Metallurgy deals with extraction and refining of metals. More than sixty elements are metals which are generally extracted from various forms of natural occurrence in the Earth's crust.

A **mineral** is a naturally occurring compound. These are mostly inorganic compounds consisting of one or more metals in association with nonmetals e.g. oxygen, sulphur etc. A mineral is solid and crystalline and has a composition varying within certain limits. It also has well defined physical properties. An **ore** is a naturally occurring aggregate of minerals from which one or more metals or minerals may be extracted economically. An ore may exhibit wide variation in composition and in physical and chemical characteristics.

When ore deposits are exploited in extractive metallurgy there is generally some waste product. This waste is composed of some minerals in the ore which are not useful from the point of view of metal extraction. These are known as **gangue** or gangue minerals. The useful minerals are sometimes called **ore minerals**.

The principal objective of this book is to introduce the readers to some of the principles of extractive metallurgy. Whenever one talks of principles of a subject, he primarily means the scientific basis of the subject. It will be so here also. However, it should be noted that some of the many extraction and refining processes are centuries old having primarily evolved as art. Serious scientific investigations of metallurgical systems began only about fifty years ago. Therefore, not all processes are yet understood completely from the scientific point of view. Yet we have now an appreciable body of knowledge about the behaviour of systems related to processes of extraction and refining of metals.

Much of the insight into the processes has been gained using principles of physical chemistry. The outcome of this is the development of the subject known as **Chemical Metallurgy** which deals with chemical fundamentals of metallurgy. Extractive metallurgy is a discipline in engineering as well. Here momentum, heat and mass transfer as well as mathematical techniques constitute the engineering fundamentals and the application of these has led to the development of the subject termed as **Process Engineering Metallurgy**. In all these developments, physical chemists, chemical and other engineers have played significant roles besides metallurgists. In this sense, extractive metallurgy is multi-disciplinary in nature.

1.1 NATURAL OCCURRENCE OF METALS

Naturally occurring minerals are mainly oxides, sulphides and halides which may be simple in terms of chemical composition (e.g. Cinnabar, HgS ; Hematite, Fe_2O_3) or rather complex (e.g. Beryl, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$); Chalcopyrite, CuFeS_2 ;

Dolomite, $\text{CaMg}(\text{CO}_3)_2$; Tourmaline, $((\text{NaLiK})_6(\text{MgFeCa})_3(\text{AlCrFe})_2\text{B}_2\text{SiO}_5)$. Some of the complex compositions may be considered as chemical association of simpler compounds. The most abundant minerals are silicates. The exact nature of association of a metallic element with other elements depends on the reactivity of the metal, distribution of other elements in the neighbourhood as well as the geological conditions to which the mineral deposits are subjected through the ages.

Metals with high chemical reactivity tend to form more stable and often more complex compounds. Those with lower reactivity tend to form relatively unstable associations. The so-called noble metals (gold, silver, platinum group metals) may be found in the native state because of their poor reactivity.

1.1.1 Sources of metals

Metals and their compounds are available from three sources. The most important source, of course, is the ore deposits in the Earth's crust. Ocean waters comprise the second source. These cover nearly seventy percent of the Earth's surface and contain, on an average, 3.5 percent dissolved solids. In addition, many regions in ocean beds are known to contain huge deposits of metal-rich nodules containing manganese and other elements. Lastly scrap metals should also be considered to be another source of metals. This man-made source is becoming more important and more freely available with industrial growth of societies. Increasing amounts of scrap are being recycled in technologically developed countries. Reclaimed and recycled lead and aluminium constitute about 50 pct. of feedstock for production of respective metals in U.K. and U.S.A.

Tables 1.1 and 1.2 show the average chemical analysis of the Earth's crust and the sea water respectively. There are several hundred billion tons of nodules in the ocean floor and they continue to form at the rate of about 10 m tons/yr. These contain principally manganese, nickel, iron, copper, cobalt and siliceous ocean floor silt and are referred to as polymetallic nodules. Although deposits of nodules can be found in almost all depths of water in the ocean, only those lying at less than 300 meters of depth are considered economic to mine. In addition, the best grades are located in the mid-pacific ocean. The average size of nodules is about 4 cm. Table 1.3 gives some figures to indicate the reserves, the composition and the relative abundance of nodules as compared to deposits in land.

TABLE 1.1 Average analysis of the Earth's crust

Element	Percent	Element	Percent
Oxygen	46.7	Chromium	0.01
Silicon	27.7	Copper	0.01
Aluminium	8.1	Nickel	0.008
Iron	5.0	Zinc	0.004
Calcium	3.6	Lead	0.002
Sodium	2.8	Cobalt	0.001
Potassium	2.6	Beryllium	0.001
Magnesium	2.1	Molybdenum	0.0001
Titanium	0.44	Tin	0.0001
Manganese	0.10	Mercury	0.00001
Zirconium	0.017	Silver	0.000001
Vanadium	0.014	Platinum	0.0000001
		Gold	0.0000001

TABLE 1.2 Average concentration of some elements present in solution in sea water

Element	Concentration g/tonne	Element	Concentration g/tonne
Sodium	10,500	Zinc	0.005—0.014
Magnesium	1,270	Copper	0.001—0.09
Calcium	400	Manganese	0.001—0.01
Potassium	380	Lead	0.004—0.005
Aluminium	0.16—1.9	Tin	0.003
Lithium	0.1	Nickel	0.0001
Silicon	0.02—0.04	Gold	0.000005
Iron	0.002—0.02		

TABLE 1.3 Reserves of metals in Pacific ocean nodules

Name of element	Wt % in nodule	Estimated reserve (10 ⁹ tonnes)	Ratio of $\frac{\text{Nodule reserve}}{\text{Land reserve}}$
Mg	1.66	25	—
Al	2.86	43	200
Ti	0.66	9.9	—
V	0.05	0.8	—
Mn	23.86	358	4000
Fe	13.80	207	4
Co	0.35	5.2	5000
Ni	0.98	14.7	1500
Cu	0.52	7.9	150
Zn	0.46	0.7	10
Zr	0.06	0.93	1000
Mo	0.05	0.77	60
Ag	0.0001	0.001	1
Pb	0.09	1.3	50

(—denotes that land reserves are unlimited)

[Source : J.L. Mero, Potential economic value of ocean floor manganese nodule deposits, National Science Foundation, Washington (1972)]

1.2 RESOURCES OF METAL-BEARING MINERALS IN INDIA

The mineral resources of India, so far as metals are concerned, can be classified into the following three categories :

Adequate to abundant : Al, Be, Cr, Fe, Mn, Mg, Ti, Zr, Th, Pb, Zn, and Rare Earths (R.E.).

Inadequate : Cu, Au, V, Ni, Cd and U.

Poor or so far not known : Sb, Bi, Co, Hg, Mo, Nb, Ta, Sr, Se, Te, Sn, Ag, W, and Pt metals.

If properly exploited the ore minerals in the first category can not only meet

*The term 'resources' means the totality of a particular mineral occurrence in a region irrespective of grade, tonnage or economics of exploitation. The term 'reserve' takes into account grades and some certainty with which the tonnage has been estimated for any particular cut-off grade.

the country's demands for these metals but may also yield surplus quantities for export. The second category refers to limited reserves. These are insufficient to meet the growing demands of the country, but, at the same time, must be exploited fully. Ore minerals in the third category usually do not justify commercial exploitation at the present stage except for strategic uses.

Obviously India's position is rather poor regarding some of the common metals such as tin, cobalt, nickel etc. However, the position regarding Cu, Zn and Pb has improved considerably after recent discoveries of new ore deposits. The country has significant reserves of iron, manganese, magnesium, aluminium, titanium etc. It also has abundant reserves of thorium, zirconium and beryllium which are metals of strategic importance.

1.3 COMMERCIAL PRODUCTION OF METALS

It should be noted that the availability of metals for use is not governed by its abundance alone. Thus, although copper is the third tonnage metal after iron and aluminium, its concentration in the Earth's crust is quite low (only about 0.01 percent). Again, although the annual consumption of iron far outstrips that of aluminium, the abundance of iron in the Earth's crust is less.

Tonnage production of a metal depends on the following factors :

Accessibility of ore deposits

Richness of ore deposits

Nature of extraction and refining processes for the metal

Physical and chemical properties of the metal, and

The demand for the metal which is governed by many factors including its physical and chemical properties.

A fundamental consideration in all the above mentioned factors, is of course, economics. A metal becomes a common one if it is readily available and easily produced with low processing cost and if it allows development of attractive properties.

Table 1.4 presents approximate world production figures for some metals. It would be seen that iron as steel is by far the most widely produced metal. This is so because iron ores are available in plenty in easily accessible deposits. Also, the processing of iron ores is relatively easy and economical. Finally, alloys of iron have a wide range of useful properties.

TABLE 1.4 World production of some metals (1985)

Metal/Alloy	Production, million tonnes/year
Raw steel	715
Pig iron	502
Aluminium	15.3
Copper (refined)	9.7
Lead (refined)	5.64
Zinc (slab)	6.75
Nickel	0.71
Tin	0.21

[Courtesy : Indian Bureau of Mines, Nagpur]

Because of the overwhelming importance of iron and steel, **Ferrous Extractive Metallurgy** is a subject on its own right. The **nonferrous metals** which are produced in large quantities include metals such as aluminium, copper, lead and zinc. The terminology 'nonferrous metals' should strictly mean all metals other than iron. Generally, however, it means the more common nonferrous metals mentioned previously. Metals such as thorium, vanadium etc., which are not so commonly used and are far more expensive, are commonly referred to as **rare metals or less common metals**.

India's share in the world production of metals is rather small. Some approximate figures are indicated in Table 1.5.

TABLE 1.5 Annual production of some metals in India (1986)

Metal/Alloy	Production (thousand metric tonnes/year)
Raw steel	12,230
Pig iron	11,590
Aluminium	240
Copper (blister)	39
Copper (electrolytic)	22
Zinc	61
Lead	30
Tin	0

[Courtesy : S. Bhattacharya, National Metallurgical Laboratory, Jamshedpur; Indian Bureau of Mines, Nagpur]

1.4 EXTRACTIVE METALLURGY— A PROCESS OF SEPARATION

Any extraction and refining process consists of some individual sequential steps, i.e. **unit steps**. Any of these unit steps can be found in more than one process. For example, electrolysis is practised for aluminium, zinc, copper and a variety of other metals. Smelting is carried out for extraction of iron, lead, copper etc. As a matter of fact, the various extraction and refining routes are formulated essentially by selective combination of these unit steps. The unit steps are classified into **unit operations** and **unit processes** in accordance with the conventions originally adopted in chemical engineering. The former refers to physical operations such as comminution, filtration, casting, distillation etc., while the latter refers to chemical processing such as leaching, smelting etc. In all subsequent discussions, the term 'process' will be used to mean both unit operation and unit process.

Production of metals of desired purity from the natural ores is principally a **separation process**. Such separation processes may be classified into two stages.

1. Separation of the compound containing the desired metal from other constituents. Crudely speaking, it is separation of ore mineral from other gangue minerals. This is known as **concentration** and it comes under the discipline of **Mineral Engineering**.

2. Separation of the desired metal from other constituents of the metallic compound and further purification of the metal. This is known as **extraction and refining** and constitutes the subject matter of **Extractive Metallurgy**.

For some metals, such as aluminium, the two stages are distinct. Pure alumina (Al_2O_3) is produced by the Bayer's process from the ore. Then aluminium metal is extracted by electrolysis. However, there is usually no separate concentration step for production of iron from high grade ores. The gangue materials are by and large separated during extraction in the blast furnace. Lean ores may, however, require beneficiation.

Chemists and chemical engineers have also been overwhelmingly concerned with various separation processes, which have been classified into two main categories.

1. **Mechanical separation processes**, such as gravity separation, filtration, magnetic separation etc. Here separation does not take place at the molecular level. Rather, aggregates of molecules (more specifically, particles) are separated.
2. **Diffusional separation processes**, such as distillation, precipitation, extraction etc. Here separation takes place by movement of individual atoms and molecules by diffusion, aided by other mass transfer processes. Some of these processes are accompanied by chemical reaction such as in leaching, smelting whereas others are purely physical separation processes, e.g. distillation, zone refining.

Again, diffusional separation processes have been subdivided into two categories.

1. Separation methods based on phase equilibria and kinetics. Here the limits of separation is set by chemical (or phase) equilibria amongst the participating phases. Examples are distillation, solvent extraction, slag-metal reactions.
2. Separation methods based on rate processes, such as gaseous diffusion and electrophoresis.

If after crushing and grinding, the constituents of an ore separate out wholly or partially, mechanical separation would enable attainment of partial concentration. Otherwise diffusional separation process is to be employed. In this connection, the terminology 'liberation' is popular amongst mineral engineers. Liberation denotes the detachment of dissimilar mineral grains upon comminution.

It may be safely generalized that unit processes and operations in extraction and refining of metals are diffusional separation processes. Mechanical separation may also be involved, but only as auxiliary feature. Moreover, it is to be noted that these separation processes are based on phase equilibria, i.e. the limits of separation would be set by chemical or phase equilibria amongst the participating phases. Finally, most of the unit steps in extractive metallurgy involve chemical reactions and hence are unit processes.

Very often the separation processes account for most of the cost of pure substance. The lower the concentration of the metal in the ore, the higher is the cost of the metal in general. Therefore, radium is costlier than gold, which is costlier than copper and so on.

1.5 CLASSIFICATION OF PROCESSES

Processes can be classified in various ways depending on the aim. In this section an attempt is made to present a comprehensive classification system with specific reference to extractive metallurgy.

Traditionally, methods of extraction and refining have been classified into the following categories:

- Pyrometallurgy
- Hydrometallurgy
- Electrometallurgy

Pyrometallurgical processes (in Greek, 'pyr' means 'more at fire') are carried out at high temperatures. Hydrometallurgy (in Greek, 'hydor' means 'more at water') is carried out in aqueous media at or around room temperature. Electrometallurgy employs electrolysis for separation at room temperature as well as at high temperature.

Another way of classification would be in terms of unit operation or unit process, as discussed already. Pyrometallurgy can be further classified as follows.

1. *Solid-state processing* : This does not involve any melting. It is typically carried out in the temperature range of 500-1200°C, as exemplified by roasting of sulphides, calcination, solid state reduction of metal oxides by H_2 and CO. Solids are mostly immiscible and hence the product of solid state processing is either pure or is a mechanical mixture. In the latter case, it requires further separation.

2. *Liquid-state processing*: This involves melting of at least the metal-containing phase and is on the whole carried out at a higher temperature. Examples are blast furnace smelting, steelmaking, distillation refining of zinc from impure lead etc. Liquid state processing separates out the metal either in pure or in impure form. Appreciable compositional changes in the liquid are possible due to miscibility, rapid diffusion and mixing.

It is worth emphasizing here that this system of classification can be extended to hydro and electrometallurgy as well. Again, processes can be classified according to type of chemical reaction, mode of energy input etc. Based on all the above discussions an attempt has been made to characterise some important unit processes and unit operations in extractive metallurgy in Table 1.6.

1.6 PROCESS DESIGN AND PROCESS ANALYSIS

In chemical engineering, the traditional method of design of unit processes or unit operations is **semi-empirical**. In this approach the process is studied in the laboratory. Important dimensionless groups are identified and correlations amongst them are obtained from laboratory data. Then predictions are made for pilot plant or commercial reactor on the basis of the above.

In **rational** or **quantitative** design methods, a different approach is employed for reactive systems. The chemical rate equations are obtained from the laboratory data. Then quantitative calculations are made for large-size reactors from the above information as well as data on heats of reactions, chemical equilibria, rates of heat and mass transfer. Such calculations are mostly complicated and call for exploitation

of numerical methods and aid of computer. This may be referred to as **rational or quantitative process analysis**.

Such process analysis calls for exploitation of scientific and engineering fundamentals. The types of calculations performed are:

- Material balance
- Heat balance
- Reaction and phase equilibria
- Reaction rates/mass transfer rates
- Heat transfer rates

Quantitative process analysis is only a step towards quantitative process design. An economic and workable design, which would be acceptable to industry also, requires a good knowledge of the process, considerations for cost as well as compliance with social constraints. For example, a process which is technically sound may be unacceptable because of high costs. Again a design, which is technically and economically feasible, may not be acceptable to the Government from social and legislative view points. In many countries there are strict pollution control acts, which are to be adhered to. If a process envisages use of raw materials which are to be imported, it may not be allowed.

A commercially successful design is an **optimal design** based on the above. Now-a-days attempts are being made to find out such optimum quantitatively by application of **optimization techniques**. However, it is usually a very difficult and complex task and has not, therefore, become common. The entire spectrum of activity connected with process design is shown schematically with the help of a block diagram in Fig. 1.1.

1.7 ORGANIZATION OF THE SUBSEQUENT CHAPTERS

The present text is concerned with:

1. brief discussions of some scientific and engineering fundamentals of importance to extractive metallurgy, and
2. presentation of simple process calculations and process analysis as illustrations of applications of principles.

The text is primarily concerned with pyrometallurgy for the following reasons.

1. Pyrometallurgy is the most important route in terms of tonnage and scope of application for extraction and refining of metals.
2. Scientific basis of room temperature systems as are encountered in hydro and many electrometallurgical processes are presented to the students in traditional chemistry courses. Behaviour of water as a fluid and a solvent is reasonably well-known. On the other hand, a student would not have much familiarity with systems encountered in pyrometallurgy unless he is specially taught these in the professional curriculum.

The text is divided into 3 parts, viz.

- (a) INTRODUCTORY
- (b) PRINCIPLES OF PYROMETALLURGY
- (c) PRINCIPLES OF HYDRO AND ELECTROMETALLURGY

TABLE 1.6 Characteristics of some unit processes and unit operations

Name of Process	Broad classification	Approximate temperature range, °C	Type of chemical reactions	Purpose of the process occurring	Mode of energy input	Contacting phases	Typical reactors employed
1	2	3	4	5	6	7	8
Roasting of sulphide	Pyromet, unit process, solid-state processing	500—1200	Oxidation	Pretreatment*	Fuel, exothermic heat of reaction	Solid, gas	Shaft furnace, fluidized bed reactor, flash roaster, rotary kiln
Calcining	—do—	—do—	Decomposition	—do—	Fuel	—do—	—do—
Carbothermic smelting	Pyromet., unit process, liquid-state processing	1200—1600	Reduction	Extraction	Fuel, electrical energy	Solid, liquid, gas	Blast furnace, retort, electric arc furnace
Metallthermic reduction of metal oxides, chlorides	—do—	900—2400	—do—	—do—	—do—	—do—	Bomb, retort
Leaching	Hydromet., unit process, solid-state	Room temp. —200	Dissolution	Pretreatment	Fuel, electrical energy	Solid, liquid	Vats, autoclaves
Distillation refining	Pyromet., unit operation, liquid-state processing	1000—2000	—	Refining	Fuel, sensible heat of input materials	Liquid, gas	Retort
Solvent extraction	Hydromet, unit process, liquid-state processing	Room temp.	Exchange	Pretreatment	Nil	Liquid	Packed bed, plate column
Electrolysis	Electromet., unit process, solid or liquid-state processing	Room temp. —900	Electrochemical	Extraction, refining	Electrical	Solid, liquid	Electrolysis tank

* Pretreatment refers to treatment for conditioning or concentrating the feed material before extraction step.

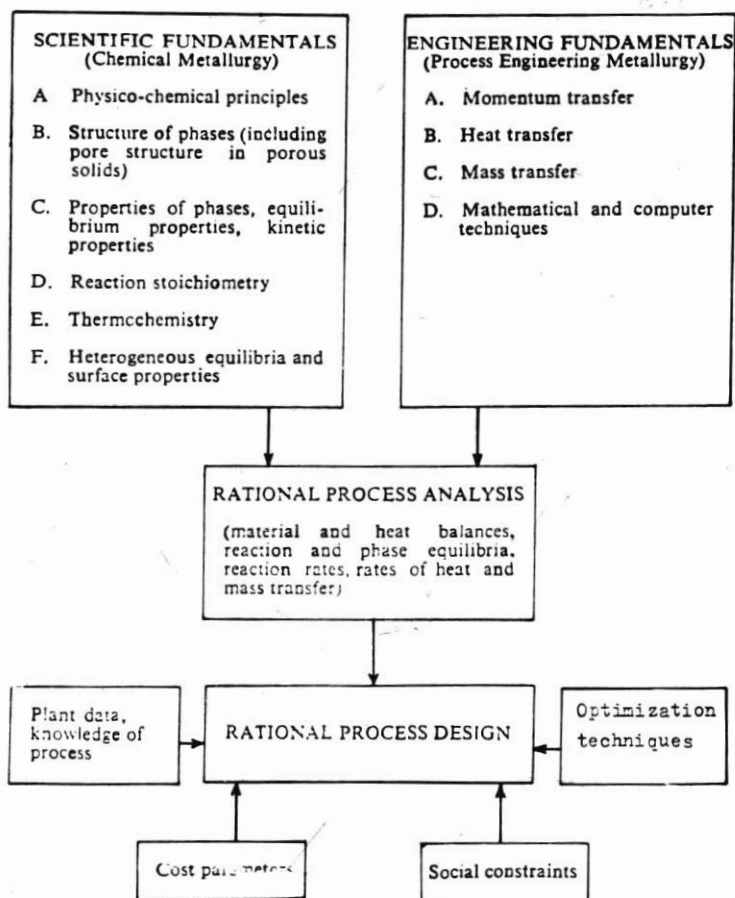


Fig. 1.1 Inputs for quantitative process design with specific reference to Extractive Metallurgy

Part (a) consists of this chapter and Ch. 2. The latter introduces the readers to methods of extraction and refining in brief. This may appear somewhat surprising. Normally, in a subject, principles are taught first and then the methods. However, in the discussion of principles, examples will be drawn all the time from processes. This necessitates that a brief exposure is given first to important methods in order that readers appreciate the principles better.

Part (b) has 7 chapters (Ch. 3-Ch. 9). The principles discussed there are of general applicability. But due to limited scope of the text, they are mostly oriented towards pyrometallurgy for the reasons cited before. The chapters are so organised that a preceding chapter would depend very little on contents of the following chapters.

Part (c) deals with principles of hydro and electrometallurgy. Here electrometallurgy precedes hydrometallurgy because the reactions in latter also are, quite often, really electrochemical in nature. Their study exploits the knowledge of electrochemistry, which is the heart of electrometallurgy.

Each chapter contains worked out examples arranged so as to illustrate application of principles just discussed. There are collections of chosen problems at the end of each chapter and a list of key references for general reading. Some useful data, taken from standard sources, are compiled in Appendix at the end of the text.

General Reading

1. F.D. Richardson, The 1964 Howe Memorial Lecture, *Trans. Met. Soc. AIME*, Vol. 230 (1964), pp. 1212-27.
2. Reinhardt Schuhmann, Jr. : *Metallurgical Engineering*, Vol. I, Addison-Wesley Publishing Co., Reading, Mass, U.S.A., 1952, Ch. 1.
3. C. Judson King, *Separation processes*, McGraw-Hill Book Co. Inc., New York, 1971, Ch. 1.
4. C.B. Alcock, *Principles of pyrometallurgy*, Academic Press, London 1976.
5. J.M. Smith, *Chemical engineering kinetics*, McGraw-Hill Book Co., New York, 2nd edition, 1970, Ch. 1 and Ch. 2.