12085CH06

Unit 6

General Principles and Processes of Isolation of Elements

Objectives

After studying this Unit, you will be able to:

- appreciate the contribution of Indian traditions in the metallurgical processes,
- explain the terms minerals, ores, concentration, benefaction, calcination, roasting, refining, etc.;
- understand the principles of oxidation and reduction as applied to the extraction procedures;
- apply the thermodynamic concepts like that of Gibbs energy and entropy to the principles of extraction of Al, Cu, Zn and Fe;
- explain why reduction of certain oxides like Cu_2O is much easier than that of Fe_2O_3;
- explain why CO is a favourable reducing agent at certain temperatures while coke is better in some other cases;
- explain why specific reducing agents are used for the reduction purposes.

Thermodynamics illustrates why only a certain reducing element and a minimum specific temperature are suitable for reduction of a metal oxide to the metal in an extraction.

The history of civilisation is linked to the use of metals in antiquity in many ways. Different periods of early human civilisations have been named after metals. The skill of extraction of metals gave many metals and brought about several changes in the human society. It gave weapons, tools, ornaments, utensils, etc., and enriched the cultural life. The **'Seven metals of antiquity'**, as they are sometimes called, are gold, copper, silver, lead, tin, iron and mercury. Although modern metallurgy had exponential growth after Industrial Revolution, it is interesting to note that many modern concepts in metallurgy have their roots in ancient practices that pre-dated the Industrial Revolution. For over 7000 years, India has had a rich tradition of metallurgical skills.

The two important sources for the history of Indian metallurgy are archaeological excavations and literary evidences. The first evidence of metal in Indian subcontinent comes from Mehrgarh in Baluchistan, where a small copper bead, dated to about 6000 BCE was found. It is however thought to be native copper, which has not been extracted from the ore. Spectrometric studies on copper ore samples obtained from the ancient mine pits at Khetri in Rajasthan and on metal samples cut from representative Harappan artefacts recovered from Mitathal in Haryana and eight other sites distributed in Rajasthan, Gujarat, Madhya Pradesh and Maharashtra prove that copper metallurgy in India dates back to the Chalcolithic cultures in the subcontinent. Indian chalcolithic copper objects were in all probability made indigenously. The ore for extraction of metal for making the objects was obtained from chalcopyrite ore deposits in Aravalli Hills. Collection of archaeological texts from copper-plates and rock-inscriptions have been compiled and published by the Archaeological Survey of India during the past century. Royal records were engraved on copper plates *(tamra-patra)*. Earliest known copper-plate has a Mauryan record that mentions famine relief efforts. It has one of the very few pre-Ashoka Brahmi inscriptions in India.

Harappans also used gold and silver, as well as their joint alloy electrum. Variety of ornaments such as pendants, bangles, beads and rings have been found in ceramic or bronze pots. Early gold and silver ornaments have been found from Indus Valley sites such as Mohenjodaro (3000 BCE). These are on display in the National Museum, New Delhi. India has the distinction of having the deepest ancient gold mines in the world, in the Maski region of Karnataka. Carbon dating places them in mid 1st millennium BCE.

Hymns of Rigveda give earliest indirect references to the alluvial placer gold deposits in India. The river Sindhu was an important source of gold in ancient times. It is interesting that the availability of alluvial placer gold deposits. Although evidence of gold refining is available in Vedic texts, it is Kautilya's *Arthashastra*, authored probably in 3rd or 4th century BCE, during Mauryan era, which has much data on prevailing chemical practices in a long section on mines and minerals including metal ores of gold, silver, copper, lead, tin and iron. Kautilya describes a variety of gold called *rasviddha*, which is naturally occurring gold solution. *Kalidas* also mentioned about such solutions. It is astonishing how people recognised such solutions.

The native gold has different colours depending upon the nature and amount of impurity present in it. It is likely that the different colours of native gold were a major driving force for the development of gold refining.

Recent excavations in central parts of Ganges Valley and Vindhya hills have shown that iron was produced there possibly as early as in 1800 BCE. In the recent excavations conducted by the Uttar Pradesh State Archaeological Department, iron furnaces, artefacts, tuyers and layers of slag have been found. Radiocarbon dating places them between BCE 1800 and 1000. The results of excavation indicate that the knowledge of iron smelting and manufacturing of iron artefacts was well known in Eastern Vindhyas and it was in use in the Central Ganga Plains, at least from the early 2nd millennium BCE. The quantity and types of iron artefacts and the level of technical advancements indicate that working of iron would have been introduced much earlier.

The evidence indicates early use of iron in other areas of the country, which proves that India was indeed an independent centre for the development of the working of iron.

Iron smelting and the use of iron was especially established in South Indian megalithic cultures. The forging of wrought iron seems to have been at peak in India in the Ist millennium CE. Greek accounts report the manufacture of steel in India by crucible process. In this process, iron, charcoal and glass were mixed together in a crucible and heated until the iron melted and absorbed the carbon. India was a major innovator in the production of advanced quality steel. Indian steel was called 'the Wonder Material of the Orient'. A Roman historian, Quintus Curtius, records that one of the gifts Porus of Taxila (326 BCE) gave to Alexander the Great was some two-and-a-half tons of Wootz steel. Wootz steel is primarily iron containing a high proportion of carbon (1.0 – 1.9%). Wootz is the English version of the word *'ukku'* which is used for steel in Karnataka and Andhra Pradesh. Literary accounts suggest that Indian Wootz steel from southern part of the Indian subcontinent was exported to Europe, China and Arab world. It became prominent in the Middle East where it was named as Damasus Steel. Michael Faraday tried to duplicate this steel by alloying iron with a variety of metals, including noble metals, but failed.

When iron ore is reduced in solid state by using charcoal, porous iron blocks are formed. Therefore, reduced iron blocks are also called sponge iron blocks. Any useful product can be obtained from this material only after removing the porosity by hot forging. The iron so obtained is termed as wrought iron. An exciting example of wrought iron produced in ancient India is the world famous Iron Pillar. It was erected in its present position in Delhi in 5th century CE. The Sanskrit inscription engraved on it suggests that it was brought here from elsewhere during the Gupta Period. The average composition (weight%) of the components present in the wrought iron of the pillar, besides iron, are 0.15% C, 0.05% Si, 0.05% Mn, 0.25% P, 0.005% Ni, 0.03% Cu and 0.02% N. The most significant aspect of the pillar is that there is no sign of corrosion inspite of the fact that it has been exposed to the atmosphere for about 1,600 years.

Radiocarbon dating of charcoal from iron slag revealed evidence of continuous smelting in Khasi Hills of Meghalaya. The slag layer, which is dated to 353 BCE – CE 128, indicates that Khasi Hill region is the earliest iron smelting site studied in the entire region of North East India. The remnants of former iron-ore excavation and iron manufacturing are visible even now in the landscape of Khasi Hills. British naturalists who visited Meghalaya in early 19th century described the iron industry that had developed in the upper part of the Khasi Hills.

There is archaeological evidence of zinc production in Rajasthan mines at Zawar from the 6th or 5th BCE. India was the first country to master zinc distillation. Due to low boiling point, zinc tends to vapourise while its ore is smelted. Pure zinc could be produced after a sophisticated 'downward' distillation technique in which the vapour was condensed in a lower container. This technique was also applied to mercury. Indian metallurgists were masters in this technique. This has been described in Sanskrit texts of 14th century.

Indians had knowledge about mercury. They used it for medicinal purpose. Development of mining and metallurgy declined during the British colonial era. By the 19th century, once flourished mines of Rajasthan were mostly abandoned and became almost extinct. In 1947 when India got independence, European literature on science had already found its way slowly into the country. Thus, in post independence era, the Government of India initiated the process of nation building through the establishment of various institutes of science and technology. In the following sections, we will learn about the modern methods of extraction of elements.

6.1 Occurrence of Metals

A few elements like carbon, sulphur, gold and noble gases, occur in free state while others are found in combined forms in the earth's crust. Elements vary in abundance. Among metals, aluminium is the most abundant. In fact, it is the third most abundant element in earth's crust (8.3% approx. by weight). It is a major component of many igneous minerals including mica and clays. Many gemstones are impure forms of Al_2O_3. For example, gems 'ruby' and 'sapphire' have Cr and Co respectively as impurity. Iron is the second most abundant metal in the earth's crust. It forms a variety of compounds and their various uses make it a very important element. It is one of the essential elements in biological systems as well.

For obtaining a particular metal, first we look for **minerals** which are naturally occurring chemical substances in the earth's crust and are obtained through mining. Out of many minerals in which a metal may be found, only a few are viable to be used as source of that metal. Such minerals are known as **ores**.

The principal ores of aluminium, iron, copper and zinc are given in Table 6.1.

Table 6.1: Principal Ores of Some Important Metals

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[Al_2(OH)_4Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

A particular element may occur in a variety of compounds. The process of isolation of element from its compound should be such that it is chemically feasible and commercially viable.

For the purpose of extraction, bauxite is chosen for aluminium. For iron, usually the oxide ores which are abundant and do not produce polluting gases (like SO_2 that is produced in case of iron pyrites) are taken. For copper and zinc, any of the ores listed in Table 6.1 may be used depending upon the availability and other relevant factors.

The entire scientific and technological process used for isolation of the metal from its ore is known as **metallurgy**. The extraction and isolation of an element from its combined form involves various principles of chemistry. Still, some general principles are common to all the extraction processes of metals.

An ore rarely contains only a desired substance. It is usually contaminated with earthly or undesired materials known as **gangue**. The extraction and isolation of metals from ores involves the following major steps:

- Concentration of the ore,
- Isolation of the metal from its concentrated ore, and
- Purification of the metal.

In the following Sections, we shall first describe the various steps for effective concentration of ores. After that principles of some of the common metallurgical processes will be discussed. Those principles will include the thermodynamic and electrochemical aspects involved in the effective reduction of the concentrated ore to the metal.

6.2 Concentration of Ores

Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as *concentration*, *dressing* or *benefaction*. Before proceeding for concentration, ores are graded and crushed to reasonable size. Concentration of ores involves several steps and selection of these steps depends upon the differences in physical properties of the compound of the metal present and that of the *gangue*. The type of the metal, the available facilities and the environmental factors are also taken into consideration. Some of the important procedures for concentration of ore are described below.

6.2.1 Hydraulic Washing

This is based on the difference between specific gravities of the ore and the *gangue* particles. It is therefore a type of *gravity separation*. In one such process, an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ore particles are left behind.

6.2.2 Magnetic Separation

This is based on differences in magnetic properties of the ore components. If either the ore or the gangue is attracted towards magnetic field, then the separation is carried out by this method. For example iron ores are attracted towards magnet, hence, non–magnetic impurities can be separted from them using magnetic separation. The powdered ore is dropped over a conveyer belt which moves over a magnetic roller (Fig.6.1) Magnetic substance remains attracted towards the belt and falls close to it.

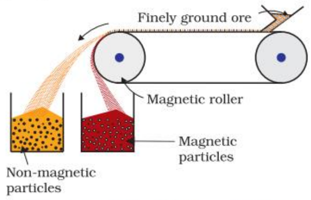

Fig. 6.1: *Magnetic separation (schematic)*

6.2.3 Froth Floatation Method

This method is used for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. *Collectors* and *froth stabilisers* are added to it. Collectors (e.g., pine oils, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilisers (e.g., cresols, aniline) stabilise the froth.

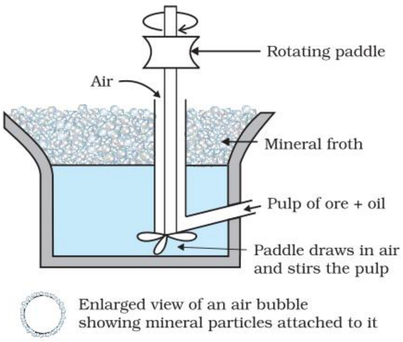

Fig. 6.2: Froth floatation process

The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles.

Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using '*depressants*'. For example, in the case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

The Innovative Washerwoman

One can do wonders if he or she has a scientific temperament and is attentive to observations. A washerwoman had an innovative mind too. While washing a miner's overalls, she noticed that sand and similar dirt fell to the bottom of the washtub. What was peculiar, the copper bearing compounds that had come to the clothes from the mines, were caught in the soapsuds and so they came to the top. One of her clients, Mrs. Carrie Everson was a chemist. The washerwoman told her experience to Mrs. Everson. The latter thought that the idea could be used for separating copper compounds from rocky and earth materials on large scale. This way an invention came up. At that time only those ores were used for extraction of copper, which contained large amounts of the metal. Invention of the *Froth Floatation Method* made copper mining profitable even from the low-grade ores. World production of copper soared and the metal became cheaper.

6.2.4 Leaching

Leaching is often used if the ore is soluble in some suitable solvent. Following examples illustrate the procedure:

(a) Leaching of alumina from bauxite

Bauxite is the principal ore of aluminium. It usually contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities. Concentration is carried out by heating the powdered ore with a concentrated solution of NaOH at 473 – 523 K and 35 – 36 bar pressure. This process is called digestion. This way, Al_2O_3 is extracted out as sodium aluminate.

The impurity, SiO_2 too dissolves forming sodium silicate. Other impurities are left behind.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq) \quad (6.1)$$

The sodium aluminate present in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, small amount of freshly prepared sample of hydrated Al_2O_3 is added to the solution. This is called seeding. It induces the precipitation.

$$2Na[Al(OH)_4](aq) + 2CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3\ (aq) \quad (6.2)$$

Sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3.

$$Al_2O_3.xH_2O(s) \xrightarrow{1470\ K} Al_2O_3(s) + xH_2O(g) \quad (6.3)$$

(b) Other examples

In the metallurgy of silver and gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air, which supplies O_2. The metal is obtained later by replacement reaction.

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-\ (aq) + 4OH^-(aq)\ (M = Ag\ or\ Au) \quad (6.4)$$

$$2[M(CN)_2]^-(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s) \quad (6.5)$$

Intext Questions

6.1 Which of the ores mentioned in Table 6.1 can be concentrated by magnetic separation method?

6.2 What is the significance of leaching in the extraction of aluminium?

6.3 Extraction of Crude Metal from Concentrated Ore

To extract metal from concentrated ore, it must be converted to a form which is suitable for reduction to metal. Usually sulphide ores are converted to oxide before reduction because oxides are easier to reduce. Thus isolation of metals from concentrated ore involves two major steps *viz.*,

(a) conversion to oxide, and

(b) reduction of the oxide to metal.

(a) Conversion to oxide

(i) *Calcination*: Calcinaton involves heating. It removes the volatile matter which escapes leaving behind the metal oxide:

$$Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3\ (s) + xH_2O(g) \quad (6.6)$$

$$ZnCO_3\ (s) \xrightarrow{\Delta} ZnO(s) + CO_2(g) \quad (6.7)$$

$$CaCO_3.MgCO_3(s) \xrightarrow{\Delta} CaO(s) + MgO(s) + 2CO_2(g) \quad (6.8)$$

(ii) *Roasting*: In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. Some of the reactions involving sulphide ores are:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \quad (6.9)$$
$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \quad (6.10)$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \quad (6.11)$$

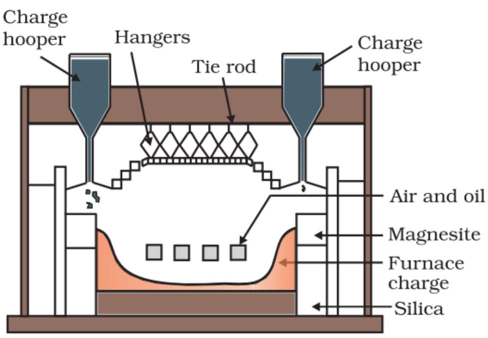

***Fig. 6.3:** A section of a modern reverberatory furnace*

The sulphide ores of copper are heated in **reverberatory furnace** [Fig. 6.3]. If the ore contains iron, it is mixed with silica before heating. Iron oxide 'slags of'* as iron silicate and copper is produced in the form of **copper matte** which contains Cu_2S and FeS.

$$\underset{\text{(slag)}}{FeO + SiO_2 \rightarrow FeSiO_3} \quad (6.12)$$

The SO_2 produced is utilised for manufacturing H_2SO_4 .

(b) Reduction of oxide to the metal

Reduction of the metal oxide usually involves heating it with a reducing agent, for example C, or CO or even another metal. The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.

$$M_xO_y + yC \rightarrow xM + y\ CO \quad (6.13)$$

Some metal oxides get reduced easily while others are very difficult to be reduced (reduction means electron gain by the metal ion). In any case, heating is required.