

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 separated from them using magnetic separation. The powdered ore is dropped over a conveyor belt which moves over a magnetic roller (Fig.6.1) Magnetic substance remains attracted towards the belt and falls close to it.

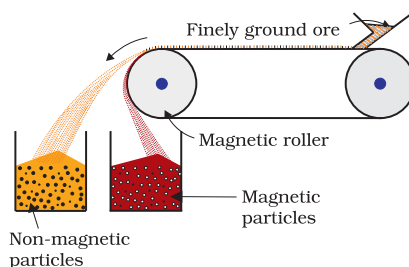
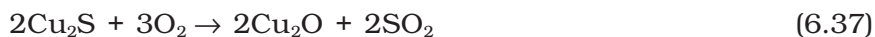


Fig. 6.1: Magnetic separation (schematic)

FeS, FeO and Cu₂S/Cu₂O to the metallic copper. Following reactions take place:



The solidified copper obtained has blistered appearance due to the evolution of SO₂ and so it is called **blister copper**.

(c) Extraction of zinc from zinc oxide

The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in the case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.



The metal is distilled off and collected by rapid chilling.

Intext Questions

6.3 The reaction,



is thermodynamically feasible as is apparent from the Gibbs energy value. Why does it not take place at room temperature?

6.4 Is it true that under certain conditions, Mg can reduce Al₂O₃ and Al can reduce MgO? What are those conditions?

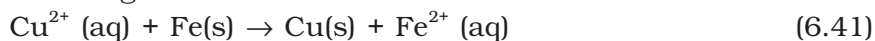
6.5
Electrochemical Principles of Metallurgy

We have seen how principles of thermodynamics are applied to **pyrometallurgy**. Similar principles are effective in the reductions of metal ions in solution or molten state. Here they are reduced by electrolysis or by adding some reducing element.

In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^\ominus = -nE^\ominus F \quad (6.40)$$

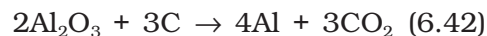
here n is the number of electrons and E[⊖] is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E[⊖] values corresponds to a positive E[⊖] and consequently negative ΔG[⊖] in equation 6.40, then the less reactive metal will come out of the solution and the more reactive metal will go into the solution, e.g.,



In simple electrolysis, the Mⁿ⁺ ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

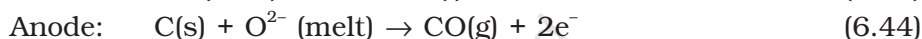
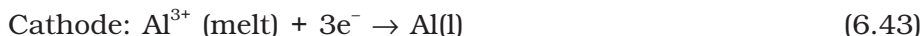
Aluminium

In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel vessel with lining of carbon acts as cathode and graphite anode is used. The overall reaction may be written as:



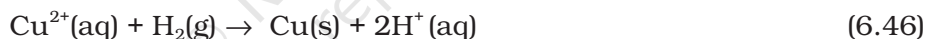
This process of electrolysis is widely known as **Hall-Heroult process**.

Thus electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are:



Copper from Low Grade Ores and Scraps

Copper is extracted by *hydrometallurgy* from low grade ores. It is leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2 (equations 6.40; 6.46).



Example 6.4

At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?

Solution

Zinc being above iron in the electrochemical series (more reactive metal is zinc), the reduction will be faster in case zinc scraps are used. But zinc is costlier metal than iron so using iron scraps will be advisable and advantageous.

6.6 Oxidation Reduction

Besides reductions, some extractions are based on oxidation particularly for non-metals. A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is abundant in sea water as common salt) .



The ΔG^\ominus for this reaction is + 422 kJ. When it is converted to E^\ominus (using $\Delta G^\ominus = -nE^\ominus F$), we get $E^\ominus = -2.2$ V. Naturally, it will require an external emf that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions (Unit-3, Section 3.5.1). Thus, Cl_2 is obtained by electrolysis giving out H_2 and aqueous NaOH as by-products. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH .

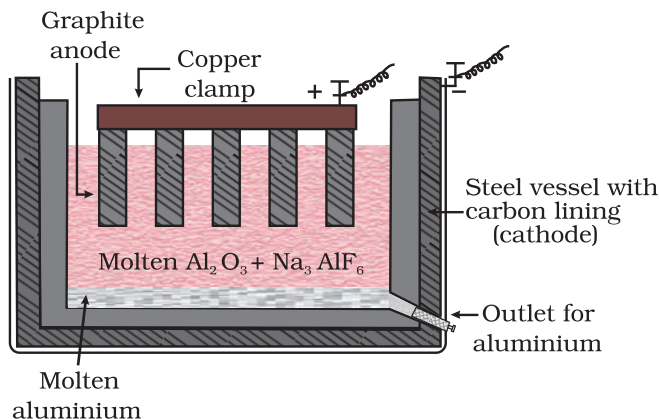
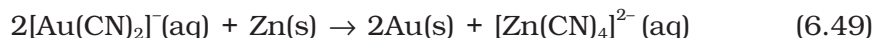
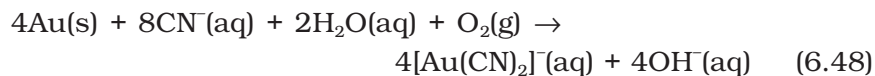


Fig. 6.6: Electrolytic cell for the extraction of aluminium

As studied earlier, extraction of gold and silver involves leaching the metal with CN^- . This is also an oxidation reaction ($\text{Ag} \rightarrow \text{Ag}^+$ or $\text{Au} \rightarrow \text{Au}^+$). The metal is later recovered by displacement method.



In this reaction zinc acts as a reducing agent.

6.7 Refining

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

- | | |
|---------------------------|-----------------------------|
| (a) Distillation | (b) Liquation |
| (c) Electrolysis | (d) Zone refining |
| (e) Vapour phase refining | (f) Chromatographic methods |

These are described in detail here.

(a) Distillation

This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

(b) Liquation

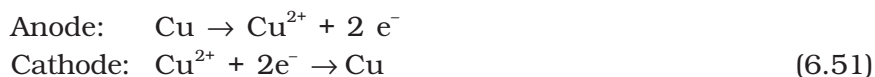
In this method a low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

(c) Electrolytic refining

In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud. This process is also explained using the concept of electrode potential, over potential, and Gibbs energy which you have seen in previous sections. The reactions are:



Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:



Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining. Zinc may also be refined this way.

(d) Zone refining

This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A mobile heater surrounding the rod of impure metal is fixed at its one end (Fig. 6.7). The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises

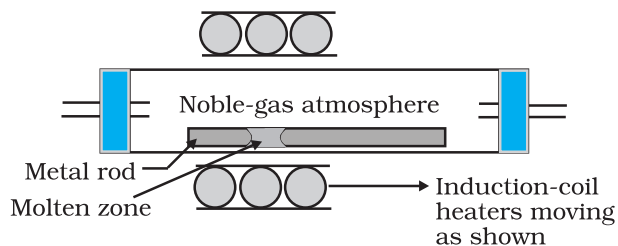


Fig. 6.7: Zone refining process

out of the melt left behind and the impurities pass on into the adjacent new molten zone created by movement of heaters. The process is repeated several times and the heater is moved in the same direction again and again. Impurities get concentrated at one end. This end is cut off. This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

(e) Vapour phase refining

In this method, the metal is converted into its volatile compound which is collected and decomposed to give pure metal. So, the two requirements are:

- (i) the metal should form a volatile compound with an available reagent,
- (ii) the volatile compound should be easily decomposable, so that the recovery is easy.

Following examples will illustrate this technique.

Mond Process for Refining Nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex named as nickel tetracarbonyl. This complex is decomposed at higher temperature to obtain pure metal.



van Arkel Method for Refining Zirconium or Titanium: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:



The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal deposits on the filament.



(f) Chromatographic methods

You have learnt about chromatographic technique of purification of substances in Class XI (Unit-12).

6.8 Uses of Aluminium, Copper, Zinc and Iron

Column chromatography is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

Aluminium foils are used as wrappers for food materials. The fine dust of the metal is used in paints and lacquers. Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides. Wires of aluminium are used as electricity conductors. Alloys containing aluminium, being light, are very useful.

Copper is used for making wires used in electrical industry and for water and steam pipes. It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin) and coinage alloy (with nickel).

Zinc is used for galvanising iron. It is also used in large quantities in batteries. It is constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40-50%). Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc. It is used in the manufacture of wrought iron and steel. **Wrought iron** is used in making anchors, wires, bolts, chains and agricultural implements. Steel finds a number of uses. Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes. Chrome steel is used for cutting tools and crushing machines, and stainless steel is used for cycles, automobiles, utensils, pens, etc.

Summary

Although modern metallurgy had exponential growth after Industrial Revolution, many modern concepts in metallurgy have their roots in ancient practices that predated the Industrial Revolution. For over 7000 years, India has had high tradition of metallurgical skills. Ancient Indian metallurgists have made major contributions which deserve their place in metallurgical history of the world. In the case of zinc and high-carbon steel, ancient India contributed significantly for the development of base for the modern metallurgical advancements which induced metallurgical study leading to Industrial Revolution.

Metals are required for a variety of purposes. For this, we need their extraction from the minerals in which they are present and from which their extraction is commercially feasible. These minerals are known as **ores**. Ores of the metal are associated with many impurities. Removal of these impurities to certain extent is achieved in **concentration** steps. The concentrated ore is then treated chemically for obtaining the metal. Usually the metal compounds (e.g., oxides, sulphides) are reduced to the metal. The reducing agents used are carbon, CO or even some metals.

In these reduction processes, the **thermodynamic** and **electrochemical** concepts are given due consideration. The metal oxide reacts with a reducing agent; the oxide is reduced to the metal and the reducing agent is oxidised. In the two reactions, the net Gibbs energy change is negative, which becomes more negative on raising the temperature. Conversion of the physical states from solid to liquid or to gas, and formation of gaseous states favours decrease in the Gibbs energy for the entire system. This concept is graphically displayed in plots of ΔG^\ominus vs T (Ellingham diagram) for such oxidation/reduction reactions at different temperatures. The concept of electrode potential is useful in the isolation of metals (e.g., Al, Ag, Au) where the sum of the two redox couples is positive so that the Gibbs energy change is negative. The metals obtained by usual methods still contain minor impurities. Getting pure metals requires **refining**. Refining process depends upon the differences in properties of the metal and the impurities. Extraction of aluminium is usually carried out from its bauxite ore by leaching it with NaOH. Sodium aluminate, thus formed, is separated and then neutralised to give back the hydrated oxide, which is then electrolysed using cryolite as a flux. Extraction of iron is done by reduction of its oxide ore in blast furnace. Copper is extracted by smelting and heating in a reverberatory furnace. Extraction of zinc from zinc oxides is done using coke. Several methods are employed in refining the metal. Metals, in general, are very widely used and have contributed significantly in the development of a variety of industries.

A Summary of the Occurrence and Extraction of some Metals is Presented in the following Table

Metal	Occurrence	Common method of extraction	Remarks
Aluminium	1. Bauxite, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6	For the extraction, a good source of electricity is required.
Iron	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4	Reduction of the oxide with CO and coke in Blast furnace	Temperature approaching 2170 K is required.
Copper	1. Copper pyrites, CuFeS_2 2. Copper glance, Cu_2S 3. Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ 4. Cuprite, Cu_2O	Roasting of sulphide partially and reduction	It is self reduction in a specially designed converter. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy for low grade ores.
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, ZnCO_3 3. Zincite, ZnO	Roasting followed by reduction with coke	The metal may be purified by fractional distillation.