Unit

4

General Principles and Processes of Isolation of Elements

4.1 Introduction

A few elements are available in free state in nature. Metal like copper, non-metals like carbon, sulphur and inert gases like helium and other are available in free form in nature. Many more metals and non-metals other than these are available naturally in combined form in the crust of the earth. As you know, that metals being important in our everyday life, they can be obtained in the form of metal from their compounds. For this, processes like extraction, isolation involving physico-chemical principles can be used to obtain metal. This total process is known as **'metallurgy'** The methods developed and used to obtain metals are based on the economical and industrial aspects. Some principles to obtain elements are same, even then, some special methods are developed depending on the nature of the ore.

Mineral is the substance available in nature, which is present in the crust of the earth and is being dug out. All the minerals available are not useful for obtaining metal because very less amount of metal is available from them. The mineral from which metals can be obtained in good proportion is called **ore.** e.g. It is not practical to obtain aluminium from aluminosilicate but it can be obtained in good proportion from its mineral bauxite. There may not be only the element to be obtained being present but undesirable and certain earthly substances are present which can be called impurities. This is called **gangue.** The main steps to obtain metal from the ore are as follows :

(1) Concentration of ore (2) Isolation of metal from concentrated ore (3) Purification (Refining) of metal.

Thus, the total procedure to isolate metals from their ores using scientific and industrial processes is called **'metallurgy'.**

In this unit, we shall study steps for effective concentration of ores, certain general principles of metallurgy in which the thermodynamical and electrochemical aspects have been included as well as to obtain metal by reduction.

4.2 Occurrence of Metals

The abundance of different elements in the crust of the earth is different. In metals, the abundance of aluminium is the highest. Its place is third in the elements available from the earth's crust. It is about 8.3% by weight. Its chief minerals are mica and china clay. Some of the gem stones are impure forms of Al_2O_3. e.g. Ruby contains Cr as impurity, sapphire contains Cd as impurity. The element available at second place is iron. It is available in many combined forms and it is also very important element. It is also present in combined form in the haemoglobin present in blood in our body. We shall study in this unit, the extraction of metals like aluminium, copper, iron and zinc. Principal ores of aluminium, copper iron and zinc metals are shown in table 4.1

Table 4.1 Principal Ores of some important metals

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

The oxide mineral is preferably selected to obtain metal from ores because SO_2 gas evolved from sulphide minerals causes pollution and their reduction is also difficult. So, bauxite for aluminium and haematite for iron etc, oxides are used. For copper and zinc, the ores mentioned in table 4.1 and their availability and the related factors are taken into consideration for the selection of ores. Before carrying out concentration of ores, they are crushed or grinded so that they become of the required size of particles.

4.3 Concentration of Ores

As we have seen earlier, there are impurities in the ores. viz. sand, clay etc. To obtain ore by removal of impurities as much as possible, is called concentration. There are many steps. The selection of these steps depends on the physical properties of the ore and the properties of the gangue. Two things are important during the concentration of ores : (1) To obtain maximum concentrated form by proper method. (2) The environment may not have any risk by the factors affecting the environment.

We shall understand one by one, all the four methods. (1) Hydraulic washing (2) Magnetic separation (3) Froth Floatation method (4) Leaching.

(1) Hydraulic washing : In this method, the principle of relative density of ore and gangue is involved so this method is also called relative density isolation. In such method, the ore is taken in a vessel and water flow is passed from the upper parts, so that the powdered ore is washed and all the light particles of the gangue are washed out. Ore is finally collected.

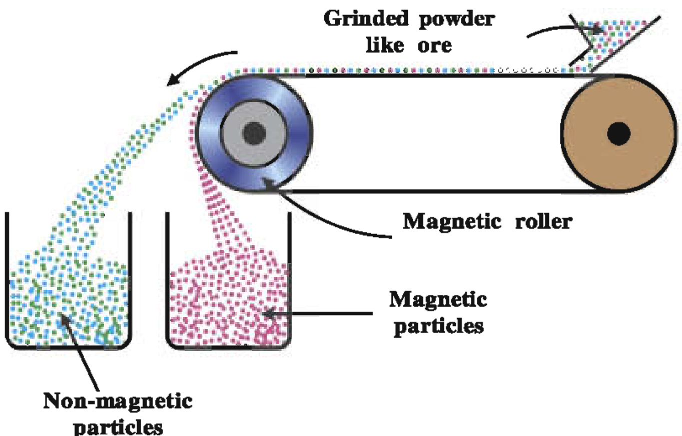

Fig. 4.1 Magnetic Separation

(2) Magnetic separation : In this method, the principle of magnetic properties of the components of the ore is involved. If any one of the ores and the gangue possesses magnetic attraction, then magnetic field can be applied. Thus, the components attracted by the magnet and not attracted by the magnet are separated. This method can be applied to the ores of iron. As shown in figure 4.1, the grinded powder like ore is placed on a magnetic roller and magnetic field is applied. The magnetic roller is also called conveyor belt which is placed on magnetic roller. As shown in figure 4.1 the components which are being attracted are dragged towards the roller while the components which are not being attracted fall away from the roller. Thus, concentration of ore can be carried out by magnetic separation.

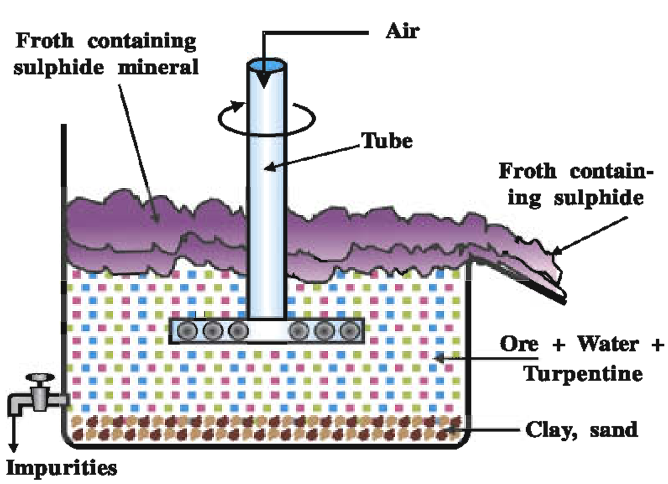

Fig. 4.2 Froth floatation method

(3) Froth Floatation method : This method is mostly used for the ores containing sulphide. The ore is grinded and brought into powder form and then suspended in water. Substances which can produce froth and concentrate the ore are added to it. viz substances like pine oil, fatty acids, xanthates, turpentine etc. are added as the substances to collect the ore. As they do not mix with water, they keep the ore concentrated and moistureless. In addition froth stabilisers like cresol, aniline are also added. The particles of the mineral are wetted by substances like pine oil and the particles of the gangue are wetted by water. As shown in figure 4.2 air is introduced in the mixture. As a result the solution gets agitated and the particles of the ore are carried on the upper part by the light froth produced. As this froth is light it is taken out by sieves skimmed off from the upper part and it is heated to obtain particles of ore. The remaining impurities remain suspended in the solution containing water. Some times two ores containing sulphide can also be separated. For this, the proportion of oil and water is properly selected and some depressants are used. viz. If NaCN is added as depressant to the ore containing ZnS and PbS, then PbS, skims off on the upper part with the froth and ZnS does not come with the froth. The reason for this may be the formation of complex - $Na_2[Zn(CN)_4]$ soluble in water from the insoluble ZnS in water.

(4) Leaching : This method is used when the ore is soluble in some suitable solvent. This method can be understood by the following illustrations.

(A) Leaching of Alumina from Bauxite : As you know bauxite is the ore of aluminium which is leaching of alumina from bauxite. We shall study further in this unit.

(B) The second example of leaching is metallurgy of silver and gold. In this, leaching of silver by NaCN and leaching of gold by KCN in presence of oxygen is carried out. The metals are obtained in displaced form by the reactions as shown below :

$$4M(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \rightarrow [4M(CN)_2]^-(aq) + 4OH^-(aq)$$

(where M = Silver or Gold)

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

4.4 Extraction of Crude Metal from the Concentrated Ore

The metal to be obtained is in the ionic form of the compound of concentrated ore, so that they can be obtained by reduction. But for this, the concentrated ore has to be converted into the suitable form so that it can be reduced. viz. Sulphide ore can be reduced only after it being converted to oxide form of ore; because the reduction of oxide is easier. Steps to obtain metal from the ore can be divided into two parts :

(1) Conversion to oxide (2) Reduction of oxide to metal

(1) Conversion to oxide : For this, two reactions have to be carried out. (i) Calcination (ii) Roasting.

(i) Calcination : The ore is heated very strongly during calcination, so that all volatile substances are removed and metal oxide is left out. e.g.

$$Fe_2O_3 \cdot XH_2O(s) \rightarrow Fe_2O_3(s) + XH_2O(g)$$

$$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$$

$$CaCO_3 \cdot MgCO_3(s) \rightarrow CaO(s) + MgO(s) + 2CO_2(g)$$

(ii) Roasting : As shown in figure 4.3, the ore is heated below the melting point of the metal in a reverberatory furnace by introducing air continuously. The roasting of sulphide containing ore takes places according to the following reactions :

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

$$2Cu_2S(s) + 3O_2(g) \rightarrow 2Cu_2O(s) + 2SO_2(g)$$

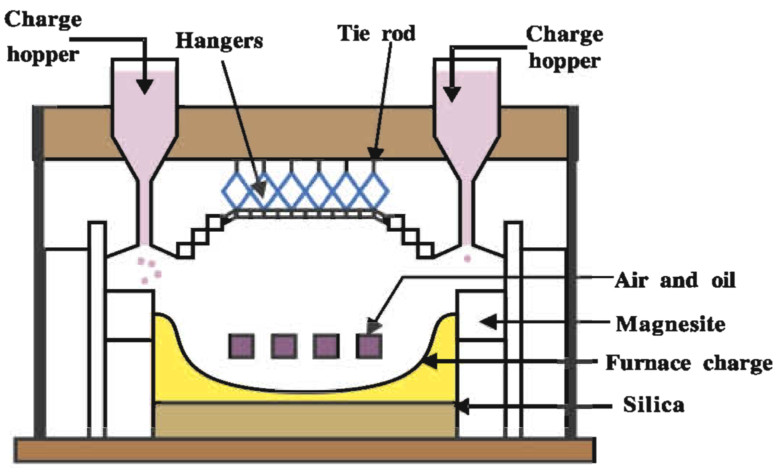

Fig. 4.3 Reverberatory furnace

If the ore of copper is containing sulphide then it is heated in reverberatory furnace. If the ore is iron containing, then silica is added to it before heating so that iron oxide combines with silica and forms iron silicate ($FeSiO_3$). It is known as **slag.**

$$FeO(s) + SiO_2(s) \xrightarrow{\Delta} FeSiO_3(s)$$

Similarly, copper metal forms one mixed substance which is a mixture of Cu_2S and FeS. It is called **"Matte".** SO_2 gas produced can be used in the manufacture of sulphuric acid.

(2) Reduction of Oxide of Ore to metal : During reduction reaction suitable reducing agent (viz. C or CO or any other metal) is used with the ore. Reducing agent like carbon combines with oxide of metal and reduces the metal oxide giving metal. viz.

$$M_xO_y + yC \rightarrow xM + yCO$$

Metal oxides can be reduced easily or with difficulty depending upon their stabilities. In the case of oxides which are easily reducible, common reducing agents are used and metal can be obtained by reduction. e.g. Fe metal from Fe_2O_3. But the reduction of stable oxides like Al_2O_3 is possible by accepting the electrons. You know that acceptance or receiving of electron is the reduction reaction. Thus, the reduction reaction by accepting electron is called **electronation.** Heat is required during both the types of reduction reactions. To understand these phenomena explanation about principles, functions etc. of thermodynamics is essential. We shall study this in detail in point no 4.5.

For understanding the thermal reduction, the necessary changes in temperature, and which substance will be suitable for reduction reaction of metal oxide, the calculation of Gibbs' free energy and its interpretation is necessary. The study of metallurgy with changes in temperature is called **"Pyrometallurgy".**

4.5 Thermodynamic Principles of Metallurgy

It is essential to have information about certain basic principles of thermodynamics. You are familiar with the terms like chemical equilibrium, equilibrium constant, Gibbs' free energy, entropy, enthalpy etc. From these, the understanding about equilibrium constant, Gibbs' free energy etc. will be useful here.

You have learnt Gibbs-Helmholtz equation $\Delta G = \Delta H - T\Delta S$, where ΔG is the change in free energy. ΔH is change in enthalpy and ΔS is the change in entropy and T is the temperature in Kelvin unit. You have also learnt the other important relation $\Delta G^0 = -RT\ln K$, where K = equilibrium constant, R = Gas constant and ΔG^0 is standard free energy change. Three values of ΔG^0 can be possible-positive, zero and negative. If the value of ΔG^0 is positive, then the reaction will not be sponatenous. If it is zero, reaction will be equilibrium state and if it is negative reaction will be spontaneous. Also the values of K can be <1, 0 and >1. If the value of K is < 1, then the proportion of products will be less in comparison to reactants i.e. product obtained will be less. If it is one, then equilibrium will be there i.e. both reactants and products will be in same proportion. If it is greater then 1 the proportion of product obtained will be more. In addition to this, Le Chatelier's principle also plays an important role.

As we have seen, the negative value of ΔG will lead the reaction to products. In the equation $\Delta G = \Delta H - T\Delta S$, if the value of temperature T is increased, the value of ΔS will increase. Consequently, the product $T\Delta S$ will also increase, so that $\Delta H - T\Delta S$ or ΔG will become negative and so the reaction will go towards product.

The value of ΔG^0 is constant at definite temperature and so in the process, after mixing reactants and products the factors like concentration, temperature, pressure, affecting the reaction should be so arranged that the value of ΔG becomes negative. If it happens so, the reaction will become spontaneous in the direction towards products. Scientist H. J. T. Ellingham had studied the relations by plotting graphs of ΔG^0 versus T, and so these graphs are known as Ellingham diagrams. They are useful but have certain limitations also. We will not study it in detail here.

When reducing agent takes part in the reaction, then its oxide is formed and metal oxide gets reduced. The function of reducing agent is to make the value of ΔG^0 negative. Thus, free energy change of oxidation-reduction reaction should be zero.

On the basis of the thermodynamic principles associated with obtaining metal, it can be said that increase in temperature will lead to negative value of ΔG^0. Hence the redox reaction should be such that the value of ΔG^0 obtained will be negative. But increase in temperature is harmful for exothermic reaction but can be advantageous for endothermic reaction. In the end, it should be kept in mind that the reducing agent should be such that its reduction reaction with metal oxide should be as spontaneous as possible. i.e. it gives maximum negative value of ΔG^0 and the efficiency of metal oxide reduction can be more. Thus, we can decide about the use of carbon, carbon monoxide, or any metal for the reduction and so the product obtained will be more or metal obtained will be more. In short, the selection of the reducing agent will depend on the magnitude of the negative value of ΔG^0. We have studied in the unit of equilibrium that to obtain maximum product the value of equilibrium constant K should be as high as possible and the corresponding values of free energy change should be as less as possible so that the process will be advantageous. Hence, we can have combination of temperature, pressure, reducing agent in such a manner that the 'optimum' state can be formulated and maximum product, i.e. maximum amount of metal, can be obtained by reduction. Such thermodynamical principles are also called physico-chemical principles.

4.6 Electrochemical Principles of Metallurgy

We have earlier learnt, the principles of thermodynamics, in obtaining metals from their oxides during pyrometallurgy. In addition to this, the principles of electrochemistry can be useful for reduction of metal ions present in the aqueous solutions or in molten states. For this electrolysis, or addition of some other metal (considering their reduction potentials) and ions of the metals can be reduced and metals can be obtained. Metal can be obtained by reduction reaction during electrolysis of molten salts, in which electrochemical principles are involved. We have studied some equations viz.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \ \Delta G^0 = -RT\ln K$$

$$\Delta G^0 = -\ nFE^0 \text{ and } E^0 = \frac{RT}{nF}\ln K$$

From these, if we think of the equation combining thermodynamics and electrochemistry, then the equation $\Delta G^0 = -nFE^0$ is useful; where n is the number of electrons associated with the reaction, F = value of Faraday = 96500 coulomb, E^0 is the standard reduction potential of the complete cell of the redox reaction and it is the difference between standard reduction potentials of the two metals and ΔG^0 = standard free energy change. The oxidation potentials of the electrodes doing reactions will be very high and positive, so their reduction potentials will be very low and negative and so their reduction will be very difficult. But if the value of E^0 is positive, the value of ΔG^0 will be negative and so the reaction will be spontaneous. Hence, if active metal is added, into the solutions of ions of the metal which is less active, the metal ions from the solution will be reduced and converted to metal- form and the added metal will be obtained as ions in the solution. viz.

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$$

Activity : Prepare solution of copper sulphate in the laboratory. Place the iron nails in this solution. After two hours, observe what has happened? The blue colour of the solution will become light blue coloured and red particles will be deposited on the iron nails. This observation is of the reaction shown above; then explain which metal is oxidised, which metal is reduced, which ions from the solution are reduced and which ions have gone into solution by oxidation. If you have studied the unit on electrochemistry, calculate E^0_{Cell} of the reaction and calculate the value of ΔG^0 from its value and prove the use of electrochemistry in metalllurgy.

Also, you do the experiment in reverse form. Place a strip of copper metal in the solution of $FeSO_4$. What happens? Explain. Give reason. This type of experiment is included in your practical book.

In electrolysis, you have studied that metal ions from the solution are deposited on cathode. Always reduction will occur at cathode. For this reduction, the electrons of the cathode have entered, metal ions receive them and metal is obtained from metal ions. Generally, cathode of any metal can be used because the metal is to be deposited on the cathode. Cathode does not dissolve, but will not allow the impurities to enter, inert cathode or the cathode prepared of the metal to be obtained is advisable for use. We shall discuss this in detail in the point of metal refining.

The electrolysis of molten solid can be carried out as above but if the melting point of molten soild is very high, some substances are added to bring it down which is known as flux and so electrolysis can be carried out at lower temperature. Cryolite (Na_3AlF_6) or calcium fluoride (CaF_2) is added in the process of obtaining Al from Al_2O_3. We shall study this in detail in the extraction of aluminium metal.

4.7 Oxidation-Reduction

You have studied the different definitions of oxidation and reduction. We shall study here one of these definitions. Oxidation means loss of electron and reduction means gain of electrons. Formation of metal ions from metal by loss of electron is oxidation reaction and formation of metal from metal ions by gain of electron is reduction reaction. This method is mostly for non-metals. We shall study the following reactions which is the reaction to obtain chlorine from sea water (brine).

$$2Cl^-(aq) + 2H_2O(l) \longrightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$$

The value of ΔG^0 is + 422 kJ for this reaction if we calculate the value of E^0 from this by the equation $\Delta G^0 = -nFE^0$ then, its value obtained is –2.186 V. As we have studied earlier, the value of E^0 being negative, the reaction will not occur in forward direction. Hence, if we apply external e.m.f. higher than –2.186 V, then the reaction will occur and Cl_2 gas will be obtained on anode and NaOH will remain in solution because H_2 will be obtained as gas at cathode. Formation of Cl_2 from Cl^- ions is oxidation reaction and will occur at anode. Suppose we electrolyse molten NaCl, then Cl_2 will be obtained on anode and Na metal will be obtained on cathode and NaOH will not be obtained in solution. As seen earlier in leaching sodium cyanide (NaCN) is used to obtain gold and silver. Formation of Ag^+ from Ag and Au^+ from Au are oxidation reactions. Hence, cyanide complex ions of gold and silver- $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ complex ions will be obtained respectively. It can be reduced by zinc metal and so gold and silver metals can be obtained viz.

$$4Au(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \longrightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

$$4Ag(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \longrightarrow 4[Ag(CN)_2]^-(aq) + 4OH^-(aq)$$

and then,

$$2[Au(CN)_2]^-(aq) + Zn(s) \longrightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$$

$$2[Ag(CN)_2]^-(aq) + Zn(s) \longrightarrow 2Ag(s) + [Zn(CN)_4]^{2-}(aq)$$

Zinc acts as reducing agent in above reactions.

4.8 Refining of Impure Metals

There is a possibility to have impurity in the metals obtained by any of the methods or processes discussed earlier. Hence, to obtain very pure metals, their refining can be carried out and refining as high as possible can be obtained. For this, the methods used for refining are applied after taking into consideration the properties of the metal, impurities present in it etc. some of these are listed below :

(1) Distillation	(2) Liquation	(3) Electrolysis
(4) Zone refining	(5) Vapour phase refining	(6) Chromatographic methods

(1) Distillation : This refining method is used for metals like zinc and mercury which have comparatively low melting points. The vapours obtained by distillation of impure metals, is cooled and the metal is obtained. The pressure is to be reduced for distillation of metal like mercury. Low pressure can be achieved by vaccum distillation method.

(2) Liquation : This method is used for the refining of metals like tin which have low melting points. For this, the impure metal is passed over a hot slopping surface, so that the pure metal having low melting point is obtained from the impurities which are melting at higher temperatures. The temperature of slopping surface can be adjusted.

(3) Electrolysis : In this, the impure metal is made anode and the strip of pure metal is made cathode. Now, these two electrodes are dipped in the aqueous solution of proper salt. If suitable electric current is passed in the solution, electrolysis takes place and pure metal is deposited on the cathode and the impure metal on the anode undergoes oxidation and enters into the solution as ions. Some noble metals are collected near the anode in the form of mud which is called anodic mud. In this method, the principle of electrochemistry is involved. You have earlier studied about standard potential of cell (E^0) and free energy change (ΔG). Hence, if the reduction potential is high, the ions in the solution are reduced and deposited as pure metal on the cathode. The impure metal at the anode, enters into the solution as ions by oxidation reaction. If suitable potential is adjusted then amount of the metal obtained is directly proportional to the quantity of the electricity passed. You have studied this in the first law of Faraday's laws of electrolysis.

Anode : $M(s) \rightarrow M^{n+}(aq) + ne^-$

Cathode : $M^{n+}(aq) + ne^- \rightarrow M(s)$

The refining of impure copper is carried out by this method in which the reactions take place as follows :

Anode : $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

combining both the reactions.

$Cu(s)$ (Impure) $\rightarrow$ $Cu(s)$ (Pure)

Thus, pure copper metal is obtained from impure metal. Metal like zinc can also be obtained in pure form by this method.

(4) Zone Refining : Semimetals like silicon and germanium can be refined by this method. The principle of this method is that, the impurities of some metals are more soluble in molten state but is less soluble in solid state. This principle is used in the zone refining method.

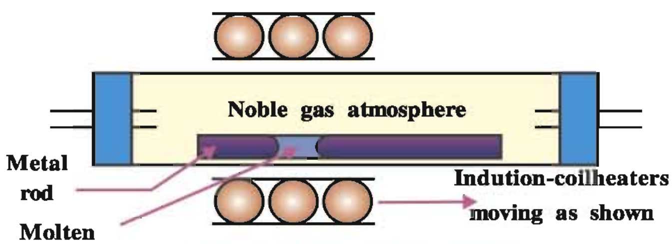

Fig. 4.4 Zone refining process

In this method spherical mobile heater is fixed at one end of the cylinder of impure semimetal. As shown in figure 4.4, the molten zone is advanced further with the heater. As the heater advances further, the impure semimetal (element) is separated from molten fluid and the impurities advance further with impure molten fluid. This method is repeated and the heater is moved in one direction only. It is cut in cylindrical form and removed. The vapourised semimetal gets cooled and obtained in pure form. The inert gas atmosphere is created with inert gas kept in the cylinder so that there is no effect of air and heat. Very pure silicon required for semiconductors is obtained by this method. In addition to this, metals/semimetals like germanium, boron, gallium, and indium are refined by this method.

(5) Vapour phase Refining : In this method, the impure metal is reacted with suitable substance and its volatile compound is prepared which is in gaseous form and so can be collected in other vessel. Then, this volatile compound is decomposed so that pure metal is obtained and the by-product obtained can be used again and can be reacted with impure metal. Thus, there are two aspects in the principle of this method : (1) To prepare volatile compound of the said metal with any other suitable substance (2) The obtained volatile compound can be easily decomposed. If it happens so, it will be easy to obtain metal. We shall see the refining of nickel. Impure nickel is reacted with hot flow of carbon monoxide gas at 330-350 K temperature so that complex compound named nickel tetracarbonyl $[Ni(CO)_4]$ is formed. In this, nickel metal combines directly with neutral ligand like carbonyl. If nickel carbonyl compound obtained this way is heated at 450-470 K temperature, it decomposes and pure nickel metal is obtained. Obtained carbon monoxide can be used again for the formation if nickel carbonyl from impure nickel metal, so that the expenses will be less. This method was developed by scientist Mond and so it is called **Mond Carbonyl process.**

Similarly, metals like zirconium or titanium can be refined by using Van Arkel method. By this method, oxygen and nitrogen present in the form of impuries in the metals like zirconium and titanium can be removed. Impure metal is heated with iodine in an evacuated vessel. The iodides of metal being volatile, are changed into vapour.

$$Zr(s) + 2I_2(g) \longrightarrow ZrI_4(g)$$

$$Ti(s) + 2I_2(g) \longrightarrow TiI_4(g)$$

The metal iodides obtained in this way are heated electrically on tungsten filament at 1800 K temperature so that they are decomposed and the pure metal is deposited on the wire.

$$ZrI_4(g) \longrightarrow Zr(s) + 2I_2(g)$$

$$TiI_4(g) \longrightarrow Ti(s) + 2I_2(g)$$

(6) Chromatographic method : In this method, the principle of adsorption is involved. The adsorption order or efficiency of different metal ions on any one adsorbent is different. Hence, if the mixture of any metal ions is passed over any suitable solid adsorbent, the components (ions) in the mixture are adsorbed in different parts of the adsorbent. These adsorbed parts in the adsorbent are separated and obtained by suitable eluent because that ion or substance becomes soluble in that eluent. You will study in detail about adsorption in the unit of surface phenomena. Solid like Al_2O_3, paper like filter paper or any suitable inert gas can be used as adsorbent. If solid substance like Al_2O_3 is used then it is filled in a glass tube and it can be used; so that the glass tube will become one column and so this chromatography is called **column chromatography.** If we cut filter paper strip and carry out separation of metal ions by suitable solvent on it, it is called **paper chromatography.** If on any suitable support, gaseous substance is used and separation is carried out, it is called **gas chromatorgaphy.** Demonstration experiments on adsorption and paper chromatography are included in your practicals book. Do it as an activity, with the help of the teacher. You will experience how interesting, nice, pleasant and innovative science is ! Some dyes, cations, anions etc. can be separated by suitable chromatographic method.

4.9 Extraction of Aluminium (Al), Copper (Cu), Iron (Fe) and Zinc (Zn) Metals

(1) Extraction of Aluminium : The extraction of Aluminium can be divided into two parts :

(A) To obtain pure alumina (Al_2O_3) from ore (bauxite)

(B) To obtain aluminium metal by reduction of alumina.

(A) To obtain pure alumina from ore (bauxite) : Bauxite is one of the principal minerals of aluminium from which aluminium is obtained. Silica (SiO_2), oxides of iron and titanium dioxide (TiO_2) are as impurities in impure bauxite. As seen earlier, the mineral bauxite is grinded and converted to small particles. Afterwards it is digested with 6 to 8% concentrated NaOH solution at 473 - 523 K temperature and 35 - 36 bar pressure. Because of this reaction amphoteric oxide Al_2O_3 reacts with base like NaOH and soluble hydrated sodium aluminate complex $Na[Al(OH)_4]$ is formed which we express as sodium tetrahydro aluminate (III) according to IUPAC. The remaining components also dissolve in sodium hydroxide and form soluble sodium silicate but hydroxides of iron and titatnium being insoluble get precipitated.

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

By filtering the solution, sodium aluminate is obtained in solution. By neutralising the solution by passing CO_2 gas, hydrated Al_2O_3 gets precipitated. At this stage, freshly prepared precipitates of Al_2O_3 or $Al(OH)_3$ are added which create induced effect in precipitation of Al_2O_3 from solution.

$$2Na[Al(OH)_4](aq) + 2CO_2(g) \longrightarrow Al_2O_3 \cdot XH_2O(s) + 2NaHCO_3(aq)$$

Sodium silicate remains in solution. Insoluble hydrated alumina is filtered. On heating it at 1470 K temperature, pure alumina is obtained.

$$Al_2O_3 \cdot XH_2O(s) \xrightarrow{1470\ K} Al_2O_3(s) + XH_2O(g)$$

(B) To obtain pure aluminium from alumina : Al_2O_3 does not conduct electricity and its melting point is very high; so that electric current can flow before getting pure aluminium metal and aluminium metal can be obtained on cathode by electrolysis. Hence, substances like cryolite (Na_3AlF_6) or CaF_2 are added to Al_2O_3. Hence, as studied earlier the physico chemical principles of thermo-dynamics are used so that the system formed is such that the value of ΔG^0 becomes more negative. This mixture is taken into an iron vessel in which there is layer of graphite on the inner side and it works as cathode. As shown in figure 4.5, carbon anodes are used and the molten $Al_2O_3 + Na_3AlF_6$ mixture is taken as electrolyte. For this, high temperature is to be maintained. Aluminium metal is obtained on graphite cathode by reduction. It is being in molten state at high temperature of the cell, aluminium comes out in the liquid form from the hole in the lower part of the cell. On cooling, aluminium metal is obtained in solid form. Thus, carbon of graphite functions as reducing agent.

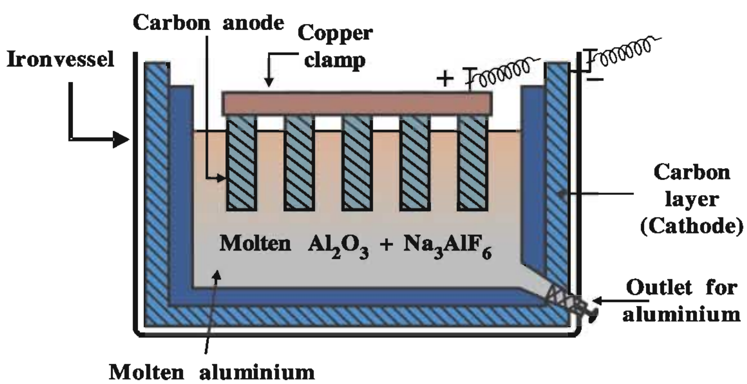

Fig. 4.5 Electrolytic cell for extraction of aluminium metal

$$2Al_2O_3(s) + 3C(s) \longrightarrow 4Al(s) + 3CO_2(g)$$

This method was discovered independently by scientists Hall and Heroult and so it is known as **Hall-Heroult process.** Oxygen liberated from Al_2O_3 at anode reacts with anode because anode is made up of carbon and temperature is high, so carbon monoxide (CO) and carbon dioxide (CO_2) are formed.

Reaction at cathode : $Al^{3+}(l) + 3e^- \longrightarrow Al(l)$

Reaction at anode : $C(s) + O^{2-}$ (Molten salt) $\longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}$ (Molten salt) $\longrightarrow CO_2(g) + 4e^-$

Thus, carbon of the anode is used up or gets corroded. According to one estimate 0.5 kilogram carbon is corroded or used up for 1 kilogram aluminium produced. Hence, the anodes of carbon are to be changed frequently. The production of alumina at the international level is about 100 million tons, India is producing about 1 million ton.

Uses of Aluminium : As aluminium is a light metal, it is used in the preparation of parts of aeroplane, household vessels, parts of cars for race. As it is good conductor of electricity, it was used in the electric wires. At present, its use has diminished. It can be used as reducing agent and metals like chromium manganese, are obtained from oxides of these metals. Alum is its important and useful compound. It also forms alloys like duralumin, magnalium, alnico and aluminium bronze are used in preparation of parts of the aeroplanes, parts of scientific balances, coinage, etc. Its thin sheets are used in cigarette cases, to keep hot substance hot and in packaging for the things instead of packaging by papers.

(2) Extraction of copper : For the extraction of copper, copper pyrites ($CuFeS_2$) is used even when many ores of copper are available. Copper available in free state, is obtained as copper metal by removal of the impurities exisiting with it. By this method, about 5% copper metal is obtained. If the ore is in carbonate or oxide form, it is heated with suitable reducing agent in fire furnace. Then it is heated with coke and sand so that copper metal is obtained by reduction of oxide; But if the ore is sulphide, it is not reduced directly as seen earlier and so it is to be converted to oxide. Sulphur dioxide gas produced during this reaction, causes pollution in atmosphere. Wet metallurgical process is used for pyrites ores of lower grade; while dry metallurgical process is used for the higher grade of pyrite ores. As copper has more attraction for sulphur, its reduction is difficult. With the increase in temperature, this attraction also increases. Iron has got more attraction for oxygen. Dry metallurgical method can be divided into five steps : (i) Concentration (ii) Roasting (iii) Smelting (iv) Bessemerisation (v) Refining.

(i) Concentration : About 2% copper is present in copper sulphide minerals available in nature. Froth floatation process is used for concentration of ore (**Recollect :** As studied earlier froth floatation process is used for concentration of sulphide ores). The grinded mineral is suspended in water and turpentine oil or cryolite oil is added to it. Then air is blown into it, so that oil sticks to the mineral and with the bubbles of the air it is collected as froth on the upper part and the impurities as well as waste is collected at the botom. The froth is skimmed off with sieves. By concentrating in this way, about 25% copper containing ore is obtained.

(ii) Roasting : The ore obtained by froth floatation method is roasted in air so that moisture as steam, sulphur and arsenic as their oxides i.e., sulphur dioxide and arsenious oxide are removed because of high temperature. During roasting, until iron sulphide is not converted into iron oxide, cuprous sulphide is not converted to its oxide.

$$2CuFeS_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 2FeO(s) + 3SO_2(g)$$

(iii) Smelting : The mixture obtained by roasting is smelted with sand (SiO_2) in blast furnace so that sand and iron oxide combine to form iron silicate ($FeSiO_3$) which is called **slag.** As it is light it floats on the mixture and so it is repeatedly removed. This iron oxide is removed as slag during the smelting.

$$2FeS(s) + 3O_2(g) \longrightarrow 2FeO(s) + 2SO_2(g)$$

$$FeO(s) + SiO_2(s) \longrightarrow FeSiO_3(s)$$

If cuprous oxide is formed with cuprous sulphide during roasting is converted to cuprous sulphide.

$$Cu_2O(s) + FeS(s) \longrightarrow Cu_2S(s) + FeO(s)$$

FeO obtained this way can be removed as slag. Then, mixture of iron sulphide (FeS) and curpous sulphide (Cu_2S) is seen there which is called matte. As it is heavy, it settles at the bottom of the vessel and the light slag of iron silicate - remains floating, so it is easy to remove it.

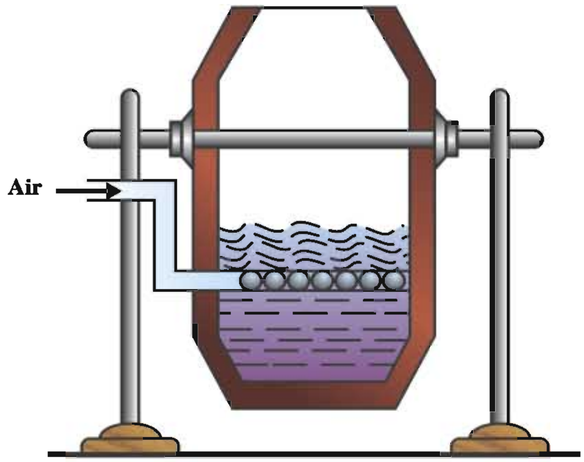

Fig. 4.6 Bessemerisation

(iv) Bessemerisation : The iron left out in the mixture is removed in Bessemerisation process. For this the fluid (mixture) obtained by smelting is poured in Bessemer's converter and required amount of sand is added. Then the converter is kept in vertical position as shown figure 4.6. Air at high pressure is introduced into it, so that iron sulphide is converted to iron oxide which combine with sand and form iron silicate (slag).

$$2FeS(s) + 3O_2(g) \longrightarrow 2FeO(s) + 2SO_2(g)$$

$$FeO(s) + SiO_2(s) \longrightarrow FeSiO_3(s)$$

During Bessemerisation, cuprous oxide is formed by oxidation of cuprous sulphide only after all the iron sulphide is converted to iron oxide. When cuprous oxide is formed in the sufficient proportion, introduction of air is stopped. Because of self oxidation between cuprous sulphide and cuprous oxide, copper is obtained in fluid state.

$$2Cu_2S(s) + 3O_2(g) \longrightarrow 2Cu_2O(s) + 2SO_2(g)$$

$$Cu_2S(s) + 2Cu_2O(s) \longrightarrow 6Cu(s) + SO_2(g)$$

Copper is taken out in fluid state, from the Bessemer converter. As this copper gets cold, bubbles of sulphur dioxide gas from the fluid are evolved. Hence, it appears that blisters are there on the surface of copper and is called **blister copper.** This copper is about 95% pure. Mainly impurities of sulphur and iron are present in it. Impurities like Zn, Si, As, Sb, Bi, Au, Pt are present in trace amounts.

(v) Refining :

(A) Thermal Refining : Blister copper is heated in presence of air in furnace, so that volatile oxides of As, Sb, etc. are removed. Silicates of Fe, Bi, Zn etc. float as slag on copper, which are removed. The remaining impurities like Ag, Au, Pt, can not be removed. During this some cuprous oxide is produced which dissolves in copper and so it becomes brittle. Hence, to stop this, powder of coal is spread on the fluid copper and the fluid is shaken with the freshly cut branches of tree. Because of the heat of copper, destructive distillation of branches of wood produces gas like methane. It reduces cuprous oxide to copper. Copper obtained this way is about 99.5% pure. It being very strong, it is used for common uses.

(B) Electrolysis : Copper obtained by thermal refining contains some impurities and so it is not a good conductor of electricity. Noble metals like Ag, Au and Pt are present in it and so it is advisable to obtain them. Hence electrolysis method is used for obtaining very pure copper. As shown in figure 4.7, solution of copper sulphate in dilute sulphuric acid is taken as an electrolyte, in a vessel. In this, small strips or rod of impure copper is dipped as the anode and strip of pure copper is dipped as cathode. As the electric current is passed through the solution, following reactions take place at anode and cathode during electrolysis.

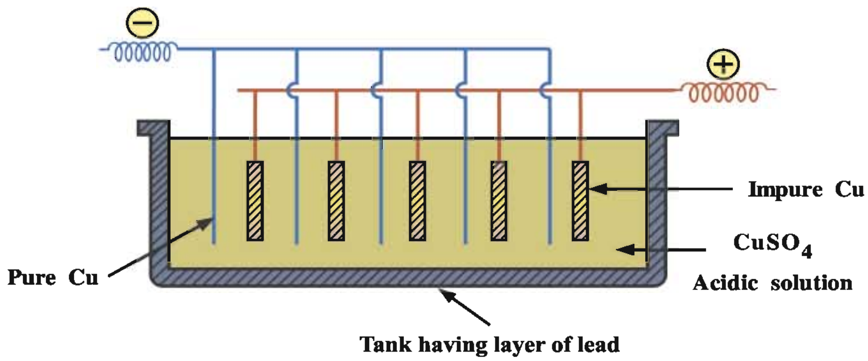

Fig. 4.7 Electrolysis of copper

Anode : $Cu(s)$ (Impure) $\longrightarrow Cu^{2+}(aq) + 2e^-$ (Oxidation)

Cathode : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (Reduction)

Net reaction : $Cu(s)$ (Impure) $\longrightarrow Cu(s)$ (Pure)

Thus, as long as electric current is passed, copper of impure copper gets oxidised and enters into the solution as copper ions and the copper ions of the solution are changed to copper metal by reduction reaction which is deposited on the cathode. As noble metals like Ag, Au and Pt are not oxidised, they are collected below the anode which is known as **anode mud.** Ag, Au and Pt metals can be obtained from it. The purity of copper obtained at the cathode is about 99.96 to 99.99%.

Uses of copper : Copper is used in preparation of electrical appliances, tubes of boiler, sheet, household vessels, currency coins and also it is added to gold ornaments so that they become strong. It is also used for obtaining metals like Ag and Au from their ions in the solutions of their salts, by reduction. In addition to this, it is also used in preparation of many more alloys. Some of the known alloys of copper are brass, bronze, german silver, Monel metal, Bell metal, Delta metal, constantant, Muntz metal, phosphor bronze, aluminium bronze etc.

(3) Extraction of Iron metal : From the ores of the iron, haematite (Fe_2O_3) is used to obtain iron. There are three steps for this.

(i) Roasting and Calcination (ii) Reduction and smelting (iii) Refining.

(i) Roasting and Calcination : The oxide form ore containing iron is first roasted by heating with some coal in a furnace, so that the volatile impurities like the moisture and carbon dioxide obtained due to decomposition of carbonate are removed. Ferrous oxide is oxidised to ferric oxide which does not combine with silica and does not form slag, in the smelt. The mixture in the furnace becomes porous.

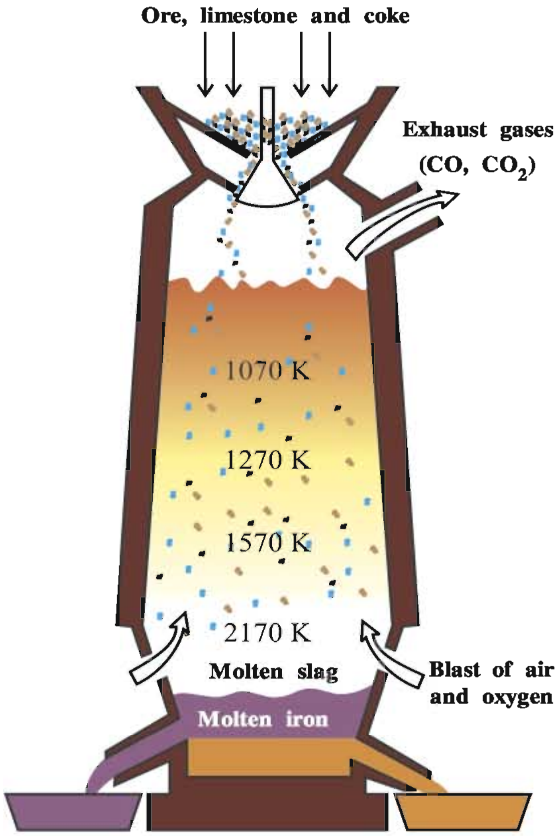

Fig. 4.8 Blast furnace

(ii) Reduction and smelting : The porous mixture obtained by roasting is mixed with lime stone. Coke, etc. are added into the blast furnace from the upper part as shown in figure 4.8. Here, oxide is reduced to iron metal. Thermodynamics is useful in understanding the reactions occuring in blast furnace e.g. How carbon monoxide formed from coke, carries out reduction ? Why such a furnace is selected ? The main function of this furnace is to carry out the following reactions :

$$FeO(s) + C(s) \longrightarrow Fe(s/l) + CO(g) \qquad (4.1)$$

The coke can carry out reduction directly. CO gas is formed by combination of carbon with oxygen available from FeO.

$$FeO(s) \longrightarrow Fe(s) + \frac{1}{2}O_2(g) \qquad [\Delta G\ (FeO, Fe)] \qquad (4.2)$$

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad [\Delta G\ (C, CO)] \qquad (4.3)$$

Reaction 4.1 is obtained by computation of simple reaction (4.2) and (4.3). Hence, the free energy change of the reaction ($\Delta_r G$) will be as follows.

$$\Delta_r G = \Delta G\ (C,CO) + \Delta G\ (FeO,\ Fe) \qquad (4.4)$$

If the value of ΔG obtained is negative, then only the reaction will occur. Hence, from the study of $\Delta_r G$ and temperature, the changes in $\Delta_r G$ can be studied and the temperatures of the reactions occurring in blast furnace can be controlled and the conditions can be so created that the reaction occurs. You have studied in standard 10 that blast furnace is a very tall furnace and there are different temperatures at different heights in the furnace. At the temperature 500-800 K (Range of low temperatures in blast furnace) the reaction takes place.

$$3Fe_2O_3(s) + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g)$$

$$Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g)$$

$$Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$$

At temperatures 900 - 1500 K, (Range of high temperatures in blast furnace), following reactions occur,

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

Calcium oxide obtained by the decomposition of lime stone combines with silica which is the impurity from the ore and forms slag which is removed as slag. Slag being in molten condition, separates from the iron. Hence, the reaction occurring at different temperatures in blast furnace can be shown as below :

(i) In the temperature range of 500-900 K.

$$\underset{\text{(Ore)}}{3Fe_2O_3(s)} + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g)$$

$$Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g)$$

$$\underset{\text{(Limestone)}}{CaCO_3(s)} \longrightarrow CaO(s) + CO_2(g)$$

$$CaO(s) + SiO_2(s) \longrightarrow \underset{\text{(Slag)}}{CaSiO_3(s)}$$

(ii) At 1270 K temperature

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

$$\underset{\text{(Coke)}}{C(s)} + CO_2(g) \longrightarrow 2CO(g)$$

$$FeO(s) + C(s) \longrightarrow Fe(s) + CO(g)$$

(iii) Molten slag is formed at 2170 K temperature.

(iv) At temperature higher than 2170 K, pig iron is formed.

Iron obtained from blast furnace contains 4% carbon and many impurities. Also, it contains S, P, Si, Mn etc. in trace. It is called **pig iron.** It can be casted into different shapes. Cast iron is different from pig iron. Cast iron can be prepared by blowing hot air in the mixture of pig iron, iron scrap and coke. The proportion of carbon in it is comparatively less (about 3%). It is hard and brittle.

(iii) Refining : Wrought iron or malleable iron is the purest form of general iron. Wrought iron is prepared from cast iron in reverberatory furnace in which there is a layer of haematite. Haematite changes carbon to carbon monoxide.

$$Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(s) + 3CO(g)$$

Limestone is added as a flux and is removed with oxidation of sulphur, silicon and phosphorus. Metal is taken out of the furnace and passed through the rollers so that slag is removed and iron metal is obtained.

Uses of Iron : The most important form of iron is cast iron which is used in stoves, rails of railway, pipes of gutter, toys etc. because it can be casted. It is used in preparation of wrought iron and steel. Wrought iron is used in preparation of anchors, wires, bolts, chains, agricultural tools, etc. Steel has many uses. Different types of steel, having desirable properties can be prepared by mixing other metals with iron. Steel containing nickel is used in ropes, automobile, parts of aeroplanes, pendulums, measurement tap etc. Steel containing chromium is used in machines for cutting and grinding and stainless steel is used in cycles, automobiles, vessels, pans etc.

(4) Extraction of Zinc : The ores of zinc are available in forms of oxide, carbonate and sulphide. From these, the zinc sulphide ore is known as zinc blende. It is mostly used in obtaining zinc metal. Zinc metal can be obtained by reduction with carbon. This, extraction takes place in four different steps : (i) Concentration (ii) Roasting (iii) Reduction (iv) Refining

(i) Concentration : As studied earlier, ZnS which is the sulphide containing ore of zinc, froth floatation process is used for its concentration. It contains galena (lead sulphide-PbS) sand etc. as the impurities. It is grinded and converted to powder form. It is taken in a vessel and water is added to it. Air is passed through after adding turpentine oil. As zinc sulphide mineral is light it comes up with the light froth obtained by bubbles of air, while other impurities remain in the solution or settle down. The froth obtained by froth floatation process is frequently removed with sieves. Concentrated ore is collected. If mineral is calamine, this method is not necessary becaue the ore does not contain galena.

(ii) Roasting : Concentrated ore-ZnS or calamine is roasted in presence of air, so that it is converted to oxide form ZnO. If the ore is ZnS, it becomes necessary to keep in mind that it is converted to ZnO as much as possible otherwise it combines with liberated SO_2 gas and changes to zinc sulphate.

$$2ZnS(s) + 3O_2(g) \xrightarrow{\Delta} 2ZnO(s) + 2SO_2(g)$$

If mineral is carbonate, ZnO is obtained as follows :

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

Thus zinc oxide is obtained.

(iii) Reduction : Zinc oxide obtained by roasting is mixed with powder form coal or anthracite coal and heated in the cylindrical retort which is made up of fire clay bricks; so strongly that it becomes red hot. One end of the retort is closed and other retort is joined with the other open part so that it works as a condensor and cools the vapour of zinc that is coming out. Many such retorts can be connected in series. It is kept bent towards its mouth. When it is heated, carbon combines with oxygen of zinc oxide and forms carbon monoxide. Carbon monoxide burns with a blue flame at the end of the china clay tube. After some time the flame becomes brighter which indicates that now the vapour of metal has started forming. A small condensor which is prepared from iron and called as prolong or nozzle. It is connected with the end of each of the china clay tube; so that zinc metal gets cooled and collected in it. This metal is taken out and is casted into blocks. The zinc metal that we get on commercial basis is called **spelter.**

$$ZnO(s) + C(s) \xrightarrow{\Delta} Zn(s) + CO(g)$$

In the distillate coming out in the beginning, impurity of cadmium is removed, because it can be easily reduced and is more volatile than zinc.

(iv) Refining : Zinc obtained by reduction, which is called spelter contains impurities like Fe, Al, As, Sb etc. which can be removed by repeated distillation. But zinc is reacted with dilute H_2SO_4, so as to obtain pure zinc. By this reaction solution of zinc sulphate is obtained. Intensive refining of this zinc sulphate is carried out. Cadmium is precipitated by zinc dust. Iron is converted to ferric state. Al, Sb, and As are separated from solutions of suitable acidity. Afterwards, the solution is filtered out so that pure zinc sulphate solution is obtained. As seen earlier in copper, here also impure zinc is made anode and pure zinc strip or rod is made cathode. The electrolyte is zinc sulphate solution containing dilute H_2SO_4. Reactions occurring at anode and cathode are as follows :

Anode : $Zn(s)\ (Impure) \longrightarrow Zn^{2+}(aq) + 2e^-$ (Oxidation)

Cathode : $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) + 2e^-$ (Reduction)

Net reaction : $Zn(s)\ (Impure) \longrightarrow Zn(s)\ (Pure)$

Uses of zinc : Zinc is used in preparation of electrical cells, in electroplating of zinc and also in galvanising. It is used in certain alloys like brass, german silver, in combination with copper. It is used as zinc powder in reduction reactions. Metals like silver (Ag) and gold (Au) can be obtained from Ag^+ or Au^{3+} ions containing solutions by reduction with zinc. It is also used for protection of metal from corrosion by electroplating them on iron strips (galvanised iron).

SUMMARY

Metals and non-metals are associated with human life from very long time. viz. metals like iron, copper, gold, mercury, and non-metals like dioxygen and dinitrogen. We use these metals in pure form or their alloys formed by metals combined with other substances. Many reactions and processes are to be used before obtaining such metals.

Metals are mostly combined in their oxide, sulphide or carbonate compounds and very rare cases the metals are in free form. Their proportions are different in the earth's crust. The substances which are obtained from earth's crust or mines are called mineral. There can be more than one mineral for a particular metal. Same amount of metal or element is not obtained from each mineral. Hence, the part in which the maximum quantity and good quality metal can be obtained is called ore. viz. Haemetite for iron, bauxite for aluminium, copper pyrites for copper and zinc blende for zinc.

The complete process to extract metal from ore is called metallurgy. In this unit, we have studied about the extraction of certain metals from their minerals or ores. The combined form of metal alongwith impurities and earthly substances is called gangue. Three important steps are there to obtain metal from ore. (i) concentration of ore, (ii) isolation of metal from concentrated ore and (iii) refining of metal. The abundance of aluminium ore available from earth's crust has position three in the order of elements available from earth's crust. The methods used for concentration of ores are developed after taking into consideration, impurities, etc., physico-chemical principles, physical and chemical properties of the metal as well as the matters which should not be harmful to environment. Amongst the methods of concentration of ore are (1) hydraulic washing (2) magneteic separation (3) froth floatation method and (4) leaching. The principle of hydraulic washing is the relative density of gangue. Principle of magnetic attraction-repulsion is involved in magnetic separation. In froth floatation process, concentration of sulphide ore by producing artificially foam is carried out. In leaching, the principle of solubility of different solutes in different solvents is involved.

Several steps are associated with extraction of crude metal from ore. viz. conversion to oxide and reduction of oxide to metal. The steps which are followed for conversion into oxides are (1) calcination (2) roasting - by which metal is obtained in oxide form. Some substances are added to remove certain substances viz. to remove iron oxide, sand (Silica) is added so that iron silicate ($FeSiO_3$) is obtained in slag form. As it is light, it can be removed. The furnaces for such functions, furnaces like reverberatory furnace, fire furnace and blast furnace are used.

After obtaining oxide of metals, they are reacted with suitable reducing agents and metals are obtained. Carbon, coal, carbon monoxide, active metal etc. can be used as reducing agents. Metallurgy studied with changes in temperatures is called pyrometallurgy. Reduction can also be carried by electrons through electric current.

The study and information about the principles of thermodynamics, chemical equilibrium, Le Chatelier's principle, as well as the study of terms like free energy change, equilibrium constant, enthalpy, entropy etc. become very essential in the process of metallurgy. For any reaction to result in products, the value of equilibrium constant should be more than 1 and the corresponding value of free energy change should be as negative as possible. Scientist Ellingham studied the relations between free energy decrease ($-\Delta G^0$) and it is known as Ellingham diagrams. The use of physico-chemical principles associated with metallurgy are explained in this unit. Oxidation means to lose electron which takes place at anode in the electrochemical cell and reduction means to gain electron which takes place at cathode in the electrochemical cell. Hence, impure metal can be oxidised with the help of anode and pure metal is reduced from the solution by reduction and gets deposited on the cathode viz. From anode of impure copper, pure copper can be obtained on the cathode. The purity of the metal obtained by this method is almost 100%. Certain metals can be converted to their complex compound forms by addition of certain substances and can be separated. Viz. reaction of metals like silver and gold with substance like sodium cyanide.

The following methods are used for refining of impure metals. (1) Distillation (2) Liquation (3) Electrolysis (4) Zone refining (5) Vapour phase refining.

Metal like mercury can be refined by distillation. Metal like tin can be refined by liquation metal like copper can be refined by electrolysis, semimetal like silicon can be refined by zone refining method and metal like nickel can be converted to gaseous compound like nickel carbonyl and then refined by vapour state method. Metals like zirconium and titanium can be refined by Van Arkel method. The ions of some metals can be obtained in pure form by chromatographic method and then metals of ions can be obtained by reduction.

In addition, the extractions of aluminium, copper, iron and zinc have been studied in this unit. This study can be shown as summary in the following table.

Sr. No.	Ore	Pure metal	Method and its name
1.	Bauxite ($Al_2O_3 \cdot XH_2O$)	Aluminium	Hall-Heroult method - by electrolysis
2.	Copper pyrites ($CuFeS_2$)	Copper	Thermal refining and electrolysis method
3.	Haematite (Fe_2O_3)	Iron	Use of blast furnace method
4.	Zinc blende (ZnS)	Zinc	Electrolysis method

In addition, in this unit, the uses of each metal, their alloys with other metals etc. are also included. The products etc. obtained by extraction of metals and non- metals plays an important role in the economic condition of the country.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which is the ore of aluminium ?

(A) Bauxite (B) Haematite (C) Copper pyrites (D) Zinc blende

(2) Which is the ore of copper ?

(A) Bauxite (B) Haematite (C) Copper pyrites (D) Zinc blend

(3) Which is the ore of zinc ?

(A) Bauxite (B) Haematite (C) Copper pyrites (D) Zinc blende

(4) Which is the ore of iron ?

(A) Bauxite (B) Haematite (C) Copper pyrites (D) Zinc blende

(5) Which metal is refined by zone refining method ?

(A) Copper (B) Zinc (C) Silicon (D) Aluminium

(6) Which metal is refined by electrolysis method ?

(A) Mercury (B) Zinc (C) Tin (D) Silicon

(7) What is name of the method used in refining of aluminium?

(A) Van Arkel (B) Bessemerisation (C) Hall-Herault (D) Heitler-London

(8) What is called the strongly heating of ore and converted to oxide ?

(A) Roasting (B) Distillation (C) Liquefaction (D) Electrolysis

(9) In which method do the ranges of temperature play an important role ?

(A) Electrolysis (B) Zone refining (C) Blast furnace (D) Liquation

(10) Which principle is involved in chromatographic separation ?

(A) Precipitation (B) Hydration (C) Decomposition (D) Adsorption

2. Answer the following questions in brief :

(1) Explain the principle of zone refining method and show which metal can be refined by it.

(2) Explain in detail roasting and calcination.

(3) Describe the use of carbon and carbon monoxide as reducing agent.

(4) Electrolysis is a reduction method. Explain.

(5) Write chemical reactions occurring in the different ranges of temperature in blast furnace.

3. **Write the answers in detail, of the following questions :**

(1) Describe in brief the methods for obtaining ore from mineral.

(2) Explain the use of physico-chemical principles in metallurgy.

(3) Describe Hall-Herault method.

(4) Explain the electrolysis of impure copper.

(5) Explain in detail, the zone refining method.

4. **Write in detail, the answers of following questions :**

(1) What is slag ? Why is it required and in extraction of which metal it is used ?

(2) Discuss the physico-chemical principles regarding cryollite and calcium fluoride used in Hall-Heroult method.

(3) Explain the terms giving suitable example-Roasting, Calcination, Refining, Electrolysis, Zone refining.

(4) Describe in detail the method to obtain pure alumina from bauxite.

(5) Give reasons for the following phenomena :

(1) The anodes of carbon have to be changed in refining of aluminium.

(2) Froth floatation method becomes inevitable for the ore containing sulphide.

(3) Iron oxide does not get reduced till there is presence of iron sulphide.

(4) Cryollite is added in refining of aluminium.

(5) In refining of metals like gold and silver, the solutions of their complex compounds are used.