6

Principles and Processes of Isolation of Elements

6.1 Introduction

Except gold, silver, platinum, carbon, sulphur and inert gases, other elements occur in nature in combined state. Most of the elements on earth have metallic nature. The biggest source of metals is the Earth's crust in which aluminium (Al) metal is most abundant (about 8.3% by wt.), next to this comes iron.

Every substance on earth is made by combination of elements. These elements can be divided in three main parts.

Table 6.1 : Percentage of main elements

S.No.	Element	Percentage (% by Wt.)
1.	Aluminium	8.3
2.	Iron	5.1
3.	Calcium	3.6

(i) **Metal–** These are solids, Metal have properties like hardness, high malleability, ductility, electrical and thermal conductivity. They have metallic lusture also. Of the known elements, 80% are metals. For example Aluminum (Al), Iron (Fe), Copper (Cu), Zinc (Zn), Silver (Ag), Gold (Au), Platinum (Pt), tec.

(ii) **Non Metal–** These elements are brittle in nature and have no lusture. They are electrically non-conducting. For example carbon, oxygen, hydrogen, nitrogen, halogen, sulphur, phosphorous, etc.

(iii) **Metalloids–** These elements have properties of both, metals and non-metals. For example, Boron, Silicon, Arsenic, Antimony, Tellurium, Bismuth, etc.

6.2 Abundance of Metals in Nature

In nature, metals are found in two states.

(i) **In free state–** These are inert in nature. They do not react with air, oxygen, moisture, CO_2 and with other elements. Example - Gold, Platinum, etc.

(ii) **In combined state–** Since most of the metals are reactive, they occur in combined state. These react with oxygen, moisture, CO_2 (oxidised or reduced) to form compounds.

Minerals– These are metallic compounds which occur in nature in combined state along with some other impurities like silica, sand, stones, etc. Places where minerals are found are known as **mine**.

Ore– Those minerals from which metals can be easily and economically extracted are known as **ores.** "It may be understood that all ores are minerals but all minierals are not ores."

In nature, metals are found generally as oxides, sulphides, sulphates, carbonates, silicates, halides, nitrates, phosphates ores. For example, Al_2O_3 with different metal impurity forms different gemstones like-

(i) **Ruby–** (Al_2O_3 having impurities of Cr)

(ii) **Blue sapphire (Neelam)–** Al_2O_3 having impurity of Co.

Table 6.2 : Main Ores of some important metals

S.No.	Metal	Ore	Chemical Composition
1.	**Aluminium**	bauxite	$Al_2O_3.2H_2O$ [or $AlO_x(OH)_{3-2x}$] where $0 < x < 1$
		feldsper	$KAlSi_3O_8$
		cryolite	Na_3AlF_6 [or $3NaF.AlF_3$]
		kaolinite	$Al_2O_3.2SiO_2.2H_2O$
		clay	$[Al_2(OH)_4.Si_2O_5]$
		diaspore	$Al_2O_3.H_2O$
		mica	$K_2O.3Al_2O_3.6SiO_2.2H_2O$
		corundum	Al_2O_3
2.	Iron	Haematite (red)	Fe_2O_3
		Limonite (brown hematite)	$2Fe_2O_3.3H_2O$ (magnetic)
		Magnetite	Fe_3O_4 (magnetic)
		Siderite	$FeCO_3$
		Iron pyrite	FeS_2
3.	Copper	Copper pyrite	$CuFeS_2$ [or $Cu_2S.Fe_2S_3$]
		Copper glance	Cu_2S
		Cuprite (ruby copper)	Cu_2O
		Malachite	$CuCO_3.Cu(OH)_2$
		Azurite	$2CuCO_3.Cu(OH)_2$
4.	Zinc	Zinc blend (sphalerite)	ZnS
		Zincite	ZnO
		Calamine (smithsonite)	$ZnCO_3$
		Willemite	Zn_2SiO_4
		Franklinite	$ZnFe^{III}_2O_4$

6.3 Extraction of Metals-Metallurgy

Generally, bauxite for Aluminium, haematite for iron, copper pyrite or cuprite for copper and zincite for zinc are chosen as ores for extraction. These ores are chosen on the basis of abundance and low cost.

Extraction of metal from its ore in a easy way is called metallurgy in which following main steps are-

(i) Crushing and grinding of the ore

(ii) Concentration of ore

(iii) Exraction of Metal

(iv) Purification of Metal

6.3.1 (i) Crushing and grinding of the ore–

First of all, suitable ore of the metal is chosen. This is in the form of small and big pieces. These are crushed is small pieces by Jaw Crusher and then again grind to finely divided particles by stamp mill or ball mill. This process is known as pulverisation. Then this pulverised ore is filtered by sieves.

6.3.2 (ii) Concentration of ore–

In general, clay, sand, stones and silicate impurities are present in the ore. These unwanted impurities are called **gangue** or matrix. Thus, the process of removal of unwanted impurities from the ore is known as concentration of ore or dressing of the ore.

Depending upon the type of the ore, available facilities and other factors, the method of concentration of ore in selected. followings are the main methods of concentration.

(1) Gravity Separation Method
(2) Magnetic Separation Method
(3) Froth Flotation Method
(4) Leaching or Chemical Separation Method

(1) Gravity Separation Method– When the density of gangue is very low as compared to the density of the ore, this method is used. The finely divided ore is agitated with water or washed with a running stream of water on steeped or Wilfley table. The heavy ore settles down rapidly and the lighter gangue is washed away. Generally, oxides and carbonate ores of iron and tin are concentrated by this method.

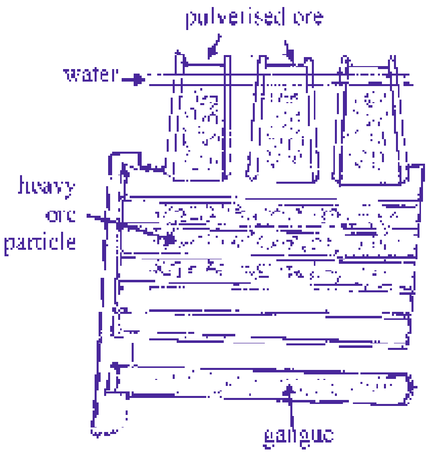

Fig. 6.1 : Wilfley Table for gravity separation

Example–

Haematite (Fe_2O_3), Cassiterite (SnO_2)

(2) Magnetic Separation– This method is used on the basis of magnetic properties of the ores obtained from minerals. In this, the ore is a mixture of two ores of which one component (in the form of impurity) is of magnetic nature. In this method pulverised ore is dropped on the one end of rubber belt moving over two pulleys, one of which is magnetic. At the other end of the belt, the magnetic component of the ore is attracted by the magnetic pulley and falls nearer to the pulley. The non-magnetic part falls farther. Ferromagnetic ores are separated by this method.

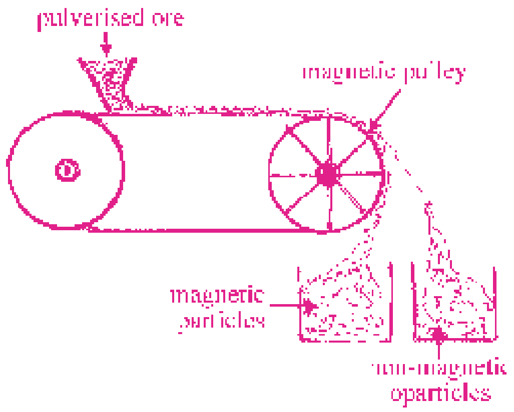

Fig. 6.2 : Concentration of ore by magnetic saparation method

For example, the ore of tin (cassiterite) contains Fe_2O_3 and $FeWO_4$ (Wolframite) and both are magnetic in nature, so this method is used in this case (Fig. 6.2)

(3) Froth-flotation Method– This method is used for sulphide ores. For example, copper pyrite ($CuFeS_2$), galena (PbS), zinc blend (ZnS), silver glance (Ag_2S), etc. are concentrated by this method.

This method is based on the principle that metallic sulphides are preferentially wetted by oil as compared to impurity like silicates, which are easily wetted by water. In this process, following substances are used :-

(i) **Frothing Agents–** These substances (oils) helps in formation of froth (foam) with air. Mainly, fatty acids, pine oil, and eucalyptus oil are good frothing agents.

(ii) **Flotation Agents–** These substances make the sulphide particles water repellant, therefore, sulphide particles float over the surfance of water. For example, sodium ethyl xanthate is main floting agent.

Formula $$\text{RO}-\underset{\underset{\text{S}}{\|}}{\text{C}}-\text{SNa}$$

R = ethyl or alkyl group

These are also called collectors.

(iii) **Stabilizers–** They stabilize the froth formed during the process. For example, cresol, aniline.

(iv) Activators– They increase the froth capacity. For example, copper sulphate ($CuSO_4$).

(v) Depressant– They are used to decrease the froth. For example, sodium cyanide (NaCN), alkali (Na_2CO_3), etc.

Description of Method– In big rectangular container, water is taken and the ore is mixed with water. To this, small quantity of oil (frothing agent) is added. Very small quantity of floating agent and stabilizer is also added. Then, the water is agitated violently with air. Because of this process, light particles of sulphide ore float-up with froth which are separated from there. Gangue is preferentially wetted by water, so it is collected at the bottom of the container. (Fig. 6.3)

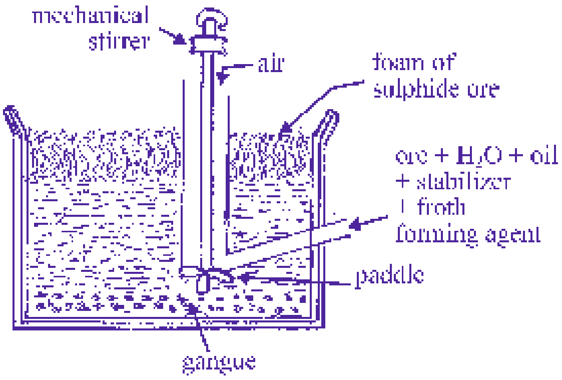

Fig. 6.3 : Froth-flotation Method

Sometimes, this method is used to separate two sulphide ores. For this, depressants are used. Depressants manage the ratio of oil and water in such a way that sulphide ores are separated. For example, sodium cyanide is used as depressant in the separation of zinc blend (ZnS) and galena (PbS). NaCN stops ZnS to go in the froth but not to PbS, therefore, they are separated easily.

Due to discovery of this method, copper ores, which contain low quantity of copper, can be concentrated easily and benificially.

(4) Leaching or chemical method of separation– In this method, the powdered ore is dissolved in suitable reagent which dissolves the ore but not the impurities. This method is used for the concentration of ores of aluminium, silver, gold, etc. Leaching is also called chemical method of concentration.

(a) Leaching of Alumina from bauxite :

(i) Bayer's Method : Specific properties of the ores can be used for their concentration. Bauxite is amphoteric in nature. When acidic impuriies like Fe_2O_3 and SiO_2 (with small amount of TiO_2) are present, then leaching is done by Bayer's method. **For example**– when pulverised bauxite is heated with NaOH at 473-523K and about 35 atmospheric pressure, then aluminium present in the ore dissolves by forming sodium meta aluminate and impurities are left behind and are filtered off.

$$Al_2O_3.2H_2O + \underset{\text{conc.}}{2NaOH} \longrightarrow \underset{\substack{\text{sodium aluminate}\\ \text{(soluble)}}}{2NaAlO_2} + 3H_2O$$

Filtered solution is diluted by water and to it freshly prepared $Al(OH)_3$ is added, so aluminium hydroxide (white ppt) is precipitated. This ppt. is filtered and dried by heating to get pure alumina (Al_2O_3).

$$NaAlO_2 + 2H_2O \xrightarrow{\text{Fresh } Al(OH)_3} \underset{\text{white ppt.}}{Al(OH)_3 \downarrow} + NaOH$$

$$2Al(OH)_3 \xrightarrow[\Delta]{\text{calcination}} \underset{\text{alumina}}{Al_2O_3} + 3H_2O$$

(ii) Alternate Method : In this, if CO_2 gas is passed in the filtrate containing sodium meta aluminate, hydrated Al_2O_3 is precipitated. For quick precipitation, freshly prepared hydrated Al_2O_3 is added (seeding).

$$2NaAlO_2 + 2H_2O + 2CO_2 \rightarrow$$
$$\underset{\text{hydrated alumina}}{Al_2O_3.H_2O} + 2NaHCO_3$$

Then hydrated alimina is filtered, dried and heated (calcination) and thus, pure anhydrous Al_2O_3 is obtained.

$$Al_2O_3.H_2O\,(s) \xrightarrow{1470\,K} Al_2O_3\,(s) + H_2O(g)$$

(iii) Hall's Method : When bauxite has impurity mainly due to presence of Fe_2O_3, then this method is used for leaching. In this method, bauxite is fused with Na_2CO_3 to give sodium meta aluminate from which pure alumina is obtainred.

$$Al_2O_3.2H_2O + Na_2CO_3 \xrightarrow{\text{fusion}}$$
$$2NaAlO_2 + 2H_2O + CO_2 \uparrow$$

$$2NaAlO_2 + 3H_2O + CO_2 \xrightarrow{325K} 2Al(OH)_3 \downarrow + Na_2CO_3$$

$$2Al(OH)_3 \xrightarrow{\text{calcination}/\Delta} \underset{\substack{\text{pure anhydrous}\\ \text{alumina}}}{Al_2O_3} + 3H_2O$$

(3) Serpeck's Method : This method is used for the purification of bauxite containing silica (SiO_2) as the main impurity. In this process, the powdered ore is mixed with coke and heated at about 1800°C in the presence of N_2 gas, aluminium nitride (AlN) is formed. AlN is hydrolysed to give aluminium hydroxide $Al(OH)_3$ which on heating gives anhydrous Al_2O_3 and silica is reduced to Si by coke, which is volatile so easily separated.

$$AlO_3.2H_2O + \underset{(\text{coke})}{3C} + N_2 \xrightarrow{1273K} 2AlN + 3CO_2 + 2H_2O$$

$$SiO_2 + 2C \longrightarrow 2CO + Si \uparrow (\text{volatile})$$

$$AlN + 3H_2O \xrightarrow{\text{Hydrolysis}} Al(OH)_3 + NH_3$$

$$2Al(OH)_3 \xrightarrow[\Delta]{\text{calcination}} Al_2O_3 + 3H_2O$$

Leaching of the ores of Silver and Gold : Leaching of the silver ore argentite or silver glance (Ag_2S) and horn silver (AgCl) is done with the dilute solution of NaCN or KCN. If the ore is argentite, the leaching take place by NaCN and O_2 of air.

$$AgCl + 2NaCN(aq.) \longrightarrow Na[Ag(CN)_2] + NaCl$$

By adding Zn metal to the above formed complex, Ag is obtained by substitution reaction;

$$Ag_2S + 4NaCN + \underset{(\text{air})}{2O_2} \longrightarrow \underset{\substack{\text{sodium dicyano}\\ \text{argentate complex}}}{2Na[Ag(CN)_2]} + Na_2SO_4$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$$

ionic reaction is as follows -

$$4Ag + 8CN^- + 2H_2O + O_2 \longrightarrow 4[Ag(CN)_2]^- + 4O\overline{H}$$

$$4[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag \downarrow$$

This process of precipitating the metal (here silver) is known as "Cementation". In the same way leaching of gold takes place by following reactions -

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Au(CN)_2] + 4NaOH$$

$$2Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Au \downarrow$$

Ionic reaction is as follows :-

$$4Au + 8C\overset{\ominus}{N} + 2H_2O + O_2 \longrightarrow 4[Au(CN)_2]^- + 4O\overline{H} \quad \ldots(6.20)$$

$$2[Au(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Au \downarrow \quad \ldots(6.21)$$

In the leaching process of Ag and Au, NaCN will first oxidise the metal, which are displaced by strong reductant Zn. This whole reaction takes place according to the principles of redox reactions. Since metal is precipitated in the aqueous solution of metal complex, this process is also called Hydrometallurgy and in the starting, cyanide complex is formed so this process is known as Cyanide process.

6.3.3 Extraction of impure metals from concentrated Ores–

By extraction of metals from concentrated ore, we obtain impure metals in free state. To get pure metal, the process is completed in two steps.

(a) To convert concentrated ore into metal oxide

(b) Reduction of metal oxide into impure metal.

(a) Conversion of concentrated ore into metal oxide : For this purpose, two methods are used-

(i) Calcination

(ii) Roasting

(i) Calcination– Calcination is a process in which the concentrated ore is heated strongly below melting point of the ore in the absence of air. It removes volatile impurities, like H_2O, CO_2, SO_2, etc. and thermally decompose hydrated oxides or hydroxides or carbonates from the ore. The remaining mass (metal oxide) becomes porous. This process is done in reverberatory furnace (Fig. 6.4). Some calcination reactions are as follows:-

$$\underset{\substack{\text{Limonite}\\ \text{(grey haematite)}}}{Fe_2O_3.3H_2O} \xrightarrow[\text{calcination}]{\Delta} Al_2O_3 + 2H_2O(g)$$

$$\underset{\text{bauxite}}{Al_2O_3.2H_2O} \xrightarrow[\text{calcination}]{\Delta} Al_2O_3 + 2H_2O(g)$$

$$\underset{\text{calamine}}{ZnCO_3} \xrightarrow[\text{calcination}]{\Delta} ZnO + CO_2(g)$$

$$\underset{\text{limestone}}{CaCO_3} \xrightarrow[\text{calcination}]{\Delta} CaO + CO_2(g)$$

$$\underset{\text{calamine}}{ZnCO_3} \xrightarrow[\text{calcination}]{\Delta} ZnO + CO_2(g)$$

$$\underset{\text{dolomite}}{CaCO_3.MgCO_3} \xrightarrow[\text{calcination}]{\Delta} CaO + MgO + 2CO_2(g)$$

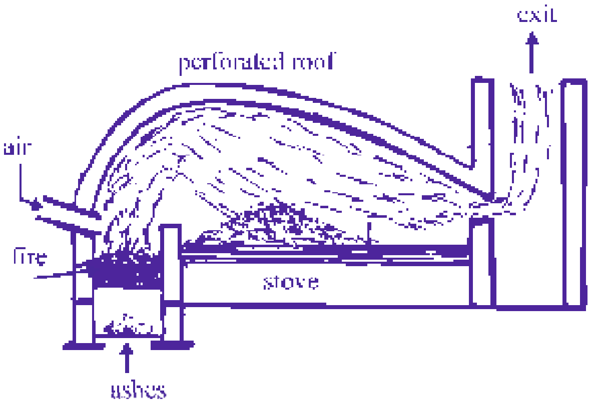

Fig. 6.4 : Reverberatory Furnace

(ii) Roasting– Roasting is a process in which the ore (usually sulphide ores) is heated at high temperature (below the m.p. of metal) in the presence of excess of air. This process is also done in reverberatory furnance. Following changes take place in the furnace -

(a) Impurity due to pohosphorous, sulphur, arsenic is expelled out as their volatile oxides.

$$P_4 + 5O_2 \xrightarrow{\Delta} 2P_2O_5(g)$$

$$S + O_2 \xrightarrow{\Delta} SO_2(g)$$

$$4As + 3O_2 \xrightarrow{\Delta} 2As_2O_3(g)$$

(b) Metal sulphide is converted to metal oxides.

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

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

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

In case of copper pyrite, some amount of silica is added by which iron silicate is separated as slag and remaining mixture is called **Copper Matte** (Cu_2S and FeS).

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

$$FeO + SiO_2 \longrightarrow \underset{\text{slag}}{FeSiO_3}$$

(c) Sometimes metal sulphides are converted to their sulphates.

$$PbS + 2O_2 \longrightarrow PbSO_4$$

$$ZnS + 2O_2 \longrightarrow ZnSO_4$$

(d) Some metal sulphides are converted to their chlorides also. Reaction of metal chloride with mercury gives amalgam.

$$Ag_2S + 2NaCl \longrightarrow 2AgCl + Na_2S$$

$$AgCl + 2Hg \longrightarrow Ag - Hg + HgCl$$

(e) In the process of roasting, organic impurities are self removed due to their combustion.

Difference between calcination and Roasting

S. No.	Calcination	Roasting
1.	It happens in the absence of air	It happens in the excess of air.
2.	In this, small molecules like H_2O, CO_2, SO_2 are expelled but no chemical change take place.	Here, chemical change takes place. During this process, oxidation, chlorination, etc. reactions are happened.

After calcination and roasting, the ore becomes porous which facilitates further reactions like reduction of metal oxides to metals.

In a reverberatory furnace (Fig. 6.4), the charge is placed on the hearth of the furnace. The roof of the furnace is concave in shape. Fuel is burn at other place in the furnace, not in direct contact with the ore. When fuel is burnt, hot flames are deflected from its roof and heat the ore. The air is controlled by the pores in the furnace. During calcination, pores are closed where as pores remain open during roasting. The furnace is used for roasting of the ores of tin, lead, copper, etc.

(f) Conversion of the oxides of metal to the metallic form–

After getting metal oxide ore by calcination/roasting, it is subjected to different reductive techniques to convert into impure metal. Some main methods are-

(a) reduction by carbon (coke) i.e. smelting

(b) reduction by aluminium (Alumino-Thermite process)

(c) auto reduction (by heating in air)

(d) electrolytic reduction (Electro-metallurgy).

After calcination/roasting, some unmelted or unfused impurities remain in the ore. These impurities are called gangue or matrix. Some substances are added to remove the gangue. These are called smelters or **flux.** The flux combines with impurities to form easily fusible product called **slag.**

$$\underset{\text{(gangue)}}{\text{Impurities}} + \underset{\text{(oxide)}}{\text{flux}} \longrightarrow \underset{\text{(slag)}}{\text{fusible product}}$$

Slag is not soluble in molten metal. It is lighter so it floats over the surface of molten metal and easily removed. Slag is generally in the form of fusible silicates or phosphates of metals. Therefore, the gangue is better removed in the form of slag as compared to direct removal from the roasted ore. Acidic impurities such as SiO_2, P_2O_5 are removed by basic flux and basic impurities such as CaO, FeO, $MgCO_3$ are removed by acidic flux. For example,

Acidic gangue (SiO_2, P_4O_{10})

Basic flux (CaO, MgO)

$$\underset{\text{gangue}}{SiO_2} + \underset{\text{flux}}{CaO} \longrightarrow \underset{\text{calcium silicate (slag)}}{CaSiO_3}$$

$$\underset{\text{gangue}}{P_4O_{10}} + \underset{\text{flux}}{6MgO} \longrightarrow \underset{\text{slag}}{2Mg_3(PO_4)_2}$$

basic gangue (CaO, MnO, MgO)

acidic flux (SiO_2)

$$\underset{\text{gangaue}}{CaO} + \underset{\text{flux}}{SiO_2} \longrightarrow \underset{\text{slag}}{CaSiO_3}$$

$$\underset{\text{gangue}}{MnO} + \underset{\text{flux}}{SiO_2} \longrightarrow \underset{\text{slag}}{MnSiO_3}$$

In other words,

$$\text{roasted ore} + \text{gangue} + \text{reductant} + \text{flux} \xrightarrow{\Delta} \text{impure metal} + \text{slag} + \text{gases.}$$

(a) Reduction by Carbon (coke)–

Smelting method : The oxides of less electropositive metals like Pb, Zn, Sn, Fe, Cu, etc. are reduced to metal by heating at high temperature with coke.

$$M_xO_y + yC \xrightarrow{\Delta} xM + yCO$$

$$ZnO + C \xrightarrow{\Delta} Zn + CO$$

$$PbO + C \xrightarrow{\Delta} Pb + CO$$

When roasted ore (metal oxides) is heated with coke at high temperature, the oxide is reduced to the metal.This process is known as Smelting. The smelting (reduction) of the oxides of iron, copper is done in Blast furnace.

$$Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO$$

$$Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$$

When metal oxide is heated intensely at high temperature with reductant to obtain metal is known as Pyrometallurgy.

(b) Reduction by aluminium (Alumino-Thermite process).

In this process, oxides like Cr_2O_3, Mn_3O_4, etc. are reduced by high electropositive metal like aluminium. Carbon and CO can not reduce these oxides easily.

$$Cr_2O_3 + 2Al \xrightarrow{\Delta/\text{thermal reduction}} 2Cr + Al_2O_3$$

This process is also known as Goldschmidt thermite process. It is pertinent to ask that why carbon reduces ZnO and Al reduces Cr_2O_3. Zinc is a good reductant even then,the reaction is not reversible. Why so ? The answer lies in the standard Gibb's free energy (ΔG^0) of the reaction.

(c) Self reduction (reduction due to heating in air)–

At high temperature, the oxides of less electropositive metals, Cu, Pb, Hg are unstable, therefore, there is no need of any other reductant. Therefore, this process is also called auto-reduction, or air reduction. For example, in Bessemer converter, the following reaction is called self-reduction.

$$2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2 \uparrow \text{(auto reduction)}$$

(d) Electrolytic Rediction (Electrometallurgy)–

In the fused melt state of oxides, hydroxides or chlorides of high electropositive metals like Na, K, Mg, Al, Ca, etc. are electrolysed and pure metal is obtained at Cathode. This is known as electrolytic reduction. This process is based on electrochemical principles. According to equation $\Delta G^o = -nFE^o$, if redox potential of the electrolytic cell is positive then value of ΔG^o becomes negative so that more active metals remain in solution and less active metal comes out of solution i.e. deposited on cathode.

For example–

$$\underset{\text{(molten state)}}{NaCl} \xrightarrow{\text{electrolysis}} \overset{+}{Na} + \overset{-}{Cl}$$

$$\text{at cathode } Na^+ + e^- \longrightarrow Na$$

$$\text{at anode } Cl^- \longrightarrow \tfrac{1}{2}Cl_2 + e^-$$

Details of electrolytic reduction of alumina is given ahead.

Thermodynamic principle of metallurgy–

For any process at standard temperature and pressure, the Gibb's Helmholtz equation is–

$$\boxed{\Delta G^o = \Delta H^o - T\Delta S^o}$$

(standard temperature is 298K and standard pressure is 1 atmosphere)

ΔH^o = standard Enthalpy change

ΔS^o = standard Entropy change

ΔG^o = standard Gibb's free energy change

According to thermodynamics, for any chemical change or reaction, to take place spontaneously, ΔG^o should be negative., It means, there should be a decrease in the free energy. Reaction change is also expresssed as-

$$\boxed{\Delta G^o = -RT \ln K}$$

Where, for any process at T temperature, K is the equilibrium constant and R is the gas constant. When reaction takes place in forward direction the value of K is positive and value of ΔG^o is negative.

Ellingham Diagram for the Choice of Reducing Agent–

The change in standard free energy ΔG^o for the formation of oxides of elements was first studied and diagramatically expressed by H.J.T. Ellingham. In the formation of oxides by consumption of one mole of oxygen (O_2), the free energy change $\Delta G^o = -RT \ln K$ were calculated. On the basis of these values of ΔG^o, graph between (ΔG^o) and temperature (T) was plotted, which is known as Ellingham diagram (Fig. 6.5). For example,

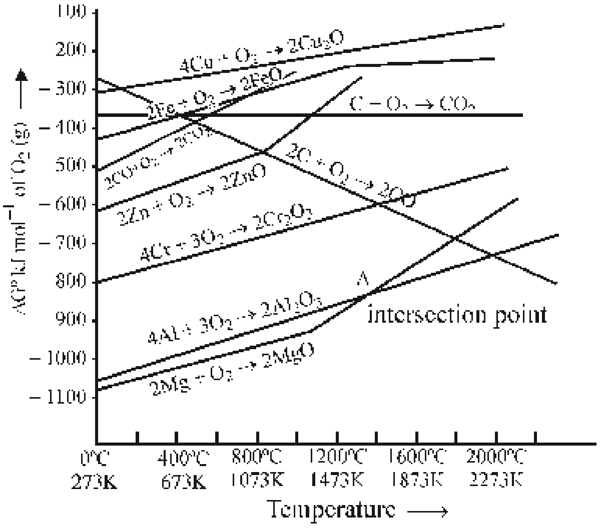

Fig. 6.5: Ellingham diagram for formation of oxides

$$2xM(s) + O_2(g) \longrightarrow 2M_xO(s)$$

For this reaction, on increasing temperature, ΔH^o values do not change much. Also, in above reaction, due to solid states, entropy decreases, it means that ΔS^o is negative for metal oxides. Therefore, with increase in temperature, value of $T\Delta S^o$ becomes positive and because of this, ΔG^o increases and the slope of the lines in Ellingham diagram is positive for the oxide formation $M_xO(s)$ reactions.

General Conclusions of Ellingham diagram (ΔG^o v/s T plots)–

(1) According to the equation, $\Delta G^o = -RT \ln K$, if the value of ΔG^o is negative, then reaction take place in forward direction. For any system (solid → liquid → gas) if there is a change in phase and disorder increase, then ΔS^o will be positive. In this situation, at high temperature, $T\Delta S^o$ value will increase i.e., ($\Delta H^o < T\Delta S^o$), which gives negative value of ΔG^o (a favourable condition for the forward reaction).

(2) If two reactions are taking place simultaneously in a system, then negative value of the resultant ΔG^o will indicate that the whole reaction will take place in forward direction.

(3) ΔG^o values are dependent upon the temperature (T) of the metal oxide formation reaction. Therefore, the Ellingham diagram gives that temperature at which the reduction of metal oxide by carbon or carbon monoxide become self reduced.

(4) Any metal will reduce the oxide of other metal which is above in Ellingham diagram.

Description of Ellingham diagram for the possibility of thermal decomposition of any ore :

(1) Ellingham diagram is useful in chosing a suitable reducing agent for reduction of metal oxides to metals.

(2) For the phase change like (solid → liquid → gas), entropy increases, so ΔS^o will be positive.

(3) For the phase change like (gas → liquid → solid), entropy decreases, so ΔS^o will be negative.

(4) Except phase change, in all other situations, Ellingham plot will be a straight line.

(5) In the plot, the point below which ΔG^o is negative shows stable metal oxide M_xO. Above this point, oxides are self-decomposed due to positive value of ΔG^o. It means that oxides with lower value of ΔG^o are more stable than oxides of higher ΔG^o value.

(6) $\Delta G^o = 0$ at the point of intersection of the plots, below this, ΔG^o is negative, and above this point of intersection, ΔG^o is positive. It means that at temperatures below the intersection point, the metal can reduce the metal oxide lying above the point of intersection.

(7) If ΔG^o is negative, i.e., if there is decrease in free energy, then that chemical change is thermodynamically possible and if ΔG^o is positive, then reaction will not take place thermodynamically.

(8) At melting point or at boiling point of metal oxides, there is sudden change in the slope of the plot for metal oxides. At this temperature, for the phase change (gas → liquid → solid), ΔS^o is more negative, so ΔG^o becomes positive.

$$\Delta G^o = \Delta H^o - [T(-\Delta S^o)]$$

$$\Delta G^o = \Delta H^o + T\Delta S^o$$

$$\Delta G^o = \text{positive (at high temperature)}^o$$

(9) At the reduction temperature, metal oxide (solid) is easily reduced to metal which is in liquid state, because ΔS^o is positive for the change from solid to liquid. (i.e. entropy increases) and this makes ΔG^o negative.

$$\Delta G^o = \Delta H^o - [T(+\Delta S^o)]$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\Delta G^o = \text{negative}$$

Limitations of Ellingham diagram :

(1) It explains only feasibility of the reaction on the basis of thermodynamics. It informs that at what temperature, metal oxide is reduced and with which reducing agent, reduction is feasible, but it does not give any information about the kinetics (velocity) of the reaction.

(2) ΔG° values are found at equilibrium between reactants and products, and according to equation $\Delta G^\circ = -RT \ln K$, value of ΔG° is based on the value of equilibrium constant K (and in the calculation of K, the active mass of solids is taken as unity means active mass of solid is not included in the calculation).

That's why this equation does not give correct value of ΔG°, when reactants or products are in solid states.

Explanation of Reduction of Haematite by Ellingham diagram–

According to Ellingham diagram (Fig. 6.6), we have-

(i) 1073K temperature represents point of intersection.

(ii) Below 1073K temperature, haematite is reduced by CO i.e.

$$\Delta G^\circ(Fe \rightarrow Fe_2O_3) > \Delta G^\circ(CO \rightarrow CO_2)$$

and reaction takes place in this way -

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\text{temp.} < 1073K} 2Fe(s) + 3CO_2(g)$$

(iii) Above 1073 K, reduction of haematite takes place by coke i.e. -

$$\Delta G^\circ(Fe \rightarrow Fe_2O_3) > \Delta G^\circ(C \rightarrow CO)$$

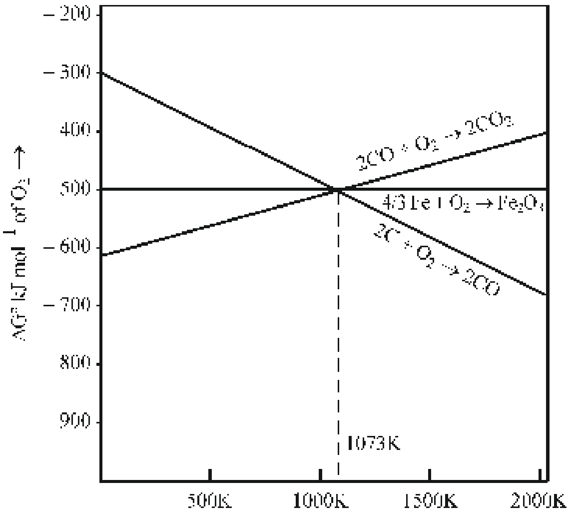

Fig. 6.6 : Ellingham diagram for the reduction of hematite by carbon or CO

and reaction is

$$\underset{\text{hematite}}{Fe_2O_3(s)} + \underset{\text{coke}}{C(s)} \xrightarrow{\text{temp.} > 1073K} 2Fe(s) + 3CO(g)$$

Reductive nature of Coke (carbon) and carbon monoxide–

If coke is taken as reducing agent, the reduction reaction is possible as follows.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad ....(i)$$

Equation (i) show that volume remain unchanged, so there is no change in entropy ($\Delta S^\circ \cong 0$), therefore ΔG° remain almost constant.

$$2C(s) + O_2(g) \longrightarrow 2CO(g) \qquad ....(ii)$$

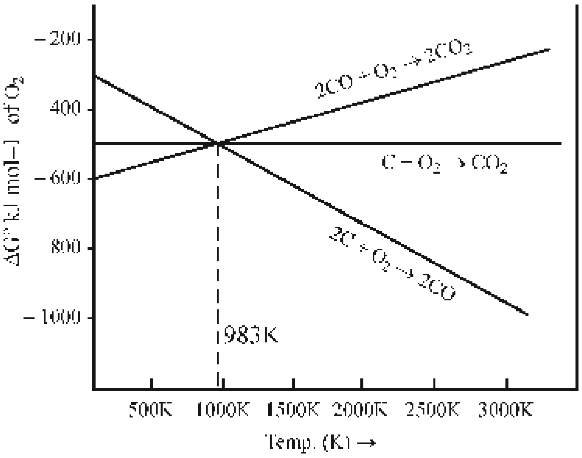

Fig. 6.7 : Ellingham diagrm for reductive nature of coke and CO

According to equation (ii) by the formation of CO, volume increases and ΔS° is positive and so ΔG° beocmes negative. Therefore, oxides is reduced by carbon.

$$2CO(g) + O_2(g) \longrightarrow CO_2(g) \qquad ....(iii)$$

According to equation (iii), in the formation of CO_2, volume is decreased, so ΔS° become negative (decrease in entropy) and ΔG° becomes prositive. Therefore, carbon acts as reducing agent by changing into carbon monoxide.

Example.

(i) $Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO$

$Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$

$FeO + CO \xrightarrow{\Delta} Fe + CO_2$

(ii) $CuO + CO \xrightarrow{\Delta} Cu + CO_2$

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

Application of extraction of Metal from Metal Oxide.

(a) Extraction of Iron from its oxide ore -

(1) **Ore-** Haematite - Fe_2O_3 (Main)

Limonite - 2 $Fe_2O_3.3H_2O$

Iron pyrite - FeS_2

(2) **Process-** After pulverisation of the haematite ore in Jaw Crusher, it is concentrated by magnetic separation method, by which gangue (non-magnetic nature) are separated.

If the ore contains moisture and carbonates, then first it is subjected to calcination process, then it is roasted in reverberatory furnace in excess of air (oxygen). By this, the impurities due to P,S, As are removed as their volatile oxides. During this process FeO is converted to Fe_2O_3.

$$4\,FeO + O_2 \longrightarrow 2\,Fe_2O_3$$

Smelting– The above roasted ore is reduced in Blast furnace. this is known as smelting - Blast furnace is made up of steel, in which there is lining of fire proof bricks. it is cylindrical and long. Its height is 30 meter and diameter is upto 6-8 meter. At the top of the furnace, cup-cone arrangement is there by which charge is poured but due to this arrangement no gas can come out. So there is another outway above the furnace by which the hot gases produced by the burning of coke and other gases are expelled. Hot air is passed is the furnace by pipes which are known as Tuyers. From top to down, the temperature of the furnace increases. Separate exit passages are there for slag and molten iron metal (raw iron/pig iron) towards the bottom of the furnace. (fig 6.8).

Calcined and roasted ore (8 part) + coke (4 part) + limestone (1 part) is known as **charge**.

Main reactions taking place in Blast furnace are -

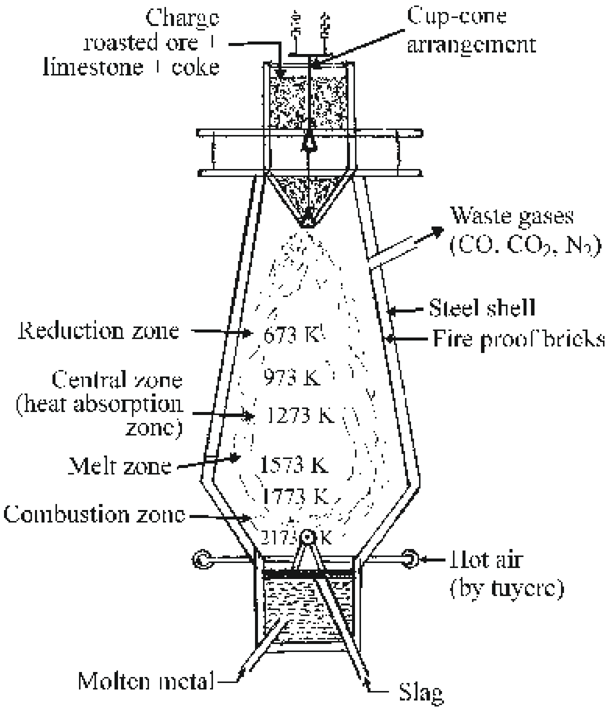

Fig. 6.8 : Blast furnace for smelting of roasted haematite

(i) **Reduction zone (approx 673K-973K) at 673K**

$$3Fe_2O_3 + CO \longrightarrow 2\,Fe_3O_4 + CO_2\uparrow$$

$$Fe_3O_4 + CO \longrightarrow 2\,FeO + CO_2\uparrow$$

$$Fe_2O_3 + CO \longrightarrow 2\,FeO + CO_2\uparrow$$

This iron is porous and solid so it is called spongy iron.

(ii) **Central Zone (heat absorption zone) :** (approx 1173k - 1473 k)

$$CaCO_3 \xrightarrow{1273\,K} CaO + CO_2\uparrow$$

$$FeO + CO \longrightarrow Fe + CO_2\uparrow$$

$$\underset{\text{flux}}{CaO} + \underset{\text{gangue}}{SiO_2} \xrightarrow{\text{temp.}>1073K} \underset{\text{slag}}{CaSiO_3}$$

(iii) **Fusion Zone-** (appox 1373K - 1573K) In this zone, spongy iron is melted and C,P,Si are absorbed.

$$CO_2 + \underset{\text{coke}}{C} \longrightarrow 2CO \quad \Delta H = +163\,kJ$$

(iv) **Combustion Zone-** (appox 1773 - 2173 K).

$$\underset{\text{coke}}{C} + \underset{\text{air}}{O_2} \longrightarrow 2CO_2 \quad \Delta H = -395.5\,kJ$$

$$FeO + C \longrightarrow Fe + CO$$

The slag, being lighter, floats on the surface of molten metal and so it is removed from time to time.

Cast Iron (Least pure form of iron)–

When hot molten iron is poured in moulds made by sand and then cooled, cast iron is obtained.

(i) If molten iron is fast cooled then carbon remains in the form of Fe_3C (cementite). This is called white cast iron.

(ii) If molten iron is cooled slowly, then most of the carbon separates out as gaphite. This is called grey cast iron which contains about 3% of carbon. It is very hard and brittle. It is non corrosive.

Wrought Iron– This is the purest form of iron. It cantaiss 0.2 to 0.5% of carbon and very small quantity of other impurities. Due to impurity, cast iron melts betwen 1423K–1523K whereas the wronght iron melts at 1823K.

Manufacturing Process – When cast iron with haematite is subjected to oxidation by hot air in reverberatory furnace, wrought iron is formed. In this process, impurity of carbon is escaped as CO and other impurties like P,S, Si are separated as their volatile oxides. Also, these impurities form slag with the added limestone as a flux. The slag is separated by roller.

$$\underset{\text{(Carbon impurity)}}{3C} + Fe_2O_3 \xrightarrow{\Delta} 2Fe + 3CO$$

$$6P + 5Fe_2O_3 \xrightarrow{\Delta} 10Fe + 3P_2O_5$$

$$P_2O_5 + Fe_2O_3 \longrightarrow \underset{\text{(slag)}}{2FePO_4}$$

(at the stage of formation of wrought iron, impurities are removed so it is in the semi-solid state. In this state it is taken out in the form of balls and hammered so the slag is squeezed out. That's why it is called wrought iron).

Steel– In this, carbon content is intermediate between that of wrought iron and cast iron i.e. in between 0.15 to 1.5%. In cast iron (2-3% carbon) and in wrougth iron (0.2 to 0.5%).

Extraction of Copper from its ore–

(1) **Ores-** Copper pyrite - $CuFeS_2$ (Main)

Cuprite or Ruby copper - Cu_2O

Copper glance - Cu_2S

Malachite - $Cu(OH)_2.CuCO_3$

(2) **Process-** Main ore of copper is copper pyrite which is a sulphide ore. The ore is first crushed in fine pieces by Jaw crusher or stamp mill and then it is concentrated by Froth - Flotation method by which gangue is separated out.

Roasting- The concentrated ore is heated in reverberatory furnnace in excess of air with small amount of silica. During this process, H_2O and other volatile impurities are removed as their oxides. Following chemical reactions tak place in the furnace -

$$2CuFeS_2 + 2O_2 \longrightarrow Cu_2S + 2FeS + 2SO_2$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$\underset{\text{gangue}}{FeO} + \underset{\text{flux}}{SiO_2} \longrightarrow \underset{\text{slag}}{FeSiO_3}$$

$$\text{and } Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

The obtained mixture of **Cu_2S and FeS is called copper matte.**

Bessemerisation–

In this process, copper oxide and copper sulphides are self reduced. This is done in Bessemer coverter (Fig. 6.9), which is pear-shaped furnace made by steel. In this there is lining of acidic SiO_2 or basic MgO which acts as flux. The nature of flux depends on the nature of gangue in matte.

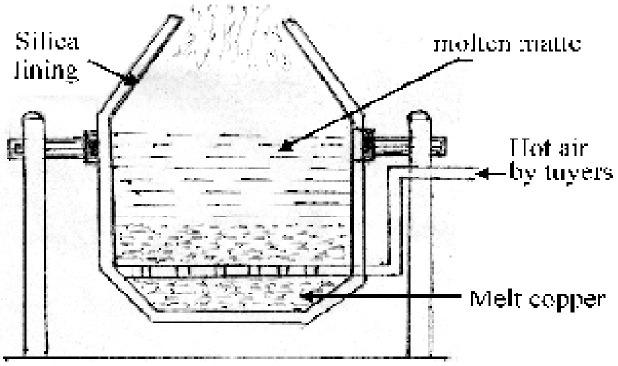

Fig. 6.9 : Bessemer converter

In the process of Bessemerisation, molten copper matte is introduced in Bassemer conveter in horizontal position. Then, blast of hot air with sand is blown through holes at the base of furnace (tuyers). The hot air is blown through the molten mass. The following reactions with air and silica take place in the Bessemer converter.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$\underset{\text{gangue}}{FeO} + \underset{\text{flux}}{SiO_2} \longrightarrow \underset{\text{slag (fusible)}}{FeSiO_3}$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$Cu_2S + 2Cu_2O \longrightarrow \underset{\substack{\text{blistered}\\ \text{copper}}}{6Cu} + SO_2 \uparrow \text{(self - reduction)}$$

The molten copper so obtained is cast into moulds of sand. It is almost pure copper. When molten copper is cooled, the dissolved SO_2 comes out in the form of bubbles which causes the appearance of blisters on the surface of molten metal. This is called blistered copper.

Extraction of Zine from Zinc oxide -

Ores - Zinc blend, ZnS (main)

- Calamine or Zinc spar - $ZnCO_3$
- Zincite - ZnO

Extraction by Readuction process :

(i) Concentration of the ore- the ore (Zinc blend) is crushed to fine poweder and concentrated by Froth - flotation process. If the ore is calamine, then magnetic separation method is used. If in the ore, iron oxide is present then magnetic separation method can be used later on.

(ii) Roasting– The concentrated ore is heated in excess of air at about 1200 K in reverberatory furnace.

The following reactions take place.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

$$ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$$

Again decomposes -

$$2ZnSO_4 \xrightarrow{1200\ K} 2ZnO + 2SO_2 + O_2$$

If ore is calamine, then roasting is not necessary, but by simply heating gives oxide. The reaction is -

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

(iii) Reduction by coke (carbon)

The roasted ore is mixed with coke and heated at 1673K in fire clay retort by which reduction of ZnO into Zn takes place.

$$ZnO + \underset{\text{coke}}{C} \xrightarrow{1673\ K} Zn + CO$$

$$ZnO + CO \longrightarrow Zn + CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

The molten metal obtained by above method contains about 97.8% of Zinc in which very small impurities of Pb, As are present. This is called impure "Zinc spelter" which is further purified by distillation method.

Electrochemical Principle of Metallurgy– According to the principle of thermodynamics, the pyrometallurgy (metallurgy at high temperature) is useful for reduction of metal oxids of less active metals but for more active metals like, Al, Mg, Na, etc. heating methods for reduction are not useful because these metals are itself strong reducing agents. Their standard reduction potential (E^o) value are high negative, therefor, for these active metals, reduction is done by electro lysis of molten salt of these metals. This can be explained by Gibb's free energy equation-

$$\Delta G^o = -nFE^o$$

Where, n = bumber of electrons transferred during reduction.

E^0= standard redox potential

F = magnitude of charge passed (1F (Farday)

= 96500 coulombs, approx)

For these more active metals, E^0 values are high negative so corresponding ΔG^o values are positive. Therefore, to separate these metals, electrolytic reduction of impure molten metal solution is done. The active metal present in solution is reduced and deposited at cathode (-ve electrode).

$$M^{n+}_{(aq)} + ne^{-} \longrightarrow M(s) \text{ (at cathode)}$$

This process is known as Electrometallurgy. In this process, on the basis of the reactivity of the obtained metals, the electrodes of these metals are used, such that electrode potential of the redox couple (E^o) become positive and thereby ΔG^o become negative. Due to this, more active metal remains in solution and less active metal comes out of solution. For example,

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

In this process, to make molten substance more conductive, suitable flux is also added.

Extraction of Aluminium from Electrolysis of fused Alumina (Al_2O_3)–

Melting point of pure alumina is 2323K which is very high and in molten state it can not be electrolysed due to its non-conducting nature. To make alumina electrically conducting, cryolite (Na_3AlF_6) and Fluorspar (CaF_2) are mixed to molten alumina (Al_2O_3). The ratio of Al_2O_3, Na_3AlF_6 and CaF_2 is 20%, 60% and 20%, respectively. The meltng point of this mixture comes down to 1173K and sufficient increase in conductivity is obtained so that alumina becomes conductor.

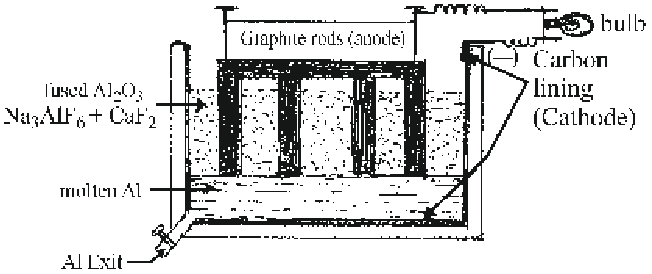

Fig. 6.10 : Electrolysis of fused alumina by Hall-Heroult process

In the Hall-Heroult process, electrolytic cell is the tank made by steel (Fig. 6.10) in which the above molten mixture is taken. On this mixture, a layer of coke (carbon) powder is deposited. This protect it to cool i.e. heat loss is stopped and carbon (graphite) anode corrosion decreases and aluminium is collected at cathode.

There is carbon lining on the inside surface of the steel tank, which itself acts as cathode. Graphite rods are suspended in the cell which acts as anode. In parallel series an electric bulb is connected which is lightened on decrease in alumina, due to increase in resistance. At this situation, alumina is added to the cell such that electrolysis remain continue.

Following two concepts are there for the electrolytic reaction -

(1) First concept, which is more popular, propounds that first alumina is ionised.

$$\text{at cathod} \left\{ \begin{array}{l} \underset{\text{(fused)}}{Al_2O_3} \xrightarrow{\text{electrolysis}} 2Al^{3+} + 3O^{2-} \\ Al^{3+} 3e^{-} \longrightarrow Al\ (1) \end{array} \right\}$$

$$\text{at anode} \left\{ \begin{array}{l} O^{2-} \longrightarrow O + 2e^{-} \\ O + O \longrightarrow O_2 \\ 4C + 3O_2 \longrightarrow 2CO + 2CO_2 \end{array} \right\}$$

$$\text{or} \quad \boxed{\begin{array}{c} 2C + O_2 \longrightarrow 2CO \\ 2CO + O_2 \longrightarrow 2CO_2 \end{array}}$$

Therefore, by these above reactions, graphite rods (anode) are corroded so they are replaced from time to time. For production of one kilogram of aluminium, 0.5 kg carbon of anode (graphite) is burnt.

(2) According to second concept, on passing electric current in cell, first cryolite is ionised -

$$\underset{\text{(molten cryolite)}}{Na_3AlF_6} \overset{\text{electrolysis}}{\rightleftharpoons} 3NaF + Al\ F_3$$

$$AlF_3 \overset{\text{electrolysis}}{\rightleftharpoons} Al^{3+} + 3F^{-}$$

$$\text{at cathod } \underset{\text{(metl)}}{Al^{3+}} + 3e^{-} \longrightarrow Al\ (1)$$

$$\text{at anode } F^{-} \longrightarrow F + e^{-}$$

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

At anode, Al_2O_3 is converted to AlF_3 which again ionises such that electrolytic process continue. Complete reaction can be written as -

$$2Al_2O_3 + 3\ C \longrightarrow 4\ Al + 2CO_2$$

By the above process, the aluminium in molten state is obtained at the bottom of the cell which is taken out by tap. Aluminium so obtained is 99.5% pure. The whole process is called Electrometallurgy.

Extraction of Copper from low grade copper (Hydrometallurgy) –

In this process, impure ore is converted into soluble complex by suitable chemical reagent. Then, strong reducing metal is added to the solution (containing the soluble complex) for displacement of the metal present in the ore, getting the pure metal. In this process, leaching is done by acid and hydrogen gas is passed so it is called hydrometallurgy. For example, low grade ores of copper contain very small amount of copper. So, leaching is done by acid/bacteria by which copper ions come in solution. In this solution, iron filings are added or hydrogen gas is passed by which copper ions are reduced to copper metal.

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

or $$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

We know from electrochemical series that zinc is more reactive than iron, so reduction by zinc takes place fast but cost of zinc is more than iron so instead of scrap zinc, scrap iron filings are used.

Extraction of elements by oxidation-reduction Method–

In this method, extraction of non-metallic elements is done. For example, chlorine is extracted from sea water or concentrated aqueous solution of NaCl which is also called 'brine' by electrolysis. Electrolysis reactions are as follows -

$$\underset{\text{brine}}{NaCl\,(aq)} \xrightleftharpoons{\text{electrolysis}} Na^- + Cl^-$$

$$H_2O \xrightleftharpoons{\text{electrolysis}} H^+ - OH^-$$

$$\underset{\text{(reduction)}}{\text{at cathode}} \quad H^+ + e \longrightarrow \tfrac{1}{2}H_2 \quad \left[\begin{array}{c}\text{potential of } H^+\\ \text{is more than the}\\ \text{potential of } Na^+\end{array}\right]$$

$$\underset{\text{(oxidation)}}{\text{at anode}} \quad Cl_{(aq)} \longrightarrow \tfrac{1}{2}Cl_2 + e^-$$

At anode, although the potential of water (E°) is less than the potential of Cl^-(aq.) and should get preference but due to over voltage of oxygen, first Cl^- is oxidised at anode. Complete reaction is -

$$2Cl^-(aq) + H_2O\,(l) \longrightarrow 2OH^-(aq) + H_2\,(g) + Cl_2\,(g),\ \Delta G^o = +422\text{ kJ}$$

According to the formula $\Delta G^o = -nFE^o$, the value of E^o for this reaction is obtained as 2.2 Volt. Therefore, for this electrolytic reaction, external e.m.f. (electromotive force) should be greater than 2.2 Volt. If other interfering factors are present, then additional e.m.f. will be needed.

If molten NaCl is taken as electrolyte instead of brine (NaCl), then Na metal is obtained at cathode and NaOH does not form because water is not present here.

$$\underset{\text{(fused)}}{NaCl} \xrightleftharpoons{\text{electrolysis}} Na^- + Cl^-$$

$$\underset{\text{(reduction)}}{\text{at cathode}} \quad Na^+ + e^- \longrightarrow Na$$

$$\underset{\text{(oxidation)}}{\text{at anode}} \quad Cl^- \longrightarrow \tfrac{1}{2}Cl_2 + e$$

In the same way, when leaching of the ores of silver and gold is done by NaCN to extract these metals, then it is also an oxidation reaction. After this, the silver (or gold) is displaced by zinc, which is a reduction. All these reactions are given earlier.

Purification or Refining of the Metal–

Metals obtained by various extraction methods are impure which is called crude metal. Following impurities are present in it which are to be removed.

(1) Un reduced metal oxide

(2) Slag and flux

(3) Other unwanted metals

(4) Non-metals like C, Si, P, As, etc.

On the basis of the nature of impurities, following methods are used for purification -

(a) Distillation

(b) Liquation

(c) Poling

(d) Electrorefining

(e) Zone refining

(f) Vapour phase refining

(i) Mond's process

(ii) van Arkel Method

(g) Chromatography

(a) Distillation : This method is used for purification of low boiling point metals in which non-volatile impurities are present. For example, zinc, mercury, etc. are purified by first they are vapourised and then condensed to get pure metal.

(b) Liquation : Low melting point metals like tin, lead, etc. are purified by this method. In this, the impure metal is placed on the sloping hearth of reverberatory furnace and heated gently in the inert atmosphere of carbon monoxide.The low m.p. metal melts and drains away, which is collected in vessel. Infusible impurities remain on the hearth.

(c) Poling : This method is used to remove impurity of copper oxide present in copper metal.In this method after taking impure molten metal in a vessel, it is stirred by green poles of wood. During this, gases which come out from green wood reduce the metal oxide. Other impurities (hydrocarbons like methane) are separated in the form of gas as SO_2, Al_2O_3 or in the form of scum (layer).

(d) Electrorefining : It is a cell device in wich thick plate of impure metal is taken as anode and thin plate of pure metal is taken as cathode. Acidified salt solution of the same metal is used as an electrolyte. On electrolysis, oxidation takes place at anode by which metal ions comes out (from anode) into solution which moves towards cathode and they accept electron and precipitated at cathode. Copper, zinc are purified by this method. For example, electrolytic purification of Copper-

Anode - thick plate of impure copper

Cathode - thin plate of pure copper

Electrolyte - Acidified solution of $CuSO_4$ (dil.$H_2SO_4 + CuSO_4$)

at anode (oxidation) $\underset{\text{(impure copper)}}{Cu(s)} \longrightarrow Cu^{2+} + 2e^-$

at Cathode (reduction) $Cu^{2+}(aq) + 2e^- \longrightarrow \underset{\text{pure copper}}{Cu(s)}$

Impurities due to less reactive metals like Ag, Au, Pt, Se, Te, etc. are settle down under the anode which is called "anode mud". Impurities of more electro-positive metals like iron, nickel, zinc, cobalt, etc. pass into solution in the form of their soluble sulphates. Copper refined by this process is 99.99% pure. The cost of the purification process comes down by recovery of these precious metals.

(e) Zone refining : This method is used to obtain very pure silicon (Si) and germanium (Ge) which are used as semiconductors. This method is based on the principle that on cooling the impure molten metal, only pure metal is crystallised. Impurities in molten state remain in the zone (i.e. impurities are more soluble in the melt than in the solid state of the metal).

In this process, the thin rod of impure metal is heated (in inert atmosphere) in circular mobile heater. Metal is melted in heater zone, when heater moves forward, impurities also move forward alongwith molten part. In this way, impurities goes to other end of the rod and pure metal crystallized out of the melt. The process is repeated several times to obtain pure metal (Fig. 6.11).

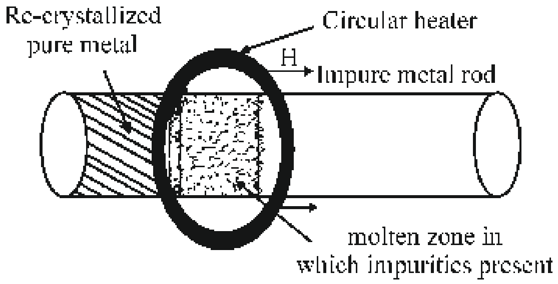

Fig. 6.11 : Zone refining (Pump Ge cash for Si)

(f) Vapour phase refining : This is a chemical process, in which metal is converted into its volatile compounds (and collected). After this, these compound are decomposed to give pure metal.

(i) Mond Process for refining Nickel- In this process, impure nickel metal is heated at 330-350K with carbon monoxide by which first nickel tetracarbonyl complex is formed. This is further heated at higher temperature (450-470K) so due to this, it decomposes and pure nickel is obtained.

$$\underset{\text{(impure nickel)}}{\text{Ni}} + 4\text{CO} \xrightarrow{330\text{–}350\text{ K}} [\text{Ni(CO)}_4]$$

$$[\text{Ni(CO)}_4] \xrightarrow{450\text{–}470\text{ K}} \underset{\text{(pure nickel)}}{\text{Ni}} + 4\text{CO}$$

(ii) van Arkel Method: This is also a chemical method in which zirconium, titanium, or bismuth, etc. metals are obtained in very pure form. In this method, the impure element is heated with iodine in vacuum. First, at low temperature, volatile iodide of these metal form which are unstable (TiI_4, ZrI_4, etc). These gaseous iodides are decomposed by passing them over an electrically heated (at 1700-1800K) filament of tungsten. The pure metal is deposited on the filament and the iodine is recycled.

$$\underset{\text{(impure)}}{\text{Zr}} + 2\text{I}_2 \xrightarrow{870\text{K}} \text{ZrI}_4$$

$$\text{ZrI}_4 \xrightarrow[\text{tangesten filament}]{1800\text{K}} \underset{\text{(pure)}}{\text{Zr}} + 2\text{I}_2$$

In the same way,

$$\underset{\text{(impure)}}{\text{Ti}} + 2\text{I}_2 \xrightarrow{500\text{ K}} \text{TiI}_4$$

$$\text{TiI}_4 \xrightarrow{1700\text{ K tungsten filament}} \underset{\text{pure}}{\text{Ti}} + 2\text{I}_2$$

(g) Chromatography : Chromatographic method is used for identification, purification and separation of those elements (in a mixture or compounds) which occur in very small amount in nature. This is an adsorption technique in which distribution between two phases of the mixture take place. In this, one phase is stationary and other phase is mobile. Mobile phase is either a liquid or a gas, whereas solid column of adsorbent is used as stationary phase. Sometimes, chromatographic paper is used as stationary phase. This method is based on the principle that different components of a mixture are differently adsorbed on the adsorbent depending upon the nature, physical state, etc. of the stationary and mobile phases.

(i) Adsorption Chromatography

(ii) Partition Chromatography

(iii) Ion-Exchange Chro matography

In adsorption chromatography, paper chromatography is used for column and distribution purpose. Details are given in the book of Class XI.

Column Chromatography : This method is useful for purification of elements which occur in very small amount in nature and there is very small difference between properties of impurities and the element. This is an effective technique used to identify and purify micro components of a mixture.

Method : In this method, a cylindrical glass column (burette may be taken) is taken with a tap at the bottom. The column is filled with a paste of an adsorbent in suitable liquid. Adsorbent should be such that it is insoluble in liquid and do not react chemically with the components (of mixture) which are to be separated. In general, alumina, silica gel, calcium carbonate, starch, cellulose, etc. are taken as adsorbent. The mixture is dissolved in a suitable solvent and this solution is slowly poured at the top of the column. On the basis of different adsorptive capacity of the components, they are adsorbed at different hights of the column. This process is called leaching (Fig. 6.12).

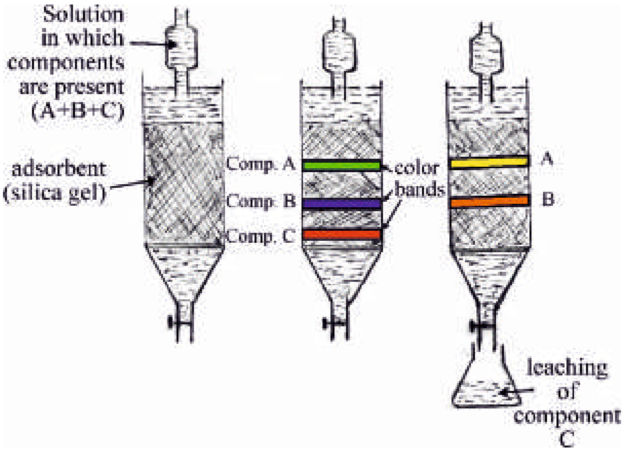

Fig. 6.12 : Adsorption chromatography (practical method)

The component which is highly adsorbed will remain nearer to upper end of the column and that which is least adsorbed will come down the column and remain at the lowest end of the column. In this way, diferent components of mixture are separated in the form of different bands on the adsorbent column. These bands are identified by colour or U.V. light These bands are cut separately and taken out. Each band is dissolved in suitable solvent to extract the component.This solution is concentrated and crystallised to obtain pure component.

Applications (uses) of Aluminium, Copper, Zinc and Iron :

(A) Uses of Aluminium

(i) as reducing agent in welding work

(ii) as rappers of chochlates and cigarettes

(iii) as electrical wires, coils of electric motor and dynamo

(iv) in the extraction of chromium and manganese

(v) aluminium powder is used in paints, for example– to develop shining in bulbs used for photography.

(B) Uses of Copper :

(i) It is a conductor of electricity so used in electric cables, copper plates, calorimeter, equipments, etc.

(ii) as hardner in ornaments of gold and silver

(iii) as fungicides (e.g. $CuSO_4$)

(C) Uses of Zinc :

(i) in batteries

(ii) in extraction of gold and silver (cyanide process)

(iii) in galvanization iron (to protect iron from corrosion)

(iv) in formation of alloys

(v) Zinc powder as reductant

(D) Uses of Iron :

(i) Cast iron : sleeper coach in railways, gutter pipes, toys, stove, etc. are made by cast iron.

(ii) Wrought iron - Wires, chains, anchor, bolts, nails, agriculture equipments, in building construction materials, etc.

S.No.	Name	Composition	Uses
1.	Stainless Steel	(73% Fe + 18%Cr +8%Ni + C)	in making of utensils, cycle, blade, cutlery, parts of automobiles,
2.	Nickel Steel	(97% Fe + 2.5% Ni + 0.5%C)	in making of parts of aeroplane, gears, wires, drilling machines.
3.	Invar	(64%Fe + 36% Ni)	in making pendulum rods, watches, meter scales, etc.
4.	Tungsten Steel	(94%Fe + 5% W + C)	in making high speed cutting tools (at high pressure)
5.	Magnanese Steel	(86%Fe + 13% Mn + C)	in making rock drills, strong treasury, rail way lines, etc.
6.	Chrome Steel	(98%Fe + 2% Cr)	in making ball bearings, axels, cutting tools such as files.

EXERCISE QUESTIONS

Multiple choice questions

(1) The impurities in the ore are collectively called -
(a) matte (b) slag
(c) flux (d) gangue

(2) Process of extracting metal from its ore is termed as -
(a) leaching (b) Concentration
(c) metallurgy (d) refining

(3) The natural material from which an element can be extracted economically is called -
(a) gangue (b) mineral
(c) ore (d) slag

(4) Bauxite is the ore of -
(a) Ba (b) Al
(c) Zn (d) Cu

(5) An example of halide ore is -
(a) Cryolite (b) bauxite
(c) galena (d) cinnabar

(6) For which ore of the metal, froth flotation method is used.
(a) Bauxite (b) Haematite
(c) galena (d) none of the above

(7) In smelting an extra substace is added which combines with impurities to form fusible product is termed as -
(a) slag (b) flux
(c) gangue (d) mud

(8) To separate ZnS and PbS, which depressant is used in froth - flotation process -
(a) $AgNO_3$ (b) NaCN
(c) H_2O (d) NaCl

(9) If the ore cantains magnetic impurities, then which method is used to separate them -
(a) Calcination (b) Magnetic separation
(c) Roasting. (d) Gravity separation

(10) Heating of an ore in the absence of air below its melting point is called.
(a) Smelting (b) leaching
(c) Roasting (d) Calcination

Short answer Questions

11. Write the name and chemical fourmula of oxide ore of aluminum and iron.
12. What is slag. Give example.
13. Write the name and chemical formula of sulphide and oxide ores of copper.
14. Give the names of two metals which occur in nature as free metals.
15. Name the metal which is most abundant in earth crust.
16. Write the name and chemical formula of the sulphide and oxide ores of zinc.
17. What is the diiference between mineral and ore. Explain with examples.
18. What is % of Carbon is cast iron and wrought iron.
19. Write composition of German silver.
20. What is anode mud.
21. What is calcination.
22. Which two parameters are plotted in Ellingham diagram.
23. What is leaching. Give example.
24. Give one example of acidic and basic flux.
25. Write the name of two impurities present in bauxite.
26. What is gangue and flux.

Very short answer question

27. What is Ruby and sapphire (Neelam).
28. Which metal is used as anode and cathode in Electrorefining.
29. Froth floatation process is used for which type of ores.
30. Which is the purest form of iron.
31. Which method is used to separate ZnS and PbS ores.
32. What is main chemical composition of Haematite.
33. What's main composition of Zinc blend.
34. Which method is widely used for refining of copper.

35. What is thermite?

36. Give name of furnace used for calcination?

37. What is cryolite.

Descriptive questions

38. Describe the Froth - Flotation process.

39. Explain the thermodynamic principle for interpretation of Ellinghan diagram using haematite ore.

40. Give details (with examples) of the calcination and Roasting. Also mention the difference between them.

41. In the metallurgy of aluminium, write the uses of following.
    - (a) Cryolite
    - (b) Coke
    - (c) Graphite rods

42. Write short notes an -
    - (a) Pyrometallurgy
    - (b) Electrometallurgy
    - (c) Hydrometallurgy.

43. Describe Hall method of obtaining alumina from bauxite and give all chemical reactions.

44. Draw diagram of Bessemer converter and why there is lining of silica for reduction of copper oxide.

45. Write the reactions taking place in reverberatory furnace in the case of copper ore. Sketch the diagram.

46. Write short notes on the following-
    - (a) gangue
    - (b) flux
    - (c) slag

47. Give details of the following methods for refining of metals.
    - (a) Poling
    - (b) Zone refining
    - (c) Electrolytic refining.

48. In the formation of Cr_2O_3, $\Delta G^0 = -540 kJ\ mol^{-1}$. and for formation of Al_2O_3, $\Delta G^0 = -827\ kJmol^{-1}$, will it be possible that Cr_2O_3 is reduced by Al. Give reasons.

49. Complete the folloiwng reactions -
    - (i) $2Cu_2O + Cu_2S \longrightarrow$ .... + ...
    - (ii) $Ag_2S + NaCN \longrightarrow$ .... + ...
    - (iii) $Al_2O_3 + NaOH \longrightarrow$ .... + ...
    - (iv) $CuFeS_2 + O_2 \longrightarrow$ .... + ...+ SO_2
    - (v) Cu_2S + ... $\longrightarrow Cu + SO_2$

Answers of multiple choice questions

1. (d), 2. (c), 3. (c), 4. (b),
5. (a), 6. (c), 7. (a), 8. (b),
9. (b), 10. (d).

❑❑❑