



**Section: Senior**

**Metallurgy**

**Date: 22-10-2014**

**Name of the student::**

**I.D.No:**

**Sec:**

The compound of a metal found in nature is called a mineral. A mineral may be a single compound or a complex mixture. Those minerals from which metal can be economically extracted are called ores. Thus all ores are minerals but all minerals are not ores.

**Ores may be divided into four groups:**

**(a) Native ores:**

Which contain the metal in free state and are found in the association of rock or alluvial impurities like clay, sand etc. Silver, gold, platinum etc, occur as native ores. Sometimes lumps of almost pure metals are also found. These are called nuggets.

**(b) Oxidised ores :**

These ores consist of oxides or oxysalts (e.g. carbonates, phosphates, sulphates and silicates ) of metals .

Oxide ores: Haematite( $\text{Fe}_2\text{O}_3$ ), Bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ), Cassiterite or tin stone( $\text{SnO}_2$ ), cuprite( $\text{Cu}_2\text{O}$ ), zincite( $\text{ZnO}$ ) etc.

Carbonate ores: Lime stone( $\text{CaCO}_3$ ), Dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), Calamine ( $\text{ZnCO}_3$ ), siderite( $\text{FeCO}_3$ ), cerussite( $\text{PbCO}_3$ ), magnesite( $\text{MgCO}_3$ ) etc.

Sulphate ores : Epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), Anglesite ( $\text{PbSO}_4$ ) etc.

Phosphate ores : Hydroxy apatite [ $(3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2)$ ], Chlorapatite [ $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$ ] etc.

Silicate ores: Asbestos ( $\text{CaSiO}_3$ ,  $3\text{MgSiO}_3$ ), Talc [ $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$ ], Albite ( $\text{Na}_3\text{AlSi}_3\text{O}_8$ ), feldspar( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ) beryl( $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) etc .

**(c) Sulphurised ores:**

Examples : Iron pyrites( $\text{FeS}_2$ ), Galena( $\text{PbS}$ ), Zinc blende ( $\text{ZnS}$ ), Cinnabar ( $\text{HgS}$ ), Copper glance( $\text{Cu}_2\text{S}$ ), chalco pyrite( $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ ).

**(d) Halide ores :**

Example : Horn silver ( $\text{AgCl}$ ), Carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), Fluorspar ( $\text{CaF}_2$ ), sylvine( $\text{KCl}$ ), Cryolite( $3\text{NaF} \cdot \text{AlF}_3$ ) etc.

### Some Important ores of metals

Metal	Ores	Composition
Aluminium	Bauxite	$\text{AlO}_x(\text{OH})_{3-2x}$ [where $0 < X < 1$ ] $\text{Al}_2\text{O}_3$
	Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	Corundum	$\text{Al}_2\text{O}_3$
	Kaolinite (a form of clay)	$[\text{Al}_2(\text{OH})_4 \text{Si}_2\text{O}_5]$
Iron	Haematite	$\text{Fe}_2\text{O}_3$
	Magnetite	$\text{Fe}_3\text{O}_4$
	Siderite	$\text{FeCO}_3$
	Iron pyrites	$\text{FeS}_2$
Copper	Limonite	$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
	Copper pyrites	$\text{CuFeS}_2$
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Cuprite	$\text{Cu}_2\text{O}$
Copper	Copper glance	$\text{Cu}_2\text{S}$
	Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Zinc blende or Sphalerite	$\text{ZnS}$
	Calamine	$\text{ZnCO}_3$
Lead	Zincite	$\text{ZnO}$
	Galena	$\text{PbS}$
	Anglesite	$\text{PbSO}_4$
Magnesium	Cerrusite	$\text{PbCO}_3$
	Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ( $\text{K}_2\text{MgCl}_4 \cdot 6\text{H}_2\text{O}$ )
	Magnesite	$\text{MgCO}_3$
Magnesium	Dolomite	$\text{MgCO}_3 \text{ CaCO}_3$
	Epsom salt (Epsomite)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
	Langbeinite	$\text{K}_2\text{Mg}_2(\text{SO}_4)_3$
	Talc	$3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$
	Spinel	$\text{MgO} \cdot \text{Al}_2\text{O}_3$
	Cassiterite (Tin stone)	$\text{SnO}_2$
Silver	Silver glance (argentite)	$\text{Ag}_2\text{S}$
	Pyrargyrite (Ruby Silver)	$\text{Ag}_3\text{SbS}_3$
	Chlorargyrite (Horn silver)	$\text{AgCl}$
	Stefinite	$\text{Ag}_5\text{SbS}_4$
	Proustite	$\text{Ag}_3\text{AsS}_3$
	Rock salt	$\text{NaCl}$
Sodium	Chile slat petre	$\text{NaNO}_3$
	Mirabilite	$\text{Na}_2\text{CO}_3$
	Glanber's salt	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
	Cryolite	$\text{Na}_3\text{AlF}_6$
Potassium	Sylvine	$\text{KCl}$
	Felspar	$\text{KAISiO}_8$
	Salt peter	$\text{KNO}_3$

### General methods of extraction of metals :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

Various metallurgical operations may be divided into three classes :

- a) Hydrometallurgy
- b) Pyrometallurgy
- c) Electrometallurgy

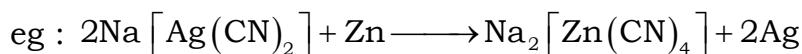
**a) Electrometallurgy :**

Highly electropositive metals (low SRP) are extracted by electrolytic reduction of their molten salts.

eg : Na, Mg , Al, K, Ca etc

**b) Hydrometallurgy :**

Extraction of metals from their aqueous solution by adding a more electropositive metal.



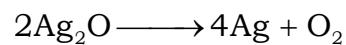
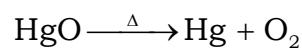
**c) Pyrometallurgy :**

Extraction of metal by heating its ore with (or) without a reducing agent.

The reducing agent may be coke, CO, more active metal, H<sub>2</sub> (or) Water gas

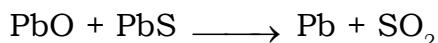
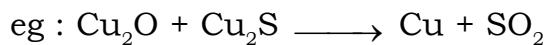
► Some metal oxides do not require any reducing agent

eg : HgO , Ag<sub>2</sub> O etc



This is due to high SRP values of metals.

► Oxides of copper, lead, Antimony, mercury etc undergo auto reduction when heated in presence of their sulphides



► Choice of a particular metallurgical process is made on the basis of SRP value of the metal which is to be extracted. This is shown in the following table.

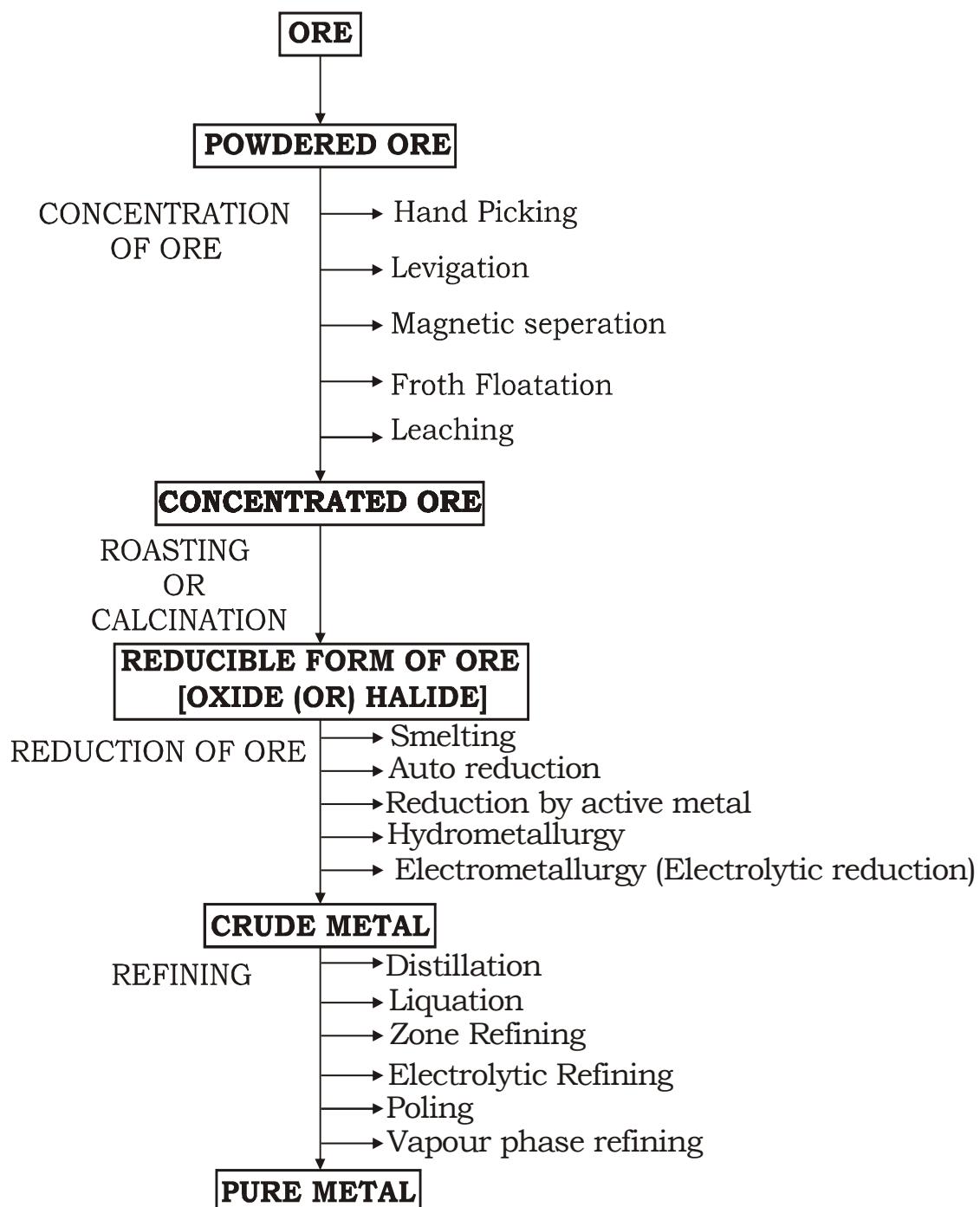
### Methods of Extraction of Metals : A Brief Review

<b>Electrode Process</b>	<b>Standard Electrode Potential/(V)</b>	<b>Main Occurrence</b>	<b>Main Method of Extraction</b>	<b>Equation for Extraction</b>
Li, Li <sup>+</sup>	-3.04	Spodumene LiAl(SiO <sub>3</sub> ) <sub>2</sub>	Electrolysis of fused LiCl with KCl added	
K, K <sup>+</sup>	-2.92	Carnallite KCl. MgCl <sub>2</sub> . 6H <sub>2</sub> O	Reduction of fused KCl with Na vapour	
Ba, Ba <sup>2+</sup>	-2.90	Witherite BaCO <sub>3</sub> , Barytes BaSO <sub>4</sub>	Electrolysis of fused BaCl <sub>2</sub>	
Sr, Sr <sup>2+</sup>	-2.89	Strontianite SrCO <sub>3</sub> , Celestine SrSO <sub>4</sub>	Electrolysis of fused SrCl <sub>2</sub>	
Ca, Ca <sup>2+</sup>	-2.87	Limestone CaCO <sub>3</sub> , Gypsum CaSO <sub>4</sub>	Electrolysis of fused CaCl <sub>2</sub> and CaF <sub>2</sub>	Most of these involve electrolytic reduction : $M^{n+} + ne^- \longrightarrow M$
Na, Na <sup>+</sup>	-2.71	Rock salt NaCl, Chile saltpeter NaNO <sub>3</sub>	Electrolysis of fused NaCl with CaCl <sub>2</sub> added	
Mg, Mg <sup>2+</sup>	-2.37	Carnallite KCl. MgCl <sub>2</sub> . 6H <sub>2</sub> O Magnesite MgCO <sub>3</sub>	Electrolysis of fused MgCl <sub>2</sub> with KCl added	
Be, Be <sup>2+</sup>	-1.70	Beryl 3 BeO. Al <sub>2</sub> O <sub>3</sub> . 6SiO <sub>2</sub>	Electrolysis of fused BeF <sub>2</sub> with NaF added	
Al, Al <sup>3+</sup>	-1.66	Bauxite Al <sub>2</sub> O <sub>3</sub> . 2H <sub>2</sub> O Silicate rocks	Electrolysis of Al <sub>2</sub> O <sub>3</sub> in molten Na <sub>3</sub> AlF <sub>6</sub>	
Mn, Mn <sup>2+</sup>	-1.18	Pyrolusite MnO <sub>2</sub> Hausmannite Mn <sub>3</sub> O <sub>4</sub>	Reduction of oxide with Al or C	3Mn <sub>3</sub> O <sub>4</sub> + 8Al $\longrightarrow$ 9M <sub>4</sub> + 4Al <sub>2</sub> O <sub>3</sub>
Ti, Ti <sup>4+</sup>	-0.95	Ilmenite TiO <sub>2</sub> . FeO Rutile TiO <sub>2</sub>	Reduction of TiCl <sub>4</sub> with Mg or Na	TiCl <sub>4</sub> + 2Mg $\longrightarrow$ Ti + 2MgCl <sub>2</sub>
Zn, Zn <sup>2-</sup>	-0.76	Zinc blende ZnS, Calamine ZnCO <sub>3</sub>	Reduction of ZnO with C or electrolysis of ZnSO <sub>4</sub>	ZnO + C $\longrightarrow$ Zn + CO
Cr, Cr <sup>2+</sup>	-0.74	Chromite FeO Cr <sub>2</sub> O <sub>3</sub>	Reduction of Cr <sub>2</sub> CO <sub>3</sub> with Al	Cr <sub>2</sub> O <sub>3</sub> + 2Al $\longrightarrow$ 2Cr + Al <sub>2</sub> O <sub>3</sub>
Fe, Fe <sup>2+</sup>	-0.44	Magnetite Fe <sub>3</sub> O <sub>4</sub> Haematite Fe <sub>2</sub> O <sub>3</sub>	Reduction of oxides with Co	Fe <sub>2</sub> O <sub>3</sub> + 3CO $\longrightarrow$ 2Fe + 3CO <sub>2</sub>
Co, Co <sup>2+</sup>	-0.28	Smaltite Co <sub>3</sub> O <sub>4</sub>	Reduction of Co <sub>3</sub> O <sub>4</sub> with Al	3Co <sub>3</sub> O <sub>4</sub> + 8Al $\longrightarrow$ 9Co + 4Al <sub>2</sub> O <sub>3</sub>
Ni, Ni <sup>2+</sup>	-0.25	Millerite NiS	Reduction of Co <sub>3</sub> O <sub>4</sub> with CO	NiO + 5CO $\longrightarrow$ Ni(CO) <sub>4</sub> + CO <sub>2</sub> Ni(CO) <sub>4</sub> $\longrightarrow$ Ni + 4CO

Sn, Sn <sup>2+</sup>	-0.14	Cassiterite SnO <sub>2</sub>	Reduction of SnO <sub>2</sub> with C	SnO <sub>2</sub> 2C → Sn + 2CO
Pb, Pb <sup>2+</sup>	-0.13	Galena PbS, C	Reduction of PbO with C	PbO + C → Pb + CO
Bi, Bi <sup>2+</sup>	+0.32	Bismuth glance Bi <sub>2</sub> S <sub>3</sub> Bismuthite Bi <sub>2</sub> O <sub>3</sub>	Reduction of Bi <sub>2</sub> O <sub>3</sub> with C	Bi <sub>2</sub> O <sub>3</sub> + 3C → 2Bi + 3CO
Cu, Cu <sup>2+</sup>	+0.34	Copperpyrites CuFeS <sub>2</sub> Cuprite Cu <sub>2</sub> O	Partial oxidation of sulphide ore	2Cu <sub>2</sub> O + Cu <sub>2</sub> S → 6Cu + SO <sub>2</sub>
Ag, Ag <sup>+</sup>	+0.80	Argentite Ag <sub>2</sub> S, Occurs as metal	Special methods involving use of sodium cyanide	Ag <sub>2</sub> S + 4NaCN → 2NaAg(CN) <sub>2</sub> + Na <sub>2</sub> S 2NaAg(CN) <sub>2</sub> + Zn → 2Ag + Na <sub>2</sub> Zn(CN) <sub>4</sub>
Hg, Hg <sup>2+</sup>	+0.85	Cinnabar HgS	Direct reduction of HgS by heat alone	HgS + O <sub>2</sub> → Hg + SO <sub>2</sub>
Pt, Pt <sup>2+</sup>	+1.20	Occurs as metal sperrylite PtAs <sub>2</sub>	Thermal decomposition of (NH) <sub>4</sub> PtCl <sub>6</sub>	(NH) <sub>4</sub> PtCl <sub>6</sub> → Pt + 2NH <sub>4</sub> Cl + 2Cl <sub>2</sub>
Au, Au <sup>2+</sup>	+1.50	Occurs as metal	Special methods involving use of sodium cyanide	Similar to that for silver 2NaAu(CN) <sub>2</sub> + Zn → 2Au + Na <sub>2</sub> Zn(CN) <sub>4</sub>

Following major steps are involved in a metallurgical operation

- (A) Dressing or concentration of the ore.
- (B) Isolation of the crude metal from its ore
- (C) Purification or refining of the metal.



#### (A) Concentration of ore:

The removal of unwanted useless impurities from the ore is called **dressing, concentration or benefaction of ore**.

Some of the important procedures are described below.

##### 1. Hydraulic washing or Gravity separation or Levigation:

It is based on the difference in the densities of the gangue and ore particles. In this, the powdered ore washed with an upward stream of running water, the lighter particles of

sand , clay etc are washed away leaving behind heavier ore particles. It is used for the concentration of oxide and native ores.

## 2. **Electromagnetic separation :**

It is used when either the ore or the impurities associated with it are magnetic in nature.

### **Examples :**

Chromite ore( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is separated from non-magnetic siliceous impurities and cassiterite ore( $\text{SnO}_2$ ) is separated from magnetic Wolframite ( $\text{FeWO}_4 + \text{MnWO}_4$ ).

## 3. **Froth floatation process.** This method is commonly used for the concentration of the low grade sulphide ores like galena, $\text{PbS}$ ; copper pyrites $\text{CuFeS}_2$ ; zinc blende, $\text{ZnS}$ etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process the following reagents are also used :

**(a) Frothers.** These form stable froth which rises to the top of the flotation cell. Oils like pine oil, camphor oil etc., are used as frothers. These are added in small quantity.

**(b) Collectors.** Potassium or sodium ethyl xanthate is used as a collector. These get attached with the particles of the sulphide ore and thus make them water-repellent. Consequently the ore particles pass on into the froth. Collectors are always added in small quantity.

**(c) Activating and depressing agents.** When a mineral contains other minerals as impurities. the addition of these agents activates or depresses the flotation property of other minerals present as impurities and thus helps in separating the impurities. For example  $\text{PbS}$  usually contains the minerals  $\text{ZnS}$  and  $\text{FeS}_2$  as impurities. Flotation is carried out by using potassium ethyl xanthate (collector) along with  $\text{NaCN}$  and  $\text{Na}_2\text{CO}_3$  (depressing agent). The addition of  $\text{NaCN}$  and  $\text{Na}_2\text{CO}_3$  depresses the flotation property of  $\text{ZnS}$  and  $\text{FeS}_2$  grains, so mainly  $\text{PbS}$  passes into the froth when air is blown in. After  $\text{PbS}$  has been collected with the froth, the process is repeated by adding  $\text{CuSO}_4$  (activator) which activates the flotation property of  $\text{ZnS}$  grains which are now removed with the froth. The acidification of the remaining material left in the floatation cell leads to the floatation of  $\text{FeS}_2$ .

**Example** How does  $\text{NaCN}$  act as a depressant in preventing  $\text{ZnS}$  from forming the froth?

**Solution**  $\text{NaCN}$  reacts with  $\text{ZnS}$  and forms a layer of  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  complex on the surface of  $\text{ZnS}$  and thus prevents it from the formation of froth.

**Example** What is the role of stabiliser in froth floatation process ?

**Solution** Froth can last for a longer period in presence of stabiliser.

## 4. **Leaching :**

Leaching is often used if the ore is soluble in some suitable solvent, e.g, acids, bases and suitable chemical reagents.

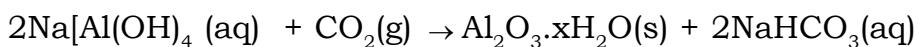
### **Example 1:**

#### **Leaching of alumina from bauxite :**

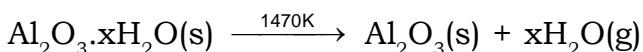
Bauxite, usually contains iron oxides and titanium oxide ( $\text{TiO}_2$ ) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of  $\text{NaOH}$  at 473 - 523 K and 35 - 36 bar pressure. This way,  $\text{Al}_2\text{O}_3$  is leached out as sodium aluminate leaving the impurities behind :



The aluminate in solution is neutralised by passing  $\text{CO}_2$  gas and hydrated  $\text{Al}_2\text{O}_3$  is precipitated.



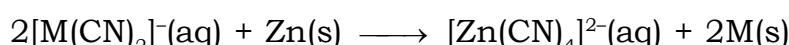
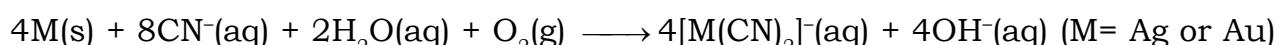
Alumina is filtered, dried.



### **Example 2:**

#### **Leaching of Gold and Silver :**

In the metallurgy of silver and that of gold, the respective metal/ore is leached with a dilute solution of  $\text{NaCN}$  or  $\text{KCN}$  in the presence of air (or  $\text{O}_2$ ) from which the metal is obtained later by displacement.



### **(B) Extraction of crude metal from concentrated ore :**

The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction as oxides are easier to reduce. Two steps are involved

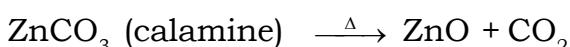
1. Conversion of ore to oxide
2. Reduction of the oxide to metal.

#### **1. Conversion of ore to oxide :**

Conversion of ore into oxide is carried out in two ways depending upon the nature of ore.

**(i) Calcination.** It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes :

**(a)** The carbonate ore gets decomposed to form the oxide of the metal, e.g.,

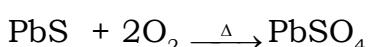
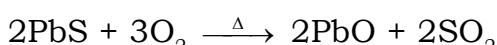


**(b)** Water of crystallisation present in the hydrated oxide ore gets lost as moisture

**(c)** Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

**(ii) Roasting:** It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or  $\text{O}_2$  below its melting point. The following changes occur:

**(a)** Roasting at moderate temperature: Some portion of the sulphide ores like galena ( $\text{PbS}$ ), Zinc blende ( $\text{ZnS}$ ) is first converted into metallic oxide and then the remaining portion is converted into metallic sulphate.



**(b)** Roasting at high temperature: Some sulphide ores, on being heated strongly in the presence of  $O_2$ , give metallic oxides.



The Sulphide ores of some of the metals like Cu, Pb, Hg, Sb etc., when heated strongly in the free supply of air or  $O_2$  are reduced directly to the metal rather than to the metallic oxides, e.g.,



**(c)** It removes easily oxidisable volatile impurities like As, S, P etc., as their oxides.

**(d)** When tin stone ( $\text{SnO}_{2(2)}$ ) is roasted, the impurities of CuS and FeS present in the ore are converted into  $\text{CuSO}_4$  and  $\text{FeSO}_4$  respectively.

## 2. Reduction of oxide to the metal

Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent, e.g., C or CO or even another metal.



Some metal oxides get reduced easily while others are very difficult to be reduced. To understand the variation in the temperature requirement for thermal reductions (pyrometallurgy) and to predict which element will suit as the reducing agent for a given metal oxide ( $\text{M}_x\text{O}_y$ ), Gibbs energy interpretations are made.

### Thermodynamic Principles of metallurgy :

$\Delta G^\circ$  for any process at any specified temperature, is given by the equation :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots \quad (1)$$

where,  $\Delta H$  is the enthalpy change and  $\Delta S^\circ$  is the entropy change for any process. Also,  $\Delta G^\circ = -RT\ln K \quad \dots \quad (2)$

where, K is the equilibrium constant at temperature, T. A negative  $\Delta G^\circ$  indicates a +ve value of K in equation (2). And this can happen only when reaction proceeds towards products. From these facts we can make the following conclusions:

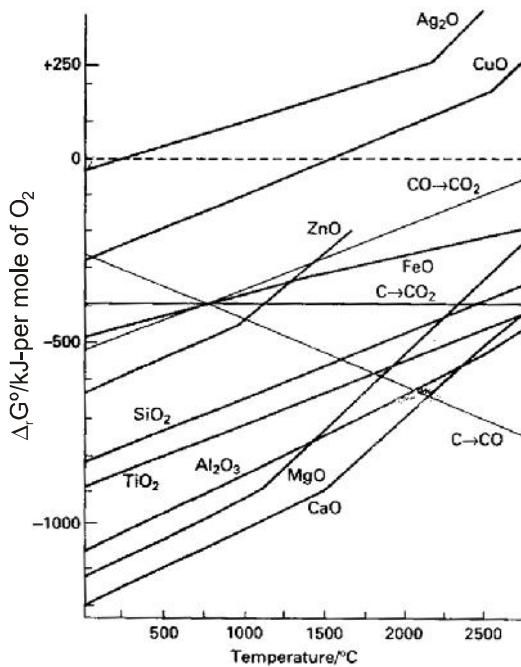
**(i)** When the value of  $\Delta G^\circ$  is negative in equation (1), only then the reaction will proceed. If  $\Delta S^\circ$  is positive, on increasing the temperature (T), the value of  $T\Delta S^\circ$  would increase ( $\Delta H^\circ < T\Delta S^\circ$ ) and then  $\Delta G^\circ$  will become -ve.

**(ii)** If reactants and products of two reactions are put together in a system and the net  $\Delta G^\circ$  of two possible reactions is -ve, the overall reaction will occur. So the process of interpretation involves coupling of the two reactions, getting the sum of their  $\Delta G^\circ$  and looking for its magnitude and sign. Such coupling is easily understood through Gibbs energy ( $\Delta G^\circ$ ) vs T plots for formation of the oxides.

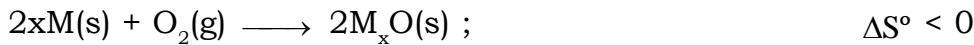
### Ellingham Diagram :

This provides an important basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham Diagram. Such diagram help us in predicting the feasibility of thermal reduction of an ore. The criterion of feasibility is

that at a given temperature, Gibbs energy of the reaction must be negative.



**(i)** Ellingham diagram normally consists of plots of  $\Delta_f G^\circ$  vs T for formation of oxides of elements i.e., for the reaction,



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

In this reaction, the gaseous amount (hence molecular randomness) is decreasing from left to right due to the consumption of gases leading to a -ve value of  $\Delta S$  which changes the sign of the second term in equation.

**(ii)** The free energy changes all follow a straight line unless the materials melt or vapours and when there is a large change in entropy associated with change of state, which changes the slope of the line.

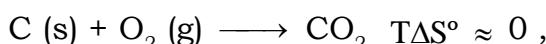
e.g. Hg – HgO line changes slope at  $356^{\circ}C$ , when Hg boils ; Mg – MgO line changes slope at  $1120^{\circ}C$  when Mg boils .

**(iii)** When the temperature is raised, a point will be reached where all graphs cross the  $\Delta G^\circ = 0$  line. Below this temperature the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of oxide is positive and the oxide becomes unstable and should decompose into metal and oxygen.

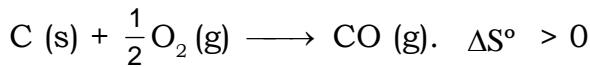
Theoretically all oxides can be decomposed to give the metal and oxygen if a sufficiently high temperature can be obtained. However in practice the oxides of Ag, Au and Hg are the only oxide can be decomposed at temperature which are easily attainable and these metals can be extracted by thermal decompositioin of this oxides.

**(iv)** In a number of processes, one metal is used to reduce the oxide of another metal. Any metal will reduce the oxide of other metals which lie below it in the. Ellingham diagram eg. Al reduces  $Fe_2O_3$ ,  $Cr_2O_3$  and  $NiO$  in the well known Thermite process, but Al will not reduce  $MgO$  at a temperature below  $1500^{\circ}C$ .

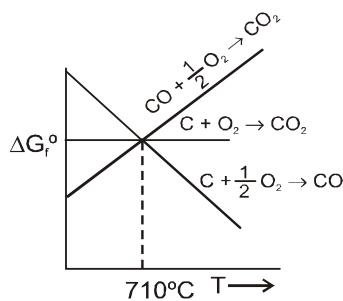
**(v)** Reduction of metallic oxides with C or CO.



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



The two lines for  $C \longrightarrow CO_2$  and  $C \longrightarrow CO$ . Cross about  $710^\circ C$ . Below this temperature  $C \longrightarrow CO_2$  is more favorable and above this temperature  $C \longrightarrow CO$  is favorable.



### Thus :

- (i) For temperatures at which the  $C \rightarrow CO$  line lies below the metal oxide line, C can be used to reduce the metal oxide and itself oxidised to CO.
- (ii) For temperature at which  $C \rightarrow CO_2$  line lies below the metal oxide line, C can be used to reduce the metal oxide and itself oxidised to  $CO_2$ .
- (iii) The temperature at which  $CO \rightarrow CO_2$ , line lies below the metallic oxide line, CO can be used to reduce the metal oxide and itself oxidised to  $CO_2$ .
- (iv) Since the  $\Delta G$  line of  $C \rightarrow CO$  sloped downwards it will eventually cross and lie below all the other graphs for (M, MO). Thus in principle carbon could be used to reduce any metallic oxide if a sufficiently high temperature were used. Reduction of  $TiO_2$ ,  $Al_2O_3$  and  $MgO$  can be carried out with the helps of C theoretically but is not attempted due to high cost and practical difficulties of using extremely high temperature. At high temperature many metal reacts with carbon forming carbides.
- (v) Many metals occurs as sulphide ores. Although C is a good reducing agent for sulphides due to the absence of compound, CS analogue to CO. Thus sulphides are normally roasted in air to form oxides before reducing with C.
- (vi)  $H_2$  is of limited use as a reducing agent for extracting metals from their oxides since  $\Delta G^\circ$  line has a +ve slope.

### Methods of Reduction :

The ore, obtained after calcination or roasting, is reduced to metal and choice of reducing agent depends upon the nature of ore. Some common reducing agents are as follows:

- i) Carbon or Carbon monoxide : For oxides of Fe, Cu, Pb, Sn, Zn, Mg, Co etc.
- ii) Electropositive metals like Na, Al, Mg or hydrogen:  
For reduction of ores of Mn, Cr, Ti, Mo, W etc
- iii) Water gas : For Ni ores
- iv) Auto-reduction : In case of Pb, Hg, Cu ores etc.
- v) Electrolytic reduction : For highly electropositive metals.

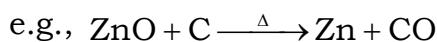
vi) Hydro metallurgy or displacement method: For Ag, Au etc.

### Some important reduction processes are described below:

#### a) Reduction by carbon:

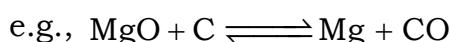
i) The metals which are less electropositive and do not form carbides with carbon, are reduced by this method e.g., oxides of Pb, Fe, Zn, Sn etc.

ii) For reduction, the ore is strongly heated with coke of coal in blast furnace, where metal is obtained in the form of vapours, or in molten state (Sn, Fe etc.)



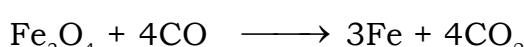
iii) Some disadvantages of carbon reduction process are that sometime metallic oxide may form carbide instead of metal e.g.,  $\text{CaO} + 3\text{C} \longrightarrow \text{CaC}_2 + \text{CO}$

In some cases reversible reaction may take place and so during cooling, formation of oxide may take place



thus carbon is not preferred for reducing CaO and MgO

iv) Carbon monoxide also acts as reducing agent,



#### Note:

i) Below  $710^\circ\text{C}$ , CO is better reducing agent than carbon and reverse is true at temperature higher than  $710^\circ\text{C}$ . It can be explained on the basis of Ellingham diagram.

ii) Carbon is good reducing agent for oxides but not for sulphides.

#### b) Reduction by Active Metals

i) Highly electrophilic metals like Na, Li, Al etc, are used to reduce the less electropositive metals like Cr, Cu, Mn etc.

ii) Reduction by powdered aluminium is known as Gold-Schmidt aluminothermic process. This process is employed in cases where metals have very high m.pt. and are to be extracted from their oxides. In this process thermite (mixture of ore and powdered aluminium), is taken in a steel crucible. The reaction is started by using ignition mixture (Mg-powder and barium peroxide). Large amount of heat is released during the reduction, which fuses both, ore and metal e.g., reduction of  $\text{Cr}_2\text{O}_3$  by Al powder takes place as follows.



Similarly



(iii) Examples of reduction by Na, K

Certain metal halides like  $\text{TiCl}_4$ ,  $\text{VCl}_4$ ,  $\text{ZrCl}_4$  etc, are reduced to metal by highly electrophilic metals like Na, K etc.



c) **Reduction by H<sub>2</sub> or Water gas (CO + H<sub>2</sub>)**

i) The oxides of metals, which are less electropositive than hydrogen may be reduced by this method. e.g.

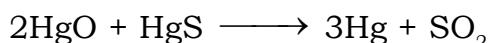
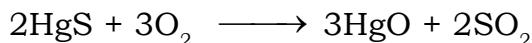


ii) Water formed during the reaction escapes out in the form of vapours.

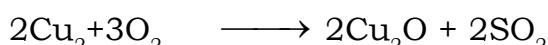
d) **Self-reduction of Auto-reduction**

Oxides of unreactive metals like those of the Hg, Pb, Cu etc, are reduced by their sulphides. Here no external reducing agent is added. eg.,

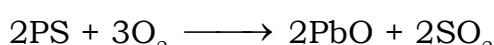
(i) extraction of Hg from cinnabar :



(ii) extraction of Cu from copper glance:



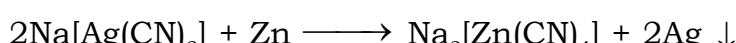
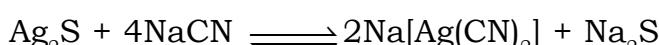
(iii) Extraction of Pb from galena.



e) **Hydrometallurgy or Displacement Method**

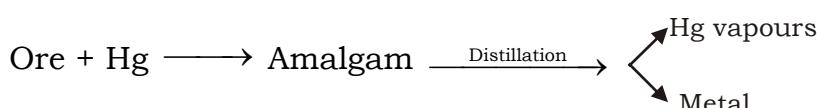
i) This method is based on the fact that a more reactive metal displaces less reactive metal from its aqueous solution.

ii) In this method, ore is converted into soluble form and more reactive metal is added in it e.g.,



f) **Amalgamation Process**

The process is used for extraction of noble metals like Pt, Au, Ag etc. Finely powdered is treated with Hg to form amalgam, Amalgam, on distillation is decomposed to metal and Hg.



g) **Electrolytic Reduction:**

The ores of highly electropositive metals (like alkali metals and alkaline earth metals) can not be reduced by common reducing agents like H<sub>2</sub>, C etc. Their (i.e., of ores of Na, K, Ca, Mg, Al etc) reduction by carbon needs very high temperature, and at such a high temperature, formation of carbide may take place. These are reduced electrolytically.

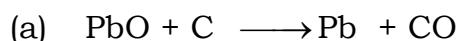
**Smelting, flux and slag:** Some of the oxides like Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, even after concentration, still contain infusible impurities which may be basic impurities (i.e., metallic oxides like

Cao, FeO, MgO etc.,) or acidic impurities (*i.e.*, non-metallic oxides like SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> etc.).

In order to remove these, the ore is mixed with coke and other substance called flux and the mixture is heated called **smelting**. Reactions taking place in smelting are :

(i) Coke or CO reduces the oxide ore to free metal.

### Examples :



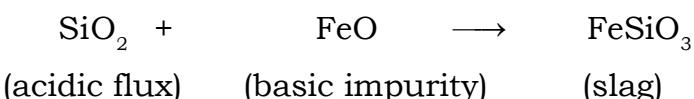
(ii) The flux combines with the impurity(gangue) and forms a fusible mass which is called **slag**. The formation of slag can be shown as :



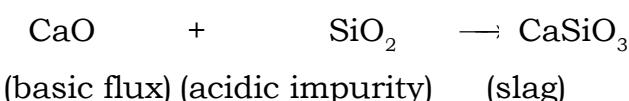
Thus a flux can be defined as “a substance which is added during the smelting of an oxide ore to remove infusible acidic or basic impurities as a fusible mass known as slag”.

**Types of flux :** Fluxes are of two types viz., acidic flux and basic flux.

**(i) Acidic flux :** It is an acidic oxide like SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub>. It is used to remove the basic impurity like CaO, FeO, MgO etc.



**(ii) Basic flux :** It is a basic oxide CaO ,MgO,Fe<sub>2</sub>O<sub>3</sub> etc., It is used to remove the acidic impurity like SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> etc.



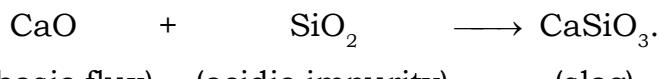
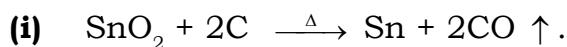
### Properties of a slag :

**(i)** Slag is a fusible mass.

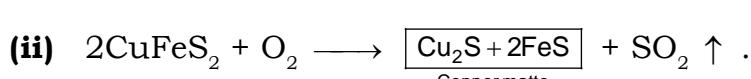
**(ii)** It has low melting point.

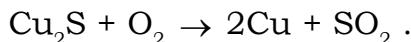
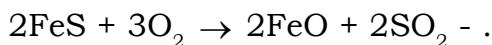
**(iii)** It is lighter than and immiscible with the molten metal.The layer of the slag on the molten metal prevents the metal from being oxidised.

### Examples of slag formation :

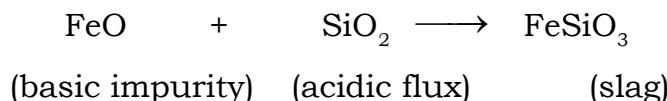


The slag of CaSiO<sub>3</sub>, being lighter, floats on the molten tin metal which can easily be removed.





Molten Cu-metal contains FeO as basic impurity which reacts with  $\text{SiO}_2$  (acidic flux) and forms a slag of  $\text{FeSiO}_3$ .



### (C) Purification or refining of impure metals :

The metals obtained by any of the methods discussed above, contain a number of impurities including other metals, unreduced oxides and sulphides of the metals, slags, etc.

Method be used for the purification of a particular metal depends on the nature of the metal to be purified and the impurities to be removed and the purpose for which the metal is to be used. The methods can be grouped into the following catagories.

#### 1. Physical methods :

**(a) Liquation process :** This process is used for the purification of the low melting metal. This process is used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy, which is obtained at the end of Parke's process and contains Pb as impurity.

The impure metal is placed on the slopping hearth of a reverberatory furnace and gently heated. When the temeprature of the furnace reaches the melting point of tin metal, this metal, on account of its lower melting point melts earlier than the impurities and hence flows down the inclined hearth and the solid infusible (non-fusible) impurities (called dross) are left behind on the hearth.

**(b) Fractional distillation prcoess .** This process is used to purify those metals which themselves are volatile and the impuritiess in them are non-volatile and vice-versa. Zn, Cd and Hg are purified by this process.

**(c) Zone refining method** (Fractional crystallisation method). This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.

Germanium metal, which is used in semiconductor devices, is refined(purified) by the zone refining method. The impure germanim metal to be refined is taken in the form of a rod. A circular heater is fitted around this rod and this heater is slowly moved along the length of the rod several times, the impurities are driven to one corner which can be discarded.

#### 2. Chemical methods : These methods include the following :

**(a) Oxidative process :** This process is used for removing the metallic (e.g., Mn,Cu,Pb,Sn,Fe,Ag etc.,) as well as non-metallic (e.g., C,P,S, Si etc.,) elements present as impurities. This process is based on the fact that when  $\text{O}_2$  or air is passed through the impure molten metal, the impurities are easily oxidised into their oxides. Then these oxides may be removed as follows :

(a) These oxide may form a scum on the surface of the metal. This scum can easily be removedby skimming.

- (b) If the oxides are volatile, they escape from the mouth of the furnace.
- (c) The oxides may form a slag with the lining on the inside surface of the furnace and may thus be removed. In the formation of the slag, the lining acts as a flux.

The oxidation of impurities can be done through the following processes :

**(i) Cupellation process :** Ag obtained by the distillation of Zn–Ag alloy contains traces of Pb as impurity. Similarly Au obtained from the auriferous quartz and alluvial deposits also contains lead as impurity. Cupellation process has been used to remove lead from Ag and Au.

**(ii) Bessemer's process :** In this process the metal containing the impurities is taken into a Bessemer's converter containing acidic or basic lining and blast of hot air is sent into it. The air converts the impurities into oxides. If these oxides are volatile, they get volatilised and thus escape from the mouth of the converter. The oxides may form a slag with the lining of the Bessemer's converter and are thus removed.

**Example :**

**Removal of FeS from the copper matte: (Bessemerisation) :** Copper–iron pyrites ( $\text{CuFeS}_2$ ), after being roasted and smelted, gives a molten mass which is called copper matte. This copper matte contains a mixture of  $\text{Cu}_2\text{S}$  and FeS. FeS is removed from this mixture (copper matte) by Bessemerisation process.

**(iii) Softening process :**

Lead obtained from galena ore (PbS) by air-reduction or carbon-reduction process, contains base metals (Cu, Bi, As Sn, Ag, Sn, Zn etc) as impurities. It is the presence of these impurities due to which that lead becomes hard and brittle. The removal of these impurities is done by the process, which is called **softening process**, since the removal of impurities makes lead soft. This process consists of heating the impure lead on the hearth of a shallow flattened reversible furnace, in a blast of air. The impurities of the base metals (except Ag) are oxidised to their respective oxides, which form a scum on the surface of lead. This scum is removed by skimming. Lead obtained by this method still contains Ag as impurities and is called argentiferous lead or commercial lead. The removal of the impurities of Ag from the commercial lead is called desilverisation of lead and is done by **Parke's process** (desilverisation of lead).

In Parke's process, the commercial lead, which contains Ag as impurities, is melted in iron pots and 1% of Zn is added to it. The molten mass is thoroughly agitated. Since Ag is about 300 times more soluble in Zn than in Pb, most of the Ag present in the commercial lead as impurity mixes with Zn, to form Zn–Ag alloy. On cooling, two layers are obtained. The upper layer contains Zn–Ag alloy in the solid state, while the lower layer has lead in the molten state. This lead contains only 0.0004% of Ag and hence is almost pure.

Zn–Ag alloy contains lead as impurity. This impurity of Pb is removed from the alloy by liquation process in which Pb melts and hence drains away from the solid alloy. Now Ag can be obtained from this purified Zn–Ag alloy by **distillation process**, in which the alloy is heated strongly in presence of little carbon in a fire-clay retort. Zn, being more volatile, distills off while Ag remains in the retort, carbon used in the process reduces the oxide of Zn, if formed. Ag obtained from Zn–Ag alloy is contaminated with a little of Pb as impurity which is removed by **cupellation**.

**(iv) Puddling process :** This process is used for the manufacture of wrought iron from cast iron. We know that cast iron contains the impurities of C, S, Si, Mn and P. When these impurities are removed from cast iron, we get wrought iron. In this process the

impurities are oxidised to their oxides not by blast of air but by the haematite ( $\text{Fe}_2\text{O}_3$ ) lining of the furnace.

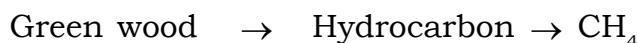
**v) Poling process :** This process is used for the purification of copper and tin.

**Examples :**

**a) Purification of impure copper :** Molten copper containing CuO as impurity is treated with powdered anthracite and then stirred with a pole of green wood. Green wood, at high temperature, liberates hydrocarbon gases, which are converted into methane ( $\text{CH}_4$ ). Methane thus obtained reduces CuO to free Cu-metal, which is about 99.5% pure and is called tough pitch copper.



**b) Purification of impure tin :**



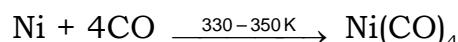
**vi) Vapour Phase thermal decomposition method :**

In this method, the metal is converted into its volatile compound and collected in some vessel. It is then decomposed to give pure metal. The two requirements for this are :

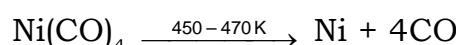
- the metal should form a volatile compound with an available reagent,
- the volatile compound should be easily decomposable, so that the recovery is easy.

**Examples:**

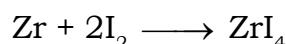
**a) Mond process for refining nickel:** In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl



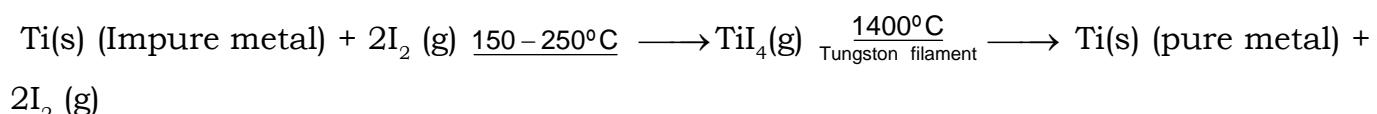
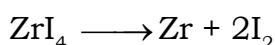
The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal:



**b) Van arkel method for refining zirconium or titanium:** This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises.



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

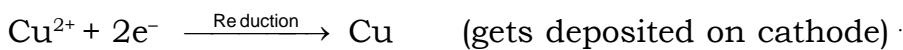


**3. Electrolytic process :** Sn, Pb, Cu, Ag, Ni, Zn, Cr etc are purified by this process. This process gives metals of high purity.

In this process, impure metal is made the anode. Pure metal is made cathode. An aqueous solution of a suitable simple salt or complex salt of the metal having some corresponding acid, if necessary, is used as an electrolytic solution. When electric current is passed through the electrolytic solution, metal from the anode is transferred to the cathode where it gets deposited. The soluble impurities go into the solution, while the insoluble impurities settle down at the bottom, below the anode (anode mud). Sometimes the anode mud contains valuable metals which can be extracted from it, e.g., the anode mud obtained in the electrolytic refining of lead contains Ag, Au, Sb, Cu etc.

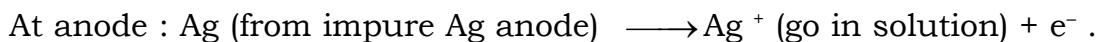
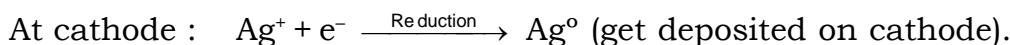
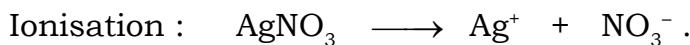
### **Example :**

**a) Purification of blister copper :** Blister copper contains many impurities like Fe, Ni, Zn, Ag, Au etc., For refining blister copper, impure copper is made anode and a thin plate of pure copper is made cathode. 15%  $\text{CuSO}_4$  containing 5%  $\text{H}_2\text{SO}_4$  is used as an electrolyte. On passing electric current. Cathode (pure Cu plate) goes on becoming thicker and thicker in size, as the reaction goes on.



The soluble impurities, like Fe, Ni, Zn, pass into solution as their sulphates, while the insoluble impurities (e.g., Ag, Au), which are not affected by  $\text{H}_2\text{SO}_4 - \text{CuSO}_4$  solution, settle down below the anode, as anode mud or anode sludge.

**b) Purification of silver :** Silver obtained by any of the methods may contain traces of Zn, Cu and Au as impurities. A block of impure Ag is made anode, while the cathode is a thin sheet of pure Ag. 6% solution of  $\text{AgNO}_3$  containing 1%  $\text{HNO}_3$  is used as an electrolytic solution. On passing electric current, pure Ag is deposited on the cathode (sheet of pure Ag). Zn and Cu, if present, pass into solution, while Au, if any, falls down as the anode mud. Reactions taking place are :



### **Metallurgy of some useful metals :**

#### **1. Extraction of Sodium:**

Two processes are in practice for extracting Na

- a. Castner's process
- b. Down's process

#### **Castner process**

**Principle** : Fused caustic soda is electrolysed

**Cathode** : Steel

**Anode** : Nickel

**Reaction at Cathode** :  $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$

**Reaction at anode** :  $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \uparrow$

Water formed at anode partially gets evaporated and partially broken and H<sub>2</sub> discharges at cathode.

The bath temperature is kept higher than the melting point of Na (318°) to dissolve Na in NaOH. Metallic sodium is taken from the cathode chamber from time to time with laddles.

### **Advantages**

- i) Since the temperature is 327°C, not much Na is vaporised
- ii) Valuable H<sub>2</sub> & O<sub>2</sub> are produced

### **Disadvantages**

- i) Costly raw material caustic soda is used
- ii) 50% of the electrical energy wasted for the hydrolysis of water.

### **b) Down's Process**

<b>Principle</b>	:	Molten NaCl is electrolysed.
Raw material	:	Anhydrous CaCl <sub>2</sub> (60%), NaCl (40%)
Temperature	:	850K
Anode	:	Graphite
Cathode	:	Iron
Cathode reaction	:	Na <sup>+</sup> + e → Na (Reduction)
Anode reaction	:	2Cl <sup>-</sup> - 2e → Cl <sub>2</sub> ↑ (oxidation)

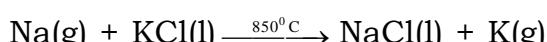
60% CaCl<sub>2</sub> added to lower the m.p of NaCl (40%) (1081 K to 850K)

### **Advantages of lowering temperature:**

- i) Lowering temperature reduces the consumption of electricity.
- ii) Molten Na at high temperature vapourises
- iii) Na & Cl<sub>2</sub> exert more corrosive action on vessel used for electrolysis at high temperature.
- iv) At higher temperature molten Na dispersed in molten NaCl and forms metallic fog which short-circuit the electrodes.

### **2. Extraction of Potassium:**

Potassium can be extracted by reducing molten KCl with metallic sodium at 850°C.



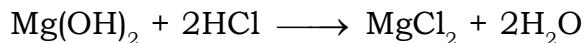
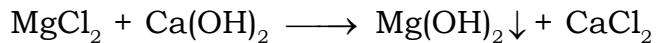
K being more volatile distills off.

### **3. Extraction of Magnesium:**

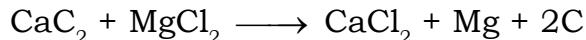
Process	:	Electrolysis
Anode	:	Graphite rod
Cathode	:	Iron pot (rectangular)
Electrolyte	:	molten MgCl <sub>2</sub> (75%), NaCl (25%)
Temperature	:	700°C
Cathode reaction	:	Mg <sup>2+</sup> + 2e → Mg



From sea water anhydrous  $\text{MgCl}_2$  is obtained by the following reactions



By thermal reduction Mg can be produced

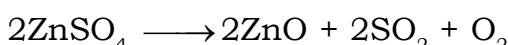
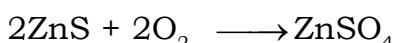
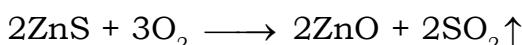


#### 4. Extraction of Zinc:

Zinc is mainly extracted from zinc blende ( $\text{ZnS}$ ). Following steps are involved

i) **Concentration**: Froth floatation process

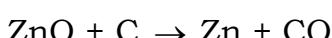
ii) **Roasting**:



iii) **Smelting**: Carbon reduction

Raw material: Powdered coke & Roasted ore

Heating process is carried out and  $\text{Zn}$ (vapour) is formed and condenses. Blue flame from the prolong is observed till the end of the reaction (due to formation of  $\text{CO}$ ).

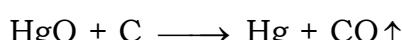
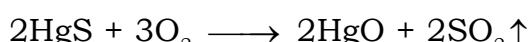


iv) **Refining**: Electro refining

Electrical refining is done by using impure  $\text{Zn}$  as the anode and  $\text{ZnSO}_4$  electrolyte and pure  $\text{Zn}$  as the cathode. The following electrolysis reaction will take place.

#### 5. Extraction of Mercury:

**Modern Process**: Cinnabar is crushed to powder and the crushed ore is then concentrated by froth floatation process. The concentrated ore is then charged in a shaft furnace through a hopper with charcoal. Furnace is fired and the following reaction takes place.

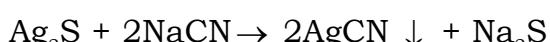


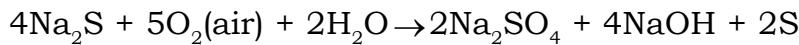
#### 6. Extraction of Silver:

Silver is mainly extracted from Silver glance or Argentite ( $\text{Ag}_2\text{S}$ ). The following steps are involved

i) **Concentration**: Froth floatation process.

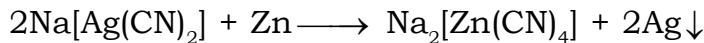
ii) **Leaching**: The concentrated  $\text{Ag}_2\text{S}$  is then treated with 0.5% solution of  $\text{NaCN}$  in presence of air.





**iii) Displacement:** Precipitation of Silver

As SRP of Zn is less than that of copper, Zn will replace Ag from the complex as follows



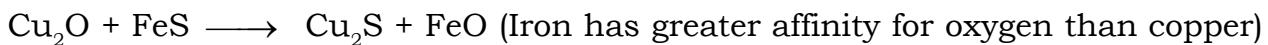
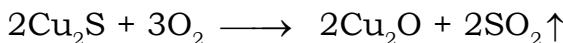
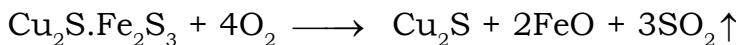
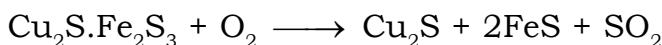
**iv) Electro-refining:** Metallic silver thus obtained contains impurities like Zn, Cu, Au etc. It is purified by electro-refining process. Impurities like Zn and Cu go into the solution while gold settles down at the anode as anode mud.

## 7. Extraction of Copper

Copper is mainly extracted from copper pyrites

i) **Concentration of the ore: Froth floatation process**

ii) **Roasting:**

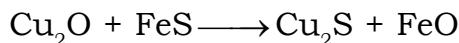
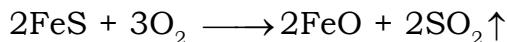


iii) **Smelting :**

**material required:** Roasted ore, Lime stone, Coke (used as fuel) and Silica (used as flux)

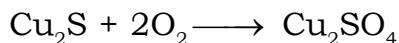
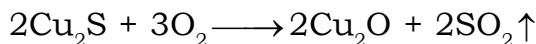
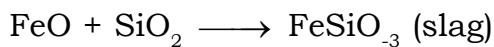
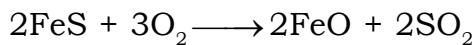
Lime stone is used to remove excess silica.

Reactions occurring are as follows

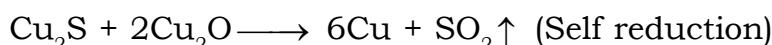


iv) **Bessemerisation:**

Reactions involved are,



When 2/3 of the cuprous sulphide is oxidised, the blast is stopped. The produced  $\text{Cu}_2\text{O}$  and  $\text{CuSO}_4$  are reduced by the rest of cuprous sulphide to give metallic copper with the evolution of  $\text{SO}_2$ .





As the molten copper cools, it gives off the dissolved of  $\text{SO}_2$  which leaves the surface of the metal with full of cavities giving the metal a blistered appearance. This is why the metal thus obtained is called **blister copper**.

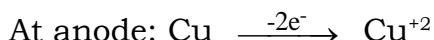
v) **Refining:** Electrorefining

Anode: Impure copper ; Cathode: Pure copper

Electrolyte: 15%  $\text{CuSO}_4$  solution + 5%  $\text{H}_2\text{SO}_4$

The impurities like Fe, Zn, Ni etc., dissolved in the solution as sulphates while gold, silver, platinum settle down below the anode as anode mud.

Reactions:



## 8. Extraction of Aluminium

Aluminium is mainly extracted from bauxite ore.

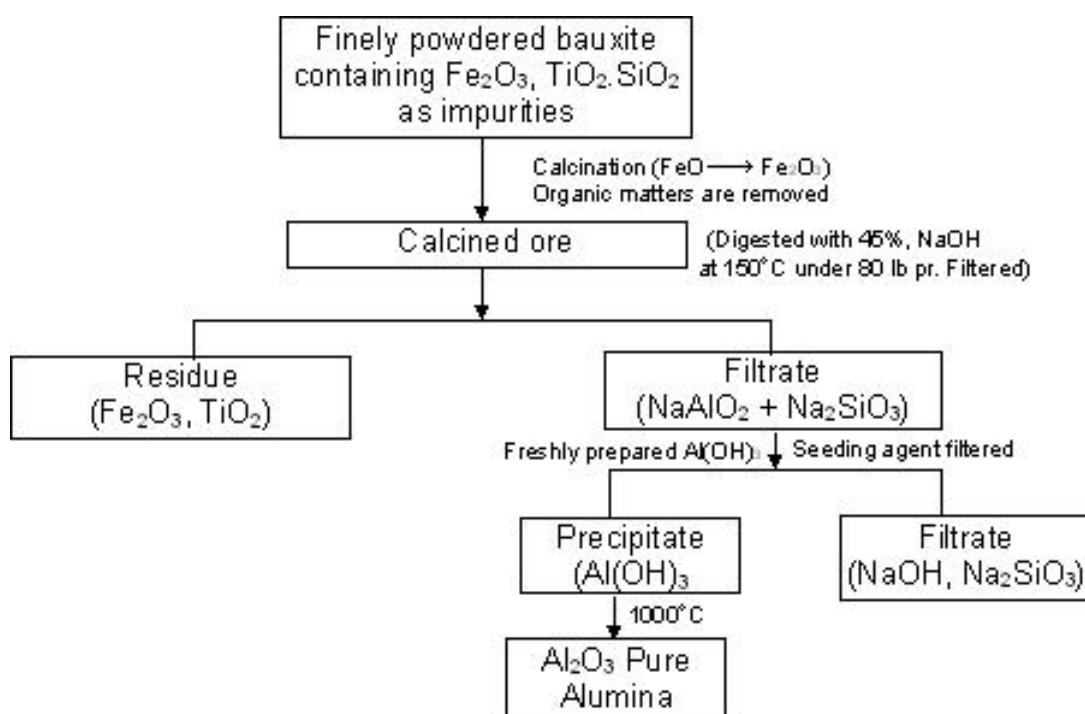
Extraction involves three stages :

- i) Purification of Bauxite
- ii) Electrolytic reduction of Alumina
- iii) Purification of Aluminium.

### i) Purification of Bauxite

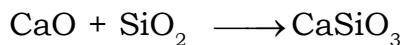
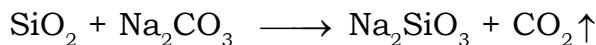
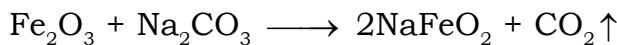
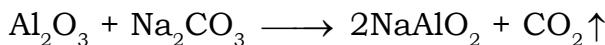
**a) Baeyer's process:** The process is used to purify red Bauxite which contains iron oxide impurity.

**Flow sheet of Baeyer's process:**

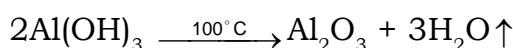
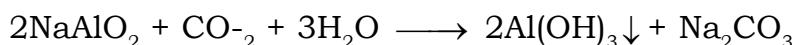


**b) Hall's process :**

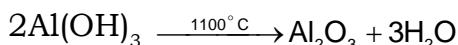
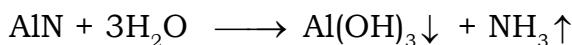
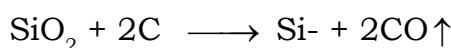
Crude bauxite at 1100°C reacts with  $\text{Na}_2\text{CO}_3$ , little  $\text{CaCO}_3$  when  $\text{CaSiO}_3$ ,  $\text{NaSiO}_2$ ,  $\text{NaFeO}_2$  etc. form



Then at 50° – 60°C  $\text{CO}_2$  is passed through  $\text{NaAlO}_2$  solution and produces thereby  $\text{Al(OH)}_3$ .  $\text{Na}_2\text{SiO}_3$  &  $\text{NaFeO}_2$  remain in solution.

**c) Serpeck's Process**

Bauxite containing high percentage of silica can be purified by Serpeck's process. In this process finely powdered bauxite is mixed with coke and the mixture is heated to 1800°C in a current of nitrogen. The AlN thus obtained is hydrolysed and  $\text{Al(OH)}_3$  is formed.

**ii) Electrolytic reduction of  $\text{Al}_2\text{O}_3$** 

Pure alumina melts at about 2000°C and is a bad conductor of electricity. If fused cryolite  $\text{AlF}_3 \cdot 3\text{NaF}$  and  $\text{CaF}_2$  (Fluorspar) is added the mixture melts at 900°C and  $\text{Al}_2\text{O}_3$  becomes a good conductor of electricity. Metallic Al is liberated at the cathode

Cathode : Carbon

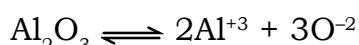
Anode : Graphite rods

Electrolyte : 60 parts cryolite + 20 parts fluorspar + 20 parts pure  $\text{Al}_2\text{O}_3$

Temperature : 900°C

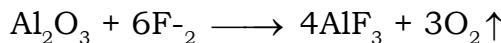
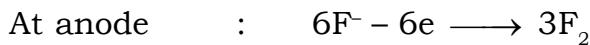
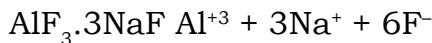
**Reactions**

According to the 1<sup>st</sup> theory the following reaction occurs



As cryolite has greater electrochemical stability it does not dissociate. It only increases the dissociation of  $\text{Al}_2\text{O}_3$

But the second theory states that, cryolite undergoes electrolytic dissociation first then  $\text{Al}^{+3}$  goes to the cathode, produce  $\text{F}_2$  at anode which then reacts with  $\text{Al}_2\text{O}_3$  produces  $\text{AlF}_3$ .



### iii) Refining of aluminium

The aluminium metal obtained by the electrolysis of fused almina is about 99.5% pure. It can be further refined by **Hoope's electrolytic process**.

## 9. Extraction of Pb :

Extracted from Sulphide ore:  $\text{PbS}$  (galena)

i) Concentration of Ore: Froth floatation process.

Air reduction (used for ore rich in lead Content)	Carbon reduction (used for ores poor in lead content)
<p><b>Step - I:</b> Ore roasted in reverberatory furnace Ore (<math>\text{PbS}</math>) Partially converted <math>\text{PbO}</math> and <math>\text{PbSO}_4</math></p> <p><b>Step - II:</b> Smelting</p> <p>Temp. of furnace increased and some more conc . ore is added. Lead metal is formed</p> $2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2$ $\text{PbS} + 2\text{O}_2 \rightarrow \text{PbSO}_4$ <p><math>\text{PbO}</math> and <math>\text{PbSO}_4</math> reduced to meta by ore, (<math>\text{PbS}</math>)</p> <p>(Self reduction)</p> $\text{PbSO}_4 + \text{PbS} \rightarrow 2\text{Pb} + 2\text{SO}_2$ $2\text{PbO} + \text{PbS} \rightarrow 3\text{Pb} + \text{SO}_2$ <p>Molten lead formed is drawn from lower part of furnace.</p>	<p><b>Step - I :</b> Concentrated ore is mixed with <math>\text{CaO}</math> and roasted.</p> $2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2$ <p>Role of lime:</p> <ul style="list-style-type: none"> <li>i) Prevents the formation of <math>\text{PbSO}_4</math></li> <li>ii) Prevents the formation of <math>\text{PbSiO}_3</math></li> </ul> $[\text{PbSiO}_3 + \text{CaO} \rightarrow \text{CaSiO}_3 + \text{PbO}]$ <p><b>Step - II:</b> smelting</p> <p>Roasted ore containing <math>\text{PbO}</math> is mixed with Coke and lime stone (flux) and smelted in blast furnace</p> $\text{PbO} + \text{C} \rightarrow \text{Pb} + \text{CO}$ $\text{PbO} + \text{CO} \rightarrow \text{Pb} + \text{CO}_2$ $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 \text{ (slag)}$

ii) Purification of metal:

Lead obtained by ether of the above two processes contains: Cu, Ag, Fe, Sb, Bi impurities.

iii) Softening process:

Impure metal is melted on reverberatory furnace. Impurities are oxidized and form scum on the surface of molten lead, which is removed.

Ag, removed by parke's or Pattinson's process

Desilverised lead further purified by electrolysis.

**Cathode:** Pure lead

**Anode:** Impure lead

**Electrolyte:**  $\text{PbSiF}_6$  with 8 to 12% of  $\text{H}_2\text{SiF}_6$ , less electropositive metals deposit fall anode as anodic mud. More electro positive metals go into solution.

## 10. Extraction of Sn:

Important ore of Sn is cassiterite:  $\text{SnO}_2$  (tinstone).

The Ore is associated with Siliceous impurities, tungstates of Iron and manganese, pyrites of copper, Iron and Zn.

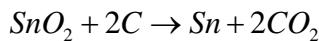
### Step - I: Concentration of Ore:

- 1) Gravity separation (Siliceous gangue are removed)
- 2)  $\text{FeWO}_4$ ,  $\text{MnWO}_4$  removed by electromagnetic separation

**Step - II: Roasting:** Removes S and As impurities as  $\text{SO}_2$  and  $\text{As}_2\text{O}_3$ .

### Step - III: Smelting:

Roasted ore is mixed with carbon (reducing agent),  $\text{CaO}$  and heated in reverberatory furnace.  $\text{SnO}_2$  is reduced to 'Sn' metal.



### Step - IV : Purification of metal.

Molten metal contains Fe, Cu, W impurities

- a) Ist: Step: Purified by liquation only Sn flows down leaving impurities Cu, Fe, W
- b) Molten metal obtained in liquation is purified by Poling
- c) Finally purified by electrolysis.

### Extraction of Sn from $\text{SnO}_2$ (Summary)

ore is concentrated by

- a) Gravity separation
- b) Electro magnetic separation
- c) Roasting

reducing agent : Coke

Flux added :  $\text{CaCO}_3$  [  $\text{CaO}$  acts as flux]

Slag :  $\text{CaSiO}_3$

Metal purified by

Liquation  $\rightarrow$  Poling  $\rightarrow$  electrolysis

☞ 'Sn' metal produces peculiar sound when ever it is bent, the cracking sound is known as **tin - cry**.

☞ 'Sn' has max . no. of natural isotopes.

☞  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  called butter of tin

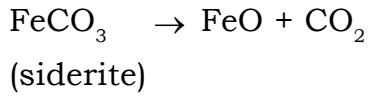
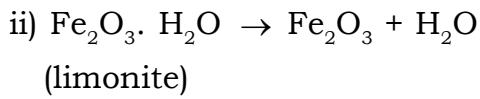
☞  $\text{SnCl}_4$  and  $(\text{CH}_3)_2\text{SnCl}_2$  are used to make film of  $\text{SnO}_2$  on glass to make it Scratch proof.

## 11. Extraction of Iron:

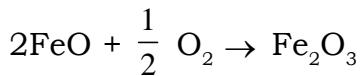
**Step - I:** Concentration of Ore: Levigation followed by Maganetic seperation.

**Step - II:** Calcination and roasting:

- i) Impurities such as P, S, C, As, Sb are removed as their volatile oxides.



Ferrous oxides is oxidised to ferric oxide.



Entire mass becomes porous.

### Step - III :

**Smelting:** carried-out in Blast furnace.

Concentrated ore is mixed with ( Coke reducing agent)

Lime stone (flux) called charge and sent into blast furnace.

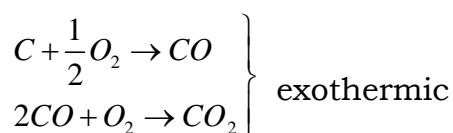
Ore :  $\text{CaCO}_3$  : Coke

8 : 1 : 4  $\Rightarrow$  Charge

Blast furnace have zone of different temperature. Different reaction occurs at different zones

**(i) Combustion zone :** (Temp – 1500 – 1600<sup>0</sup> C)

(bottom of furnace)

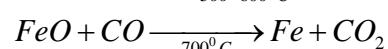
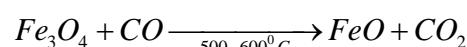
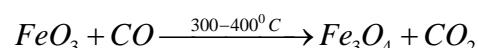


$\text{CO}_2$  rises upwards and partially get reduced to CO with carbon

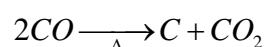


**(ii) Reduction Zone:** Temp 250<sup>0</sup>C – 700<sup>0</sup>C

The upper most zone of the furnace reduction of Iron Oxide takes place by up coming 'CO'



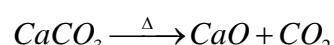
Heat involved during reduction decomposes part of CO to C. The Iron formed is called spongy Iron.

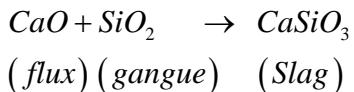


**(iii) Slag formation zone:** (Temp: 800<sup>0</sup>C – 1000<sup>0</sup>C)

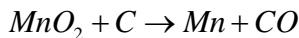
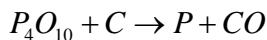
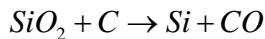
Middle portion of furnace

Lime stone ( $\text{CaCO}_3$ ) decomposes





Other impurities, Silicates, Phosphates & manganates are converted to Si, P, Mn respectively

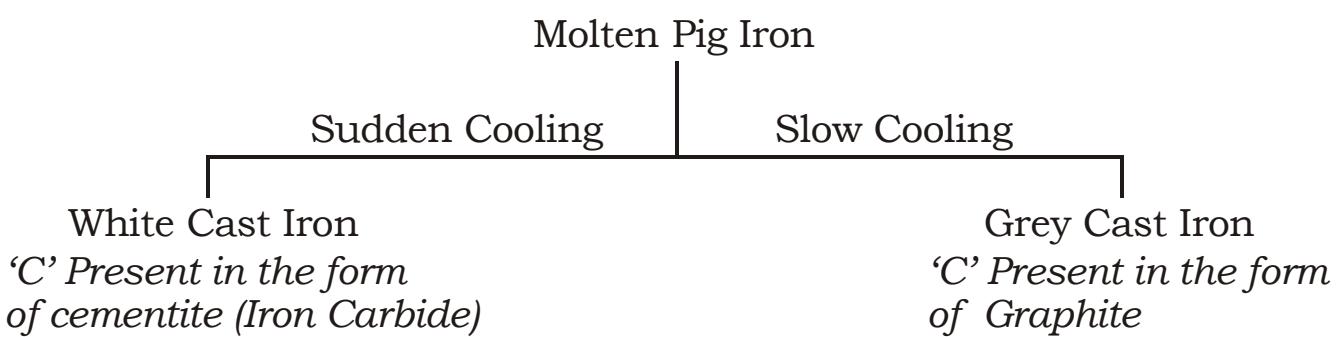


Si, P, Mn are partially absorbed by slag and partially by Iron.

**(iv) Zone of fusion:** Temp (1200 – 1500° C)

Just above combustion zone spongy Iron containing impurities C, Si, P, Mn melts at 1300°C collected at the bottom molten metal is covered by slag which prevents oxidation of iron by blast of air.

Iron obtained from blast furnace is called Pig Iron  $\Rightarrow [93\% Fe + 5\% C + 2\% Si, P, Mn]$



Types of iron	Cast Iron	Wrought Iron	Steel
<b>Composition</b>	Fe = 93 – 95% C = 2.5 – 5% 2% impurities	(all most pure) Fe = 99.5 – 99.8 % C = 0.25 – 1% 0.30% impurities	Fe = 98 – 99.5 % C = .25 – 2%
<b>M.P</b>	1200°C	1500°C	1300°C – 1400°C

### Alloys

Alloys are homogeneous mixture of elements with metallic properties

#### Advantages of alloys :

Alloys exhibit special properties which are largely different from constituent metals. some important characteristics are

- i) Resistant to corrosion
- ii) Harder than pure metals
- iii) High electrical resistance eg : Nichrome
- iv) Light and strong eg: Aluminium alloys
- v) Colour can be varied by changing composition.

### **Some important Alloys**

<b>S.No.</b>	<b>Name</b>	<b>Composition</b>	<b>Application</b>
1	Stainless Steel	Fe, Cr, Ni	Surgical instruments
2.	Invar	Fe, Ni	Pendulums
3.	Alnico	Fe, Al, Ni, Co	Bar magnets
4.	Brass	Cu, Zn	Utensils
5.	Bronze	Cu, Zn, Sn	Statues
6.	Gun Metal	Cu, Sn, Zn	Gears
7.	Bell Metal	Cu, Sn	Bells
8.	German Silver	Cu, Zn, Ni, Fe	Cutlery
9.	Solder, Pewter	Pb, Sn	Soldering