

**METALLURGY**

**Minerals** : Naturally occurring chemical substance in which metal exist either in its free state or in combined state is called mineral.

**Ore** : Mineral from which metal can be conventionally & economically extracted is called ore & impurities associated with it is called gangue or matrix

**TYPES OF ORES :**

- **Sulphide Ores** : Galena :  $\text{PbS}$ , Cinnabar :  $\text{HgS}$ , Cinnabar :  $\text{HgS}$   
Zinc blende :  $\text{ZnS}$ , Chalcopyrite :  $\text{CuFeS}_2$   
Copper glance :  $\text{CuS}_2$ , Fool's Gold :  $\text{FeS}_2$
- **Oxide Ores** :  
Bauxite :  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  Haematite :  $\text{Fe}_2\text{O}_3$   
Limonite :  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  Tin stone or Cassiterite :  $\text{SnO}_2$
- **Carbonate Ores** : Siderite :  $\text{FeCO}_3$  Calamine  $\text{ZnCO}_3$   
Malacite :  $\text{Cu}(\text{OH})_2\text{CuCO}_3$  Dolomite  $\text{CaCO}_3 \cdot \text{MgCO}_3 \cdot 2\text{H}_2\text{O}$   
lime stone :  $\text{CaCO}_3$
- **Sulphate Ores** : Gypsum :  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  Anhydrite  $\text{PbSO}_4$   
Glauber's salt :  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  Mohr's salt :  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
- **Halide Ores** : Rock salt :  $\text{NaCl}$  Cryolite :  $\text{Na}_3\text{AlF}_6$   
Fluorspar :  $\text{CaF}_2$  Carnallite :  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- **Nitrate Ores** : Chile Saltpetre :  $\text{NaNO}_3$  Indian Salt petre :  $\text{KNO}_3$
- **Native Ores** : Those metals which are chemically less reactive. They occur in the earth crust in form of free state (lumps)  
e.g : Cu, Ag, Au, Hg, Pd, Pt, Bi

**Pulverization** : The crushing of ore to powdered state is called pulverisation.

**General principles & processes involved in the extraction of metal from its ore :**

The extraction of metal from its ore is completed in three steps :

**Step I** : concentration or Dressing or Beneficiation of ore

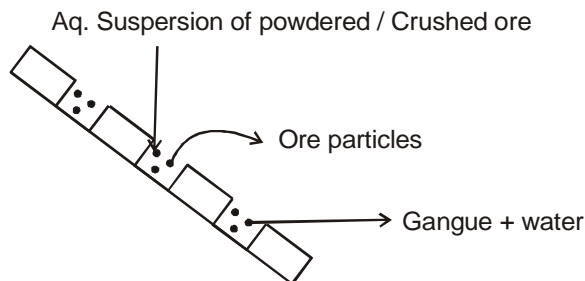
**Step II** : Extraction of crude metal from conc. ore

**Step III** : Refining of impure metal.

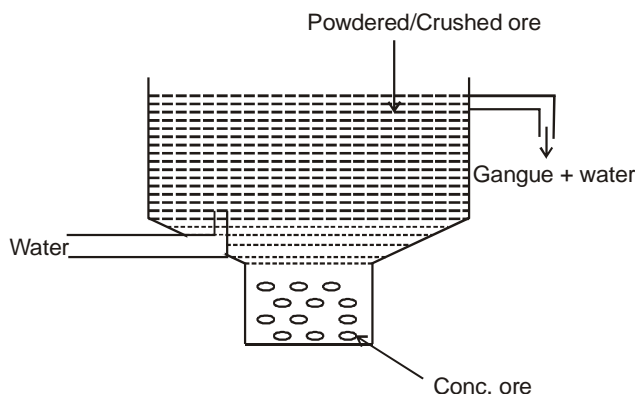
**Step I : Concentration or Dressing or beneficiation of Ore**

(a) **By Gravity separation** : Ore particles are heavier than the gangue particles. This is used for the separation of most of the gangue particles :

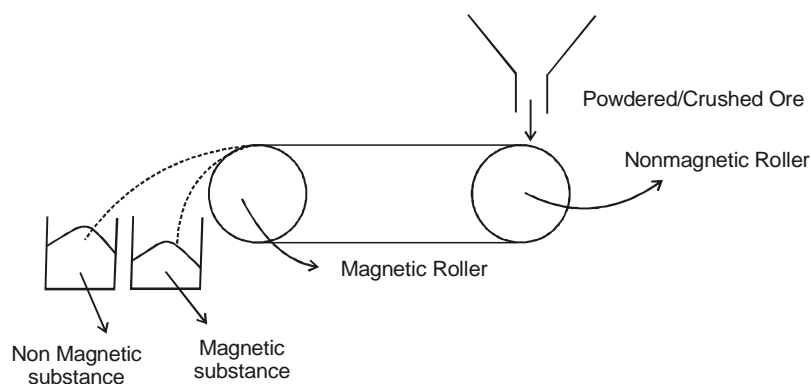
⇒ By Wilfley Table Method



⇒ By Hydraulic Classifier



(b) By Magnetic separator :



Cassiterite or Tinstone contains impurities of wulframite or wulframates of Fe & Mn.

⇒ Tin stone :  $\text{SnO}_2 \rightarrow$  Diamagnetic

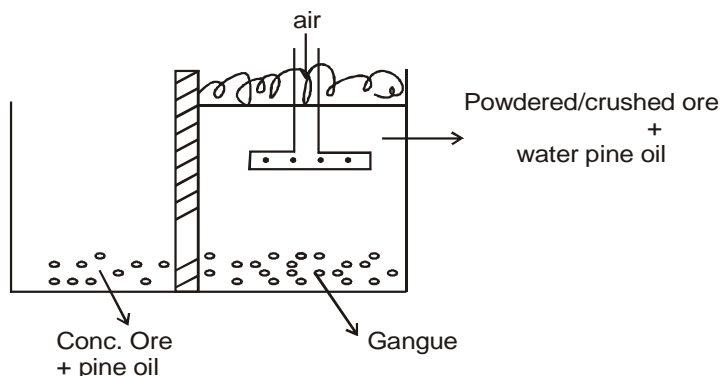
⇒ Wulframites or wulframates of

Fe & Mn :  $\text{FeWO}_4$ ,  $\text{MnWO}_4 \Rightarrow$  Paramagnetic.

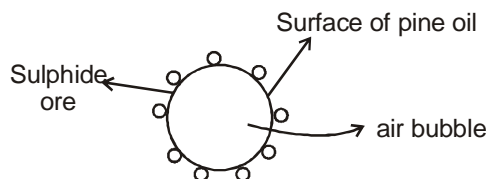
Wulframates of Fe & Mn from Tin stone by magnetic separator.

(c) **By Froth Floatation Process** : This method is used for the concentration of sulphide ores.

- It is based on the concept that the sulphide ores are preferentially wetted by pine oil, camphor oil while gangue particles are preferentially by water.
- This is based on the physical phenomenon of adsorption.

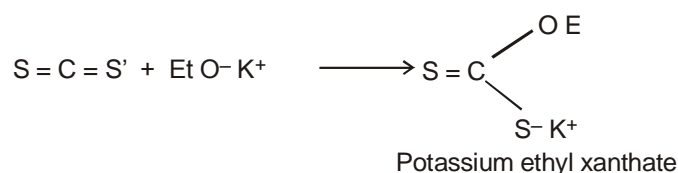
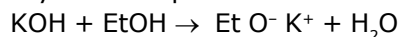


**Frother** : Pine oil, Camphor oil



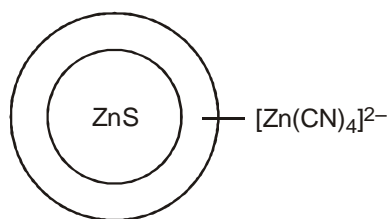
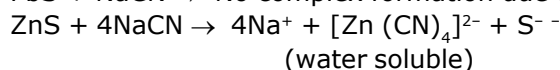
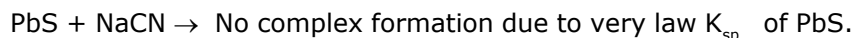
**Froth Stabilizers** : They reduce surface tension of water e.g. cresols, amines.

**Collector** : Sodium or Potassium xanthates. It combines with sulphide ore & makes them water repellent so that its affinity towards pine oil increases (Adsorption tendency increases)



**Depressant** : KCN or NaCN

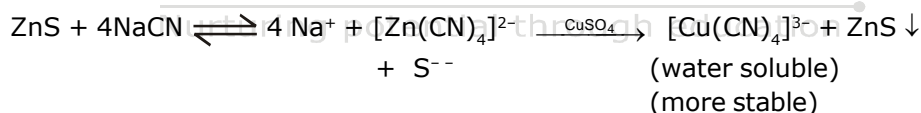
ZnS is found to be an impurity with the lead sulphide. Therefore to separate out PbS from ZnS depressant KCN or NaCN added.



Thus, ZnS becomes water soluble & it remains with gangue while PbS comes out with the froth.

**Activator** :  $\text{CuSO}_4$

From galena (PbS.ZnS) ZnS is removed



& ZnS is taken out by froth floatation second time.

(d) **By electrostatic Method** : This method is very specific for the separation of ZnS from galena (lead sulphide) because ZnS is poor conductor of electricity & PbS is good conductor of electricity.

(c) **Leaching**

### Step II : Extraction of Crude Metal from concentrated Ore :

It's completed in two stages :

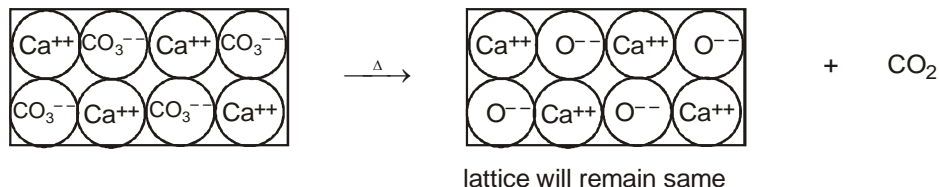
(a) Conversion of concentrated ore into metal oxide.

(b) Reduction of metal oxide/concentrated ore into free metal

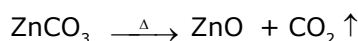
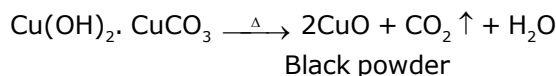
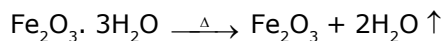
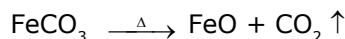
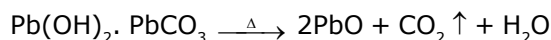
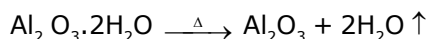
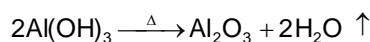
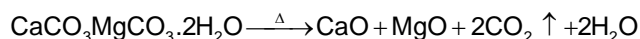
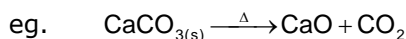
(a) **Conversion of concentrated ore into metal oxide :**

**Calcination :** (Carbonates ore)

- Calcination is carried out for carbonate, hydrated metal oxide & metal hydroxide ores.
- It is carried out in the absence of air i.e., heating in absence of air.

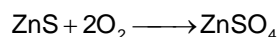
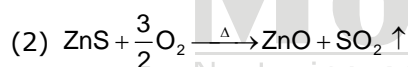
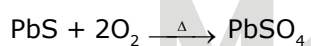
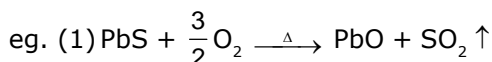


- Due to calcination ore becomes porous.
- Volatile organic impurities get evaporated



**Roasting :** In the presence of air the sulphide are heated in free supply of air below m.p. Impurities of sulphur, phosphorus, arsenic & antimony are converted into their corresponding volatile oxide & thus get removed.

Moisture & Water of crystallisation are also removed.

**(b) Reduction of Metal oxide / conc. ore into free metal .**

This can be carried out

- |                                   |   |
|-----------------------------------|---|
| (i) chemical reduction            | (ii) By self reduction or auto reduction or Air Reduction |
| (iii) Metal - displacement method | (iv) By electrolytic Reduction      (v) By amalgamation.  |

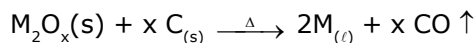
(i) & (ii) method are collectively known as Pyrometallurgy

e.g. Sn, Pb, Fe, Hg, Cu, B, Zn, (Based on Ellingham diagram)

(iii) step is called hydrometallurgy — Cu, Ag, Au are extracted

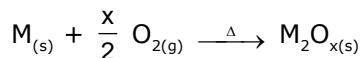
(iv) step is called Electrometallurgy, Alkali, Alkaline earth metals & Al & base electrolysis

(v) is used for Ag & Au

**(I) CHEMICAL REDUCTION :****1. Smelting i.e., carbon Reduction - Reduction of metal oxide by coke, coal & CO**

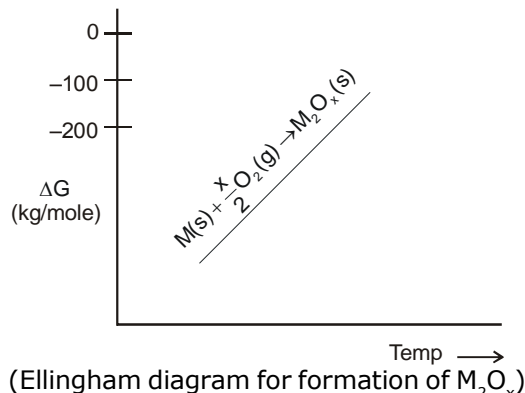
$$\therefore \Delta G = \Delta H - T\Delta S$$

If  $\Delta H$  is greater than zero then reduction will be feasible on increasing temperature i.e.,  $|T\Delta S| > |\Delta H|$

**Ellingham diagram -**

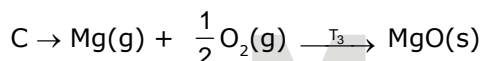
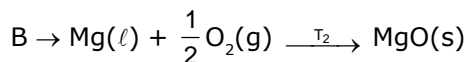
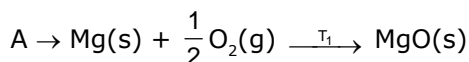
$$\Delta G = \Delta H - T\Delta S$$

$\therefore$  For forward rxn  $\Delta S < 0$

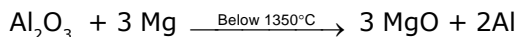
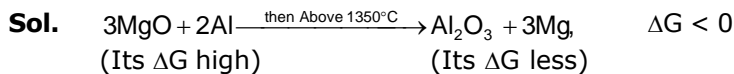
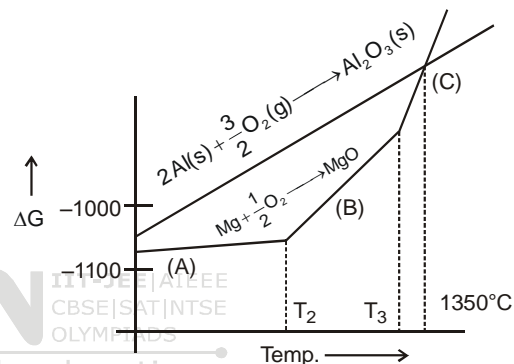


Ellingham diagram is a plot of formation of an element oxide between  $\Delta G$  &  $\Delta T$

**Ex.** Which of the following statements are true :

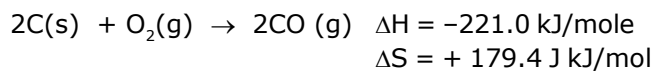


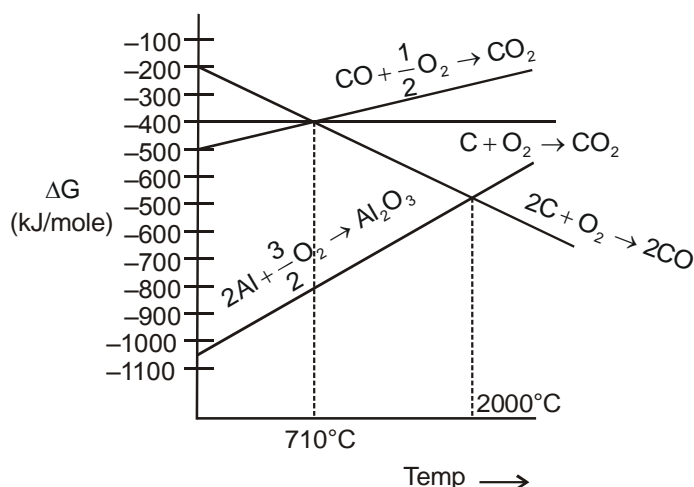
- I : Below  $1350^\circ$  Mg can reduce  $Al_2O_3$   
 II : Above  $1350^\circ$  C Mg Will reduce  $Al_2O_3$   
 III : Below  $1350^\circ$  Al can reduce MgO  
 IV : Above  $1350^\circ$  Al can reduce MgO  
 V : At  $1350^\circ$  C there is no change in free energy i.e.,  $\Delta G = 0$



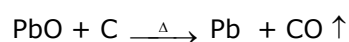
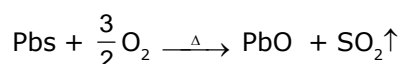
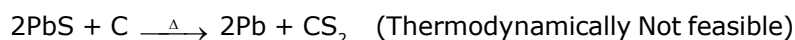
At  $1350^\circ$  C both reactions have same G  $\therefore \Delta G = 0$

To carry out smelting below  $800^\circ C$ , CO is used as reducing agent while above  $800^\circ C$ , smelting is carried out by coke.





- Aluminium can be extracted from Alumina by carbon reduction but the method is highly uneconomical because -
  - As the smelting occurs above 2000°C hence a part of the aluminium will go into vapour phase (M.P. = 2520°C)
  - At this high temperature the liberated Al will combine with the carbon & aluminium carbide will be formed.
  - $\Delta H_{\text{for}}$  of alumina is high - ve value  
 $\therefore$  It is thermodynamically more stable & reduction is more difficult
- To extract metal from sulphide ore is carried out by firstly roasting it into metal oxide & followed by its smelting. Metal sulphide or sulphide ore is not directly smelted to metal.



} Thermodynamically feasible

$$\Delta G_f \text{ of PbS} = -21.9 \text{ kcal/mol}$$

$$\Delta G_f \text{ of CS}_2 = +17.15 \text{ kcal/mol}$$

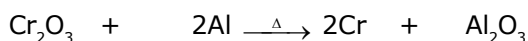
$$\Delta G_f \text{ of PbO} = -45.1 \text{ kcal/mol}$$

$$\Delta G_f \text{ of SO}_2 = -71.7 \text{ kcal/mol}$$

$$\Delta G_f \text{ of CO} = +32.8 \text{ kcal/mol}$$

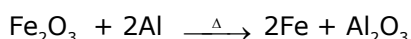
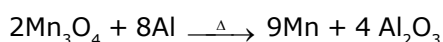
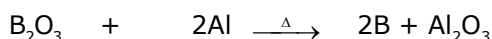
## (b) Gold Schmidt Thermite Reduction :

### Thermite : Al powder



$$(\Delta G_f = -540 \text{ kJ/mole})$$

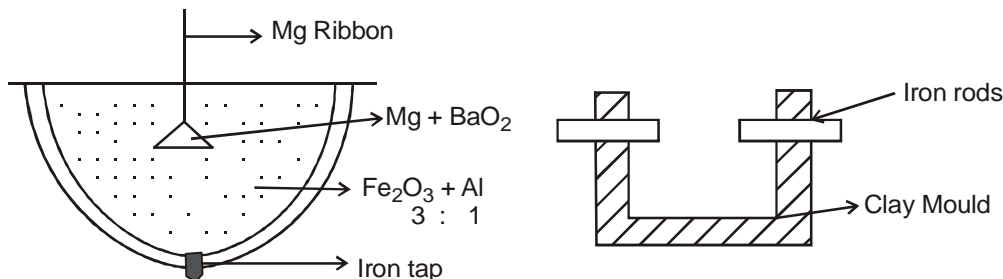
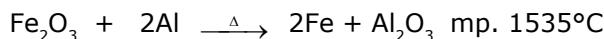
$$(\Delta G_3 = -827 \text{ kJ/mole})$$



This method is used for reduction of those metal oxides which are highly stable if they are reduced by

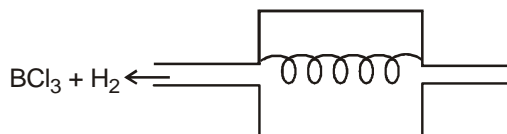
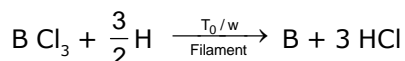
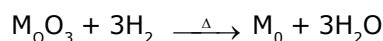
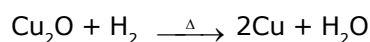
coke it will occur at very high temperature & at this high temperature the liberated metal will combine with the coke & carbide will be formed hence Al powder i.e., thermite is used

### Gold schmidt thermite Welding

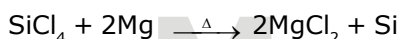


### (c) Reduction by Hydrogen :

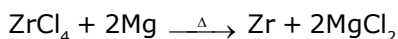
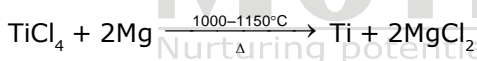
Because of inflammable nature of hydrogen its use as a reducing agent is very restricted.



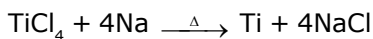
### Reduction by other metals :



Kroll process used for extraction of Ti & Zr



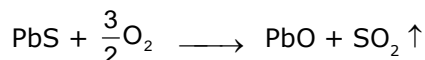
### I.M.I Process (Imperial Metal Industries)



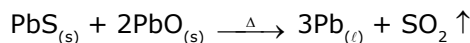
### (ii) By Self reduction or Auto reduction or Air Reduction :

This method is used for extraction of copper, lead, mercury i.e., it is used for the extraction of metal from their sulphide ores.

In this method the sulphide ore is roasted in free supply of air to its metal oxide & then air supply is cut off followed by heating by increasing temperature & metal is extracted by self reduction.

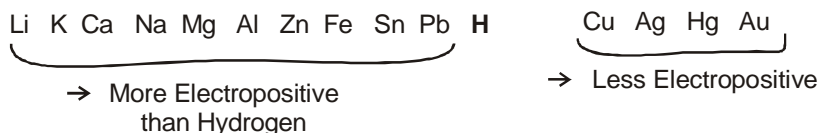


Now air supply is cut off followed by heating



Self reduction is responsible for acid rain than roasting because  $\text{SO}_2$  dissolves in air, (3927cc  $\text{CO}_2$  in 1000cc of  $\text{H}_2\text{O}$ )

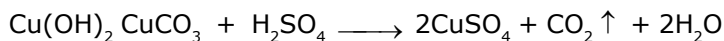
**(iii) By Metal Displacement Method or By Hydrometallurgy :**



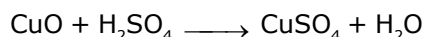
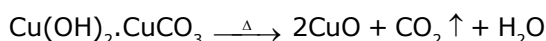
In this method the concentrated ore is treated/ leached with specific chemical reagent that converts the ore into water soluble salt. Now, on adding more electropositive metal into the aqueous salt solution the metal (less electro positive) is displaced

e.g.

Extraction of Copper from Malacite :

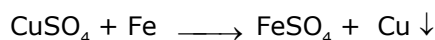


or



$\text{H}_2\text{SO}_4 \Rightarrow$  leaching agent, it leached out Cu as  $\text{CuSO}_4$

Now, on adding more electropositive metal :



(Reducing agent)

$$\therefore E^\circ_{\text{Cu}^{++}/\text{Cu}} = +0.34$$

$$E^\circ_{\text{Fe}^{++}/\text{Fe}} = -0.40$$

$$\therefore E^\circ_{\text{Cell}} = 0.74 \Rightarrow \Delta G < 0$$

- Iron is found to be an impurity in the copper ores hence if Zn is added to extract copper, iron will also be displaced along with copper & that is why iron is used.
- Both metals which extracted & by which we extracted are water insoluble

**(iv) Electro Metallurgy :** The metal is extracted by passing electricity into its fused salt or in aqueous solution.

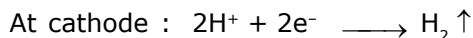
**Extraction of sodium :**

$\Rightarrow$  By electrolysis of Aq. NaCl solution :





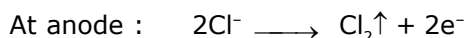
- On passing electricity



$$\therefore E^\circ_{\text{H}^+ / 1/2\text{H}_2} = 0; \Delta G = -nFE^\circ$$

$$E^\circ_{\text{Na}^+ / \text{Na}} = -2.7 \text{ V}; \Delta G = -nFE^\circ$$

$\therefore \text{Na}^+$  does not discharge at cathode

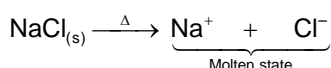


$$E^\circ_{1/2\text{Cl}_2 / \text{Cl}^-} = -1.36 \text{ Volt}$$

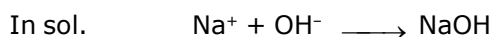
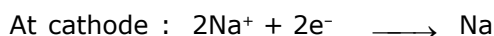
$$E^\circ_{1/2\text{O}_2 / \text{OH}^-} = -0.44 \text{ V}$$



$\Rightarrow$  By electrolysis of fused NaCl :



On Passing electricity

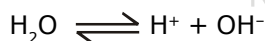


### ***In general :***

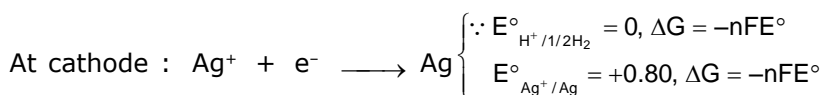
Alkali metals, Alkaline earth metals & Aluminium are extracted by electrolysis of their fused salt or molten salts. Metal is not extracted by electrolysis of their aq. salt solution because at cathode hydrogen gas is liberated.

$\Rightarrow$  Extraction of Silver :

- By electrolysis of Aqueous  $\text{AgNO}_3$  solution.

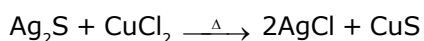


On passing electricity,

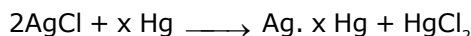


**Conclusion :** The metals which are less electropositive than Hydrogen like Cu, Ag, Au can be obtained by electrolysis of their aqueous salt solution.

- (v) **By Amalgamation :** (Extraction of Ag & Au by using Mercury) or **Refining Method**



Now, on adding excess of Mercury :

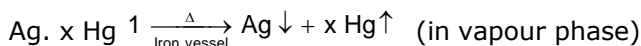


or



Native ore      Amalgam

Now the silver amalgam is heated in a vessel made of iron.



Mercury does not form amalgam with iron & platinum therefore iron vessel are used.

**Flux** : Flux are those substances which combine with acidic or basic impurities & form fusible mass called slag.

Acidic flux -  $\text{SiO}_2$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{B}_2\text{O}_3$  or  $\text{Na}_2\text{B}_{11}\text{O}_7$

Basic flux -  $\text{CaO}$ ,  $\text{MgO}$

Slag - It is a fusible mass,

**Characteristic of slag :**

- (i) It is obtained as a fusible mass.
- (ii) It is lighter & immiscible with the extracted the molten metal & hence it can easily be skimmed off.
- (iii) Its m.p. is less than the extracted metal.
- (iv) It prevents air oxidation of the molten metal.

• **Refining of impure metal :**

(A) By physical Methods :

- (a) liquation
- (b) Distillation
- (c) Zone refining

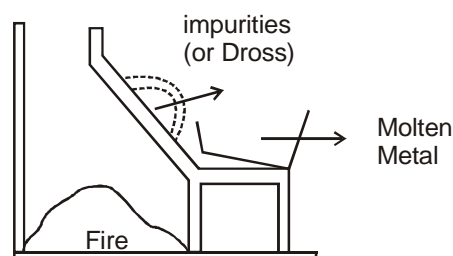
(B) By Chemical Methods

- (a) Oxidation
- (b) Poling
- (c) Vapour Phase Refining
- (C) By Electrolytic Refining

**(A) By Physical Method :**

**(a) Liquation Method :**

|            |       |        |
|------------|-------|--------|
| Impurities | Metal | M.P.   |
|            | Sn    | 232°C  |
|            | Fe    | 1535°C |
|            | Mn    | 1244°C |
|            | W     | 3380°C |

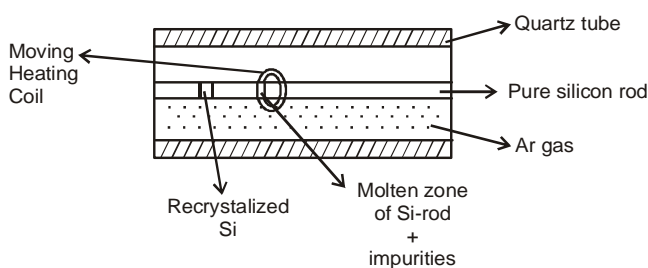
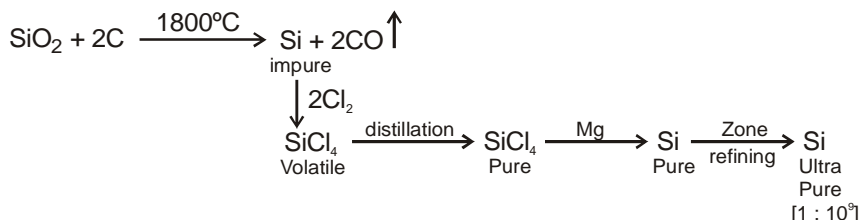


This method is used for refining of those metal which have very low m.p. in comparison to impurity present in them.

e.g.  $\rightarrow$  Sn, Pb, Hg, Bi, Zn

(b) **Distillation Method :** It is used for refining of those metals which are volatile & hence it is used for refining of Zn, Cd, Hg (i.e., is of filled d orbital metal)

(c) **Zone Refining :** (Si, Ge, Pb, B, Ga, In)



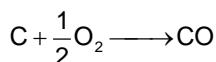
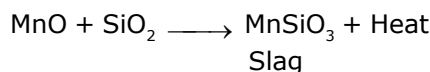
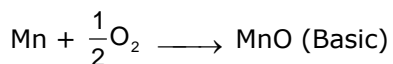
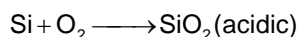
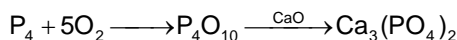
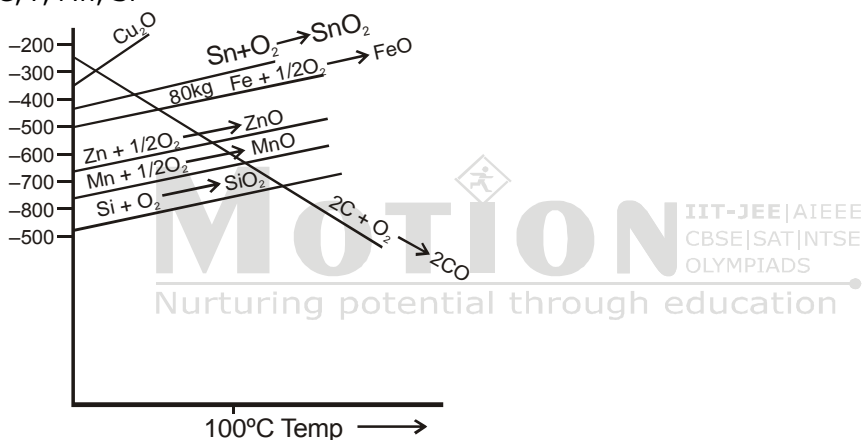
**Concept :** Impurities are more soluble in the melt than in the solid state.

(B) **By Chemical Methods :**

(a) **Oxidation : (Fe, Sn, Pb)**

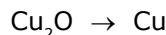
eg. **Pig iron :** M.P. 1080

**Impurities :** C, P, Mn, Si



This method is used for the refining of metals in which impurities are more oxidisable than metal itself. When impurities oxidise they are converted into either volatile oxides or non volatile oxides. Non-volatile oxides are removed either by slag formation or by removing their skum. Oxidation is known by various names : baseremization (Fe), Cupellation (Ag), Softening (Pb) or Puddling (for iron), tossing (for iron)

- (b) **Polling** : When along with impurities the metal to be refine is also oxidised part then this method is used. In this method the molten impure metal is steared with green wood log, The hydrocarbons released from the log reduce metal oxide into metal while impurity oxides are not reduced. This method is used for refining of Cu & Tin. In both metals during poling iron get oxidised into FeO which in turn is oxidised into  $\text{Fe}_2\text{O}_3$  while in case of Sn,  $\text{SnO}_2$  is reduced to tin (Sn) & in case of Cu copper (I) oxide i.e., cuprous oxide is reduced to Cu,



- (c) **Vapour Phase Refining** : Impure metal is allowed to react with a suitable reagent such that a volatile unstable compound is formed & then the compound is decomposed to pure free metal when it is subjected to heat.

- Mond's Process : used for refining of Ni



- (C) **By Electrolytic Refining** :

**Anode** : Impure metal

**cathode** : Pure metal

**Electrolyte** : Aq. salt sol. of metal/fused metal salt + Acid

**Anode Mud** : Metals which are less electropositive than the metal to be refined.

In electrolyte : More electropositive metals are found.

eg. in Cu : Ag, Au, Fe, Zn

In electrolyte

**MOTION** **TIN** IIT-JEE|AIEEE  
CBSE|SAT|NTSE  
OLYMPIADS  
Nurturing potential through education

**Important Ore** : Tin stone or Cassiterite  $\text{SnO}_2$  (diamagnetic)

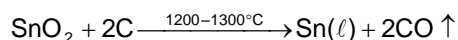
Extraction :

### I. Concentration or Dressing or Beneficiation of Ore :

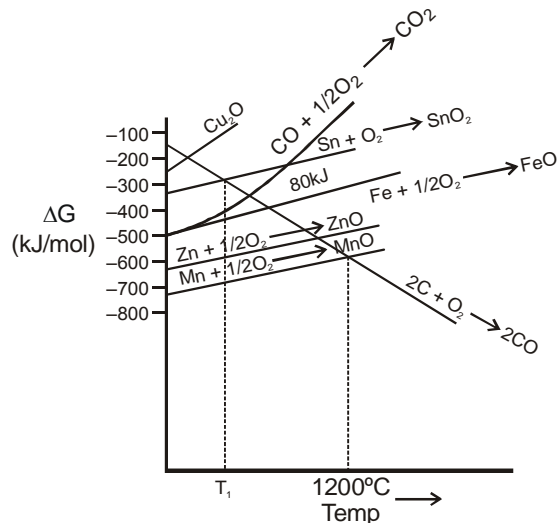
- By Gravity separation
- By Magnetic separator

### II. Extraction of crude Metal from concentrated ore :

- Calcination
- Reduction of metal oxide into free metal  $\Rightarrow$  Smelting



Coke reduce  $\text{SnO}_2$  above  $1200^\circ\text{C}$  while  $\text{CO}$  is not used above  $1200^\circ\text{C}$ . If Fe impurities is not present then coke can reduce it also at  $T_1$  temp.



III. **Refining** : Thus obtain Tin has impurities of Mn (m.p.  $1244^\circ\text{C}$ ), Fe ( $1535^\circ\text{C}$ ) & W ( $3380^\circ\text{C}$ ) while M.P. of Sn is  $232^\circ\text{C}$

a  $\rightarrow$  *liquation* : Impurities remain in the form of Dross.

b  $\rightarrow$  *Polling*

(C) **Electrolytic Refining :**

**Anode :** Impure Tin

**Cathode :** Pure Tin

**Electrolyte** Aq.  $\text{SnSO}_4$  sol. + dil.  $\text{H}_2\text{SO}_4$

**In Anode Mud** : CO (It is obtained as biproduct in metallurgy of Sn)

**In electrolyte** : Fe & Mn

**Ex.** In which metal's metallurgy tungston is obtained as biproduct ?

**Sol.** Tin

## LEAD

**Imprtant Ores** : Galena ( $\text{PbS}$ ), Cerussite ( $\text{PbCO}_3$ ), Anylesite ( $\text{PbSO}_4$ )

**Extraction of lead from galena :**

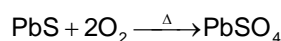
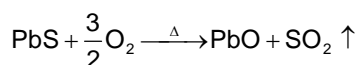
I. Concentration or Dressing or Beneficiation of ore : Froth floatation in presence of NaCN because PbS is always with Zns

II. Extraction of Crude Metal from concentrated ore :  
Lead is extracted from concentrated galena by two methods

(A) **By self Reduction or Air Reduction or by Auto Reduction** : when galena is rich in lead content / PbS content.

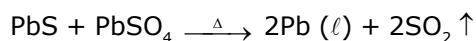
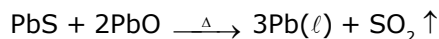
(B) **By Carbon reduction** : When galena is poor in lead content / PbS content.

**A :** **By Self Reduction** (when ore is rich in lead content)

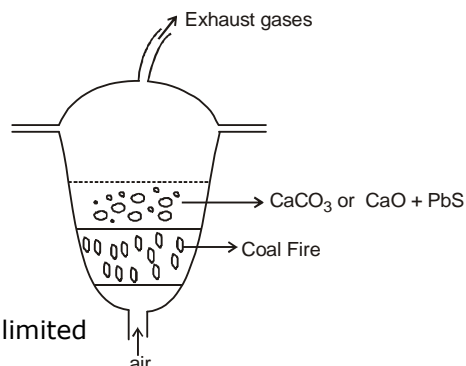
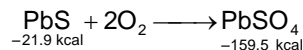
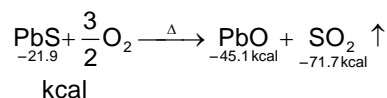


Now, air supply is cut off followed by heating of reasted mass with or without more concentrated

Galena, by raising temp. ( $\Delta G = \Delta H - T\Delta S$ )



**B : By Carbon Reduction** - It is completed in two stages.



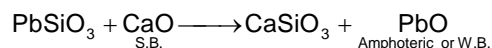
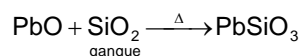
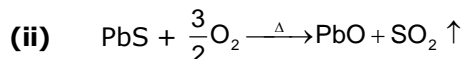
This method is completed in two stages :

**I<sup>st</sup> stage :** Conversion of PbS into PbO by heating it into limited supply of air in a furnace called "Sinterer",

As the formation of PbSO<sub>4</sub> is thermodynamically more feasible hence the concentrated galena is roasted in limited supply of air in sinterer.

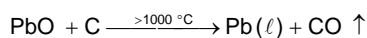
**Role of CaCO<sub>3</sub> or CaO :**

(i) Prevents the formation of lead sulphate because it diffuses the passed air into it

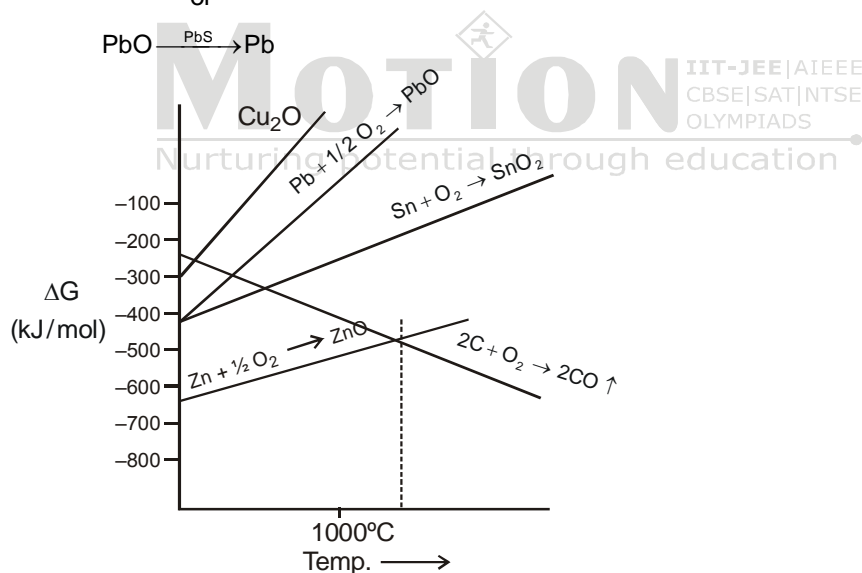


Thus by roasting of PbS, lead oxide is obtained. It regenerates PbO from lead silicates if it is formed

**II<sup>nd</sup> stage : Smelting or Carbon Reduction of PbO**



or



**III. Refining :** Thus obtained lead contains impurities of Cu, Ag, Au, Zn, As, Sb, Bi & Sn.

**a. Liquation** — It removes mainly impurities of Cu.

**b. softening** — Removal of impurities by air oxidation.

Impure lead obtained after softening is called Argentiferous lead which contains 1 - 2% Ag.

**c. Desilverization of Argentiferous lead :** It completes by two processes

**(i) Pattinson's Process :** In this method by repeated Fractional crystallisation of lead from argentiferous lead is carried out till the concentration of silver raised to 2.6% at which it forms unreacted mixture with lead that melts at  $303^{\circ}\text{C}$  while m.p. of pure lattice is  $327^{\circ}\text{C}$

**(ii) Parke's Process :** It is based on principle of solvent extraction, Distribution law, partition law.

**Solvent used :** Molten zinc.

The characteristics of Zinc to be used as a solvent

(a) Silver is about 300 times more soluble in Zn than Pb

(b) Zn is lighter than lead

(c) Zn is immiscible with lead

(d) M.P. of Zn is  $420^{\circ}\text{C}$  and that of Pb is  $327^{\circ}\text{C}$

(e) Zn is volatile while Ag is non-volatile.

**d. Electrolytic Refining by Bett's Process :**

**Anode :** Impure lead

**Cathod ;** pure lead

**Electrolyte :** Molten/ Fused ( $\text{PbSiF}_6 + \text{H}_2\text{SiF}_6 + \text{Gelatin}$ )

**Anode Mud :** Cu, Ag, Au

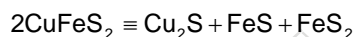
**In Electrolyte :** Zn, Sn, Bi

**Plumbosolvency :** Dissolution of Pb into water in presence of air. plumbosolvency increases in the presence of  $\text{CH}_3\text{COOH}$ ,  $\text{NO}_3$ ,  $\text{NO}_2$

To prevent plumbosolvency in electrolytic refining of lead, molten salt is used.

## COPPER

**Important Ores :** Native Ore, Sulphide ore - Chalcopyrite ( $\text{CuFeS}_2$ )



Chalcocite or copper glance :  $\text{Cu}_2\text{S}$

Bornite or Peacock Ore ;  $\text{Cu}_5\text{FeS}_4$  ( $2\text{CuFeS}_4 \equiv 5\text{Cu}_2\text{S} + \text{FeS} + \text{FeS}_2$ )

• Oxide ore

• Carbonate ore :

Malacite (green)  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$

Azurite (blue)  $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$

Copper can be extracted by anyone of the following methods.

(i) By self Reduction or by auto reduction.

(ii) By Hydrometallurgy

(iii) By carbon Reduction

(iv) By electrolysis of aq. copper sulphate

(v) Reduction of copper oxide by hydrogen.

• Self Reduction or Auto reduction is the commercial method of reduction

**Extraction of Copper from chalcopyrite by self Reduction or Auto Reduction or Air Reduction :**

**I. Concentration :** By froth floatation Process.

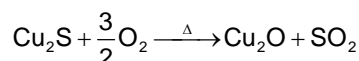
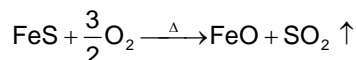
**II. Extraction of Crude Metal from concentrated ore.**

A. Roasting :

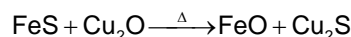


B. Smelting :

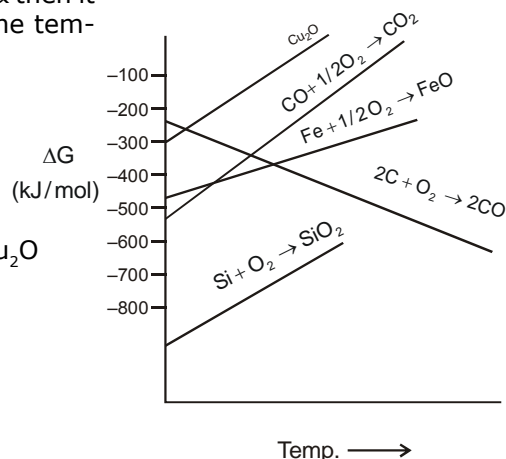
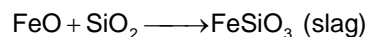
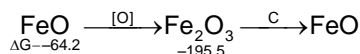
The roasted mass is mixed with silica & some coke & then it is heated in presence of air in a blast furnace in the temperature range of 1400 – 1450° C



remaining FeS which is not Oxidised react. with  $\text{Cu}_2\text{O}$

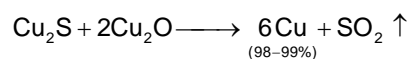
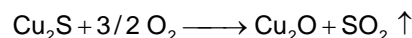
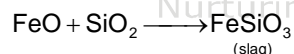
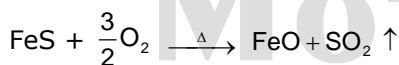
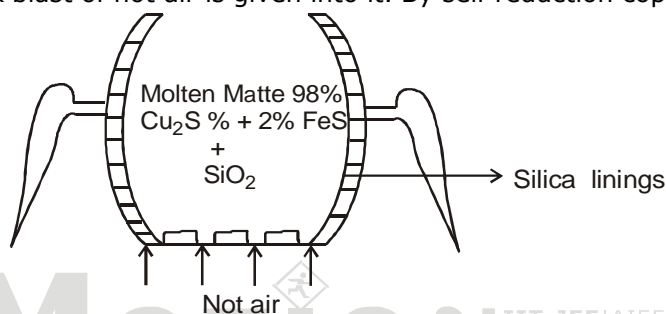


Silica removes FeO in form of slag.

**Role of coke :**

When smelting is over the furnace contains 98% of  $\text{Cu}_2\text{S}$  copper (I) sulphide & 2% FeS & this molten mass is called matte over which layer of slag exist.

**(c) Bassemerization :** The molten matte is mixed with some silica & it is taken into Bassemer converter having silica linings & blast of hot air is given into it. By self reduction copper is obtained.



Blister copper because it escapes  $\text{SO}_2$ ,  $\text{N}_2$  &  $\text{O}_2$

Here copper (II) oxide is not formed because it is thermodynamically not feasible.

Thus obtained copper is called Blister copper & it is 98 – 99% pure. Blister appearances are due to escape of  $\text{SO}_2$ ,  $\text{N}_2$  &  $\text{O}_2$  from molten copper.

**III. Refining :** Blister copper contains impurity of Ag, Au, Fe, Se, Te, Pt & Sb

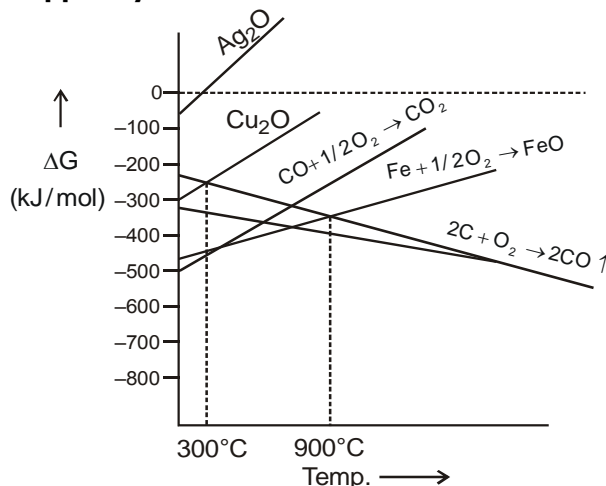
a. Poling



- b.** Electrolytic Refining ;  
 Anode : Impure copper  
 cathode ; Pure copper  
 Electrolyte ; Aq.  $\text{CuSO}_4$  sol. + dil.  $\text{H}_2\text{SO}_4$   
 In Anode Mud/ Slime : Ag, Au, Pt, Se, Te  
 In Electrolyte : Fe  
 (Sb during oxidation it completely removes)

The main source of selenium (Se) & tellurium (Te) is Anode mud obtained from Cu refining.  
 Se has photoreceptor property hence it is used in xerox machine. Se is also used as decolouriser for glass.

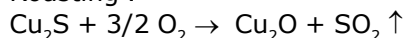
### Extraction of Copper by carbon Reduction from Chalcocite.



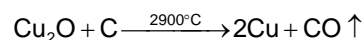
### I. Concentration : By Froth Floatation

### II. Extraction of Copper from conc. ore

#### (a) Roasting :



#### (b) Smelting

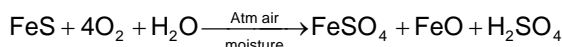
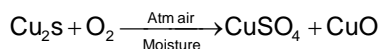


⇒ Both CO & C can reduce  $\text{Cu}_2\text{O}$  into Cu.

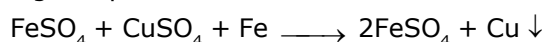
### Extraction of Copper by Hydrometallurgy

- From Malachite (discussed in discussion of hydrometallurgy)
- From Chalcopyrite ( $\text{CuFeS}_2$ )

Chalcopyrite ore is left open in presence of atmospheric air & moisture for a year long which oxidises copper (I) Sulphide into copper sulphate & FeS into  $\text{FeSO}_4$ . Now, aq. solution of  $\text{CuSO}_4$  &  $\text{FeSO}_4$  scrap iron / Fe is added copper is displaced.



On adding scrap Fe/Fe :



### Extraction of copper by electrolysis of Aq. $\text{CuSO}_4$ solution :

At cathode copper is liberated

Extraction of Copper by Reducing  $\text{Cu}_2\text{O}$  with Hydrogen :

Coke, CO, CS can reduce  $\text{Cu}_2\text{O}$  to Cu.

## SILVER

**Ores :** (a) Native ore

(b) Sulphide Ores : (i) Argentite or silver glance ( $\text{Ag}_2\text{S}$ )  
(ii) Pyrargyrite or Ruby silver  $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$

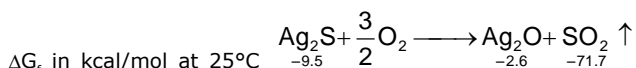
(c) Halide Ores : Chorargyrite or Horn silver ( $\text{AgCl}$ )

(d) As a by Product :

- From ext of Pb.
- From ext of Cu
- From ext. of Zn.

### Extraction of Silver :

## Feasibility of extraction of Ag by self Reduction from silver glance



It is very slow reaction. By increasing temperature  $\Delta G$  of  $\text{Ag}_2\text{O}$  becomes +ve

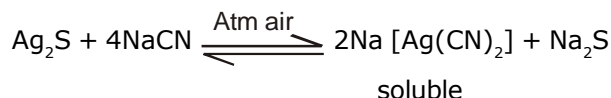
∴ It is not thermodynamically feasible.

- Extraction of Ag by self reduction from silver glance or argentite is thermodynamically not feasible because
  - (i) by increasing temp. the roasting of  $\text{Ag}_2\text{S}$  is thermodynamically not favourable.
  - (ii) The content of  $\text{Ag}_2\text{S}$  is too poor to carry out self reduction.

### Extraction of silver by Cyanidation or Mac Arthur forest method

**From Argentite or silver glance :**

- (i) concentration
- (ii) Concentrated silver glance / Argentite is leached with 0.4 to 0.64 aq. NaCN solution which leached out (converts) Ag into soluble Cyno complex in presence of air.



The role of air is to oxidise  $\text{Na}_2\text{S}$  so that reaction proceed in the forward direction.

**From native Ore :** Native ore is leached with 0.4 – 0.6% aq. NaCN solution in presence of air & soluble cyno complex is formed.

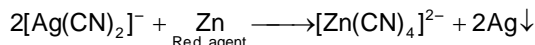


The role of oxygen is to oxidise Ag

**From Horn silver :**



Now on adding Zn powder into the soluble complex



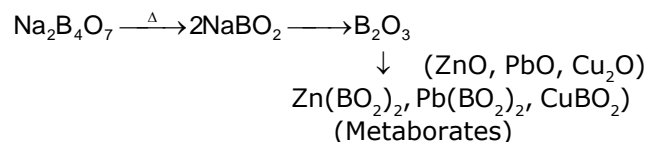
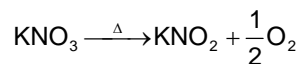
In place of Zn powder copper is not used because of its less reducing character.

**By Amalgamation :** (Already discussed)

**Refining :** Pb, Zn, Cu, Au are impurities.

- (i) Here two flux are used : Potassium Nitrate or Borax Ag is refined by using flux of Pot. Nitrate ( $\text{KNO}_3$ ) or Borax. If  $\text{KNO}_3$  is used it oxidises the impurities or if Borax is used it will remove impurities in the form of

meta borates



- (ii) **Cupellation** : Air is blown into molten impure Ag which oxidises Pb into litharz (PbO) & which is blown away by air pressure.

When Ag content is more then this method is used unless Park's Method is used.

### Cupellation

Removal of lead as an impurity from Ag by air oxidation

### Park's

Removal of Ag as an impurity from Pb by using solvent extraction

- (iii) **Electrolytic Refining :**

Anode : Impure Ag  
 Cathode : Pure Ag  
 Electrolyte : Aq. AgNO<sub>3</sub> + dil. H<sub>2</sub>SO<sub>4</sub>  
 In Anode mud/slime : Au  
 In Electrolyte : Cu, Zn

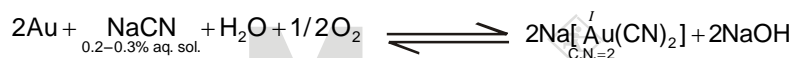
## GOLD (Au)

**Ores** : Native Ore (in form of Plaur gold & in form of Vein gold  
gold trapped in rocks)

**As a by Product** : From ext. of Cu  
 From ext. of Pb  
 from ext. of Ag

### Extraction of Gold :

- (ii) By Cyanidation or By Mac. Arthur Forest Method :



On Adding zn powder In it



### Refining :

By electrolytic Method :

Anode : Impure Au  
 Cathode : pure Au  
 Electrolyte : Aq. sol. of AuCl<sub>3</sub> + dil. HCl  
 In Anode Mud :  
 In Electrolyte : Ag

**Fineness or Purity of Gold** : 24 carats = 100% gold

For making gold jwelleries it is alloyed with Ag & Cu

### In Extraction of Gold

(I) concentration : By Panning based on principle of Gravity separation

Au = 19.3 gm/cc

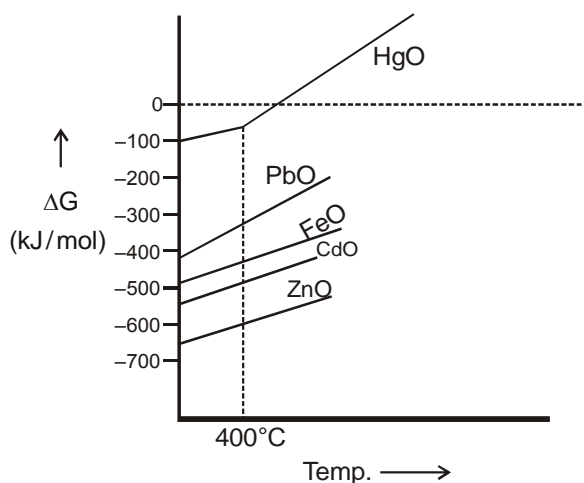
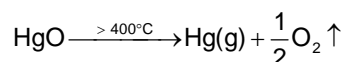
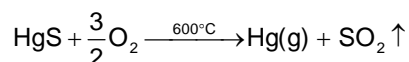
SiO<sub>2</sub> = 2.5 gm/cc

**MERCURY****Ores :** • Native Ore

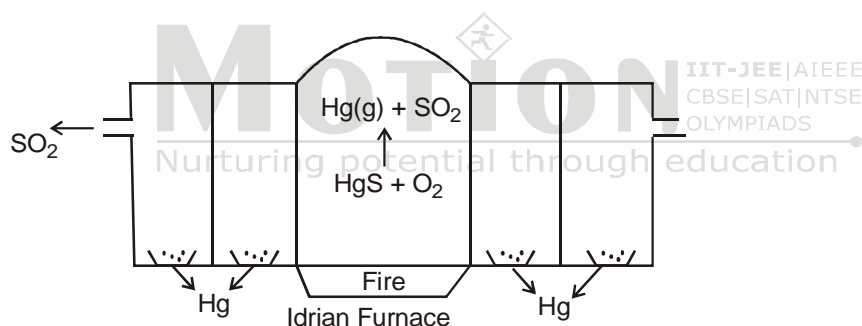
- Cinnabar (HgS) : Bright Red coloured

**Extraction from Cinnabar**

(i) Concentration : By Froth Floatation Process

(II) Extraction of Hg from concentrated Ore : By self Reduction or Auto Red<sup>n</sup> or Air Reduction

Self Reduction is carried out in

**"Idrian Furnace"**

III Refining : Now impurities are : Zn, Cd, Pb, Fe

Mercury is refined by

(a) Air oxidation

(b) Now impure mercury is treated with 5%  $\text{HNO}_3$  to remove left impure metal oxides into soluble nitrates

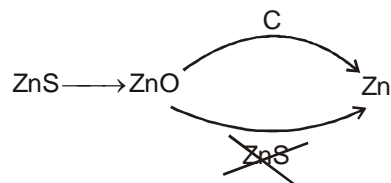
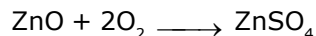
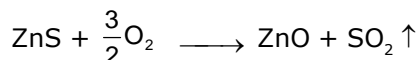
(c) Lastly mercury is refined by vacuum distillation

**ZINC**

**Ore :** Zinc blends : ZnS  
 Calamine : ZnCO<sub>3</sub>  
 Zincite : ZnO

**Extraction of Zinc from Zinc Blends :**

- (i) Concentration : By Froth Floatation  
 (ii) Extraction of Zinc from concentrated ore :  
 (a) Roasting :

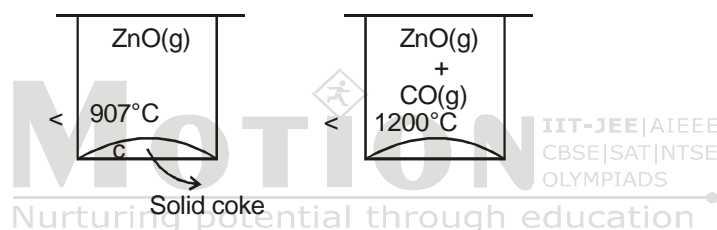
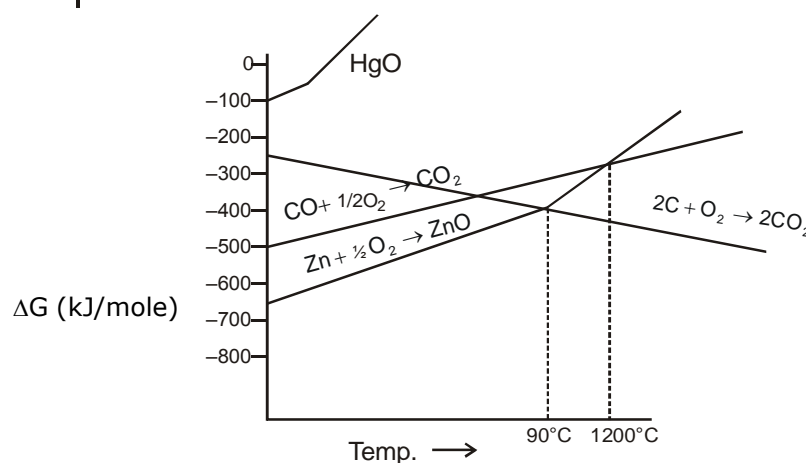


To prevent the formation of ZnSO<sub>4</sub>, ZnS is roasted in limited supply of air. So that only ZnO can be formed.

(b) smelting :

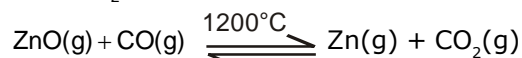
Zn : M.P. 420°C  
 B.P. 907°C

ZnO sublimes at 400°C



∴ CO is preferred.

- Zinc is obtained by reduction of ZnO only above 907°C.
- As ZnO sublimes above 400°C therefore its reduction above 907°C will be more efficiently be carried out by CO.
- To obtain zinc from gaseous product cooling is carried out but during cooling a part of zinc gets reoxidised into ZnO.
- To prevent reoxidation of zinc during its isolation from gaseous oproduct
  - (i) Zinc is obtained by shock colling or rapid cooling
  - (ii) Reduction is carried out in presence of excess of coke. so that the formed CO<sub>2</sub> can be reduced into CO.



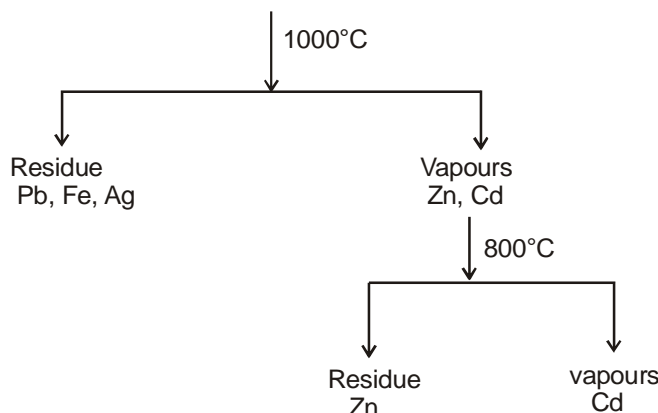
Thus obtained zinc is called spelter which contain impurities of Cd, Ag, Pb & Fe, Ag.

**III Refining :**

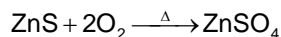
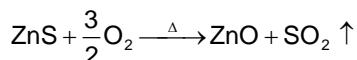
In spelter 99% zinc is pure from this zinc (pure) is obtained by vacuum distillation.

spelter (Zn, Cd, Pb, Fe, Ag)

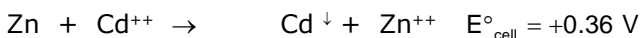
B.p. 907°C 765°C 1751°C 2750°C 2155°C



- Extraction of zinc By electrolysis of Aq.  $\text{ZnSO}_4$  solution :  
from zinc Blende :
- (I) Concentration : By Froth Floatation :
- (II) Ext. by Electrolysis of  $\text{ZnSO}_4$  solution.
- (A) Roasting - Free supply of air (because to make  $\text{ZnSO}_4$ )



- (B) Electrolysis of Aq.  $\text{ZnSO}_4$
- The roasted mass is leached with dil.  $\text{H}_2\text{SO}_4$  to convert it into  $\text{ZnSO}_4$
- Zn powder is added into aq.  $\text{ZnSO}_4$  solution to remove impurities of Cd.
- Now electrolysis of aq.  $\text{ZnSO}_4$  is carried out by using Al cathode and Pb anode.



- Ex.** In extraction of zinc by electrolysis of Aq.  $\text{ZnSO}_4$  solution from zinc blends, why zinc powder is added.
- To reduce ZnO
  - for self reduction.
  - To remove impurities of Cd
  - To ppt. Cd

**Sol.** c,d

**Ex.** In this, in electrolysis what metals are used for anode & cathode ?

**Sol.** Cathode : Aluminium (Al)

Anode : Lead (Pb)

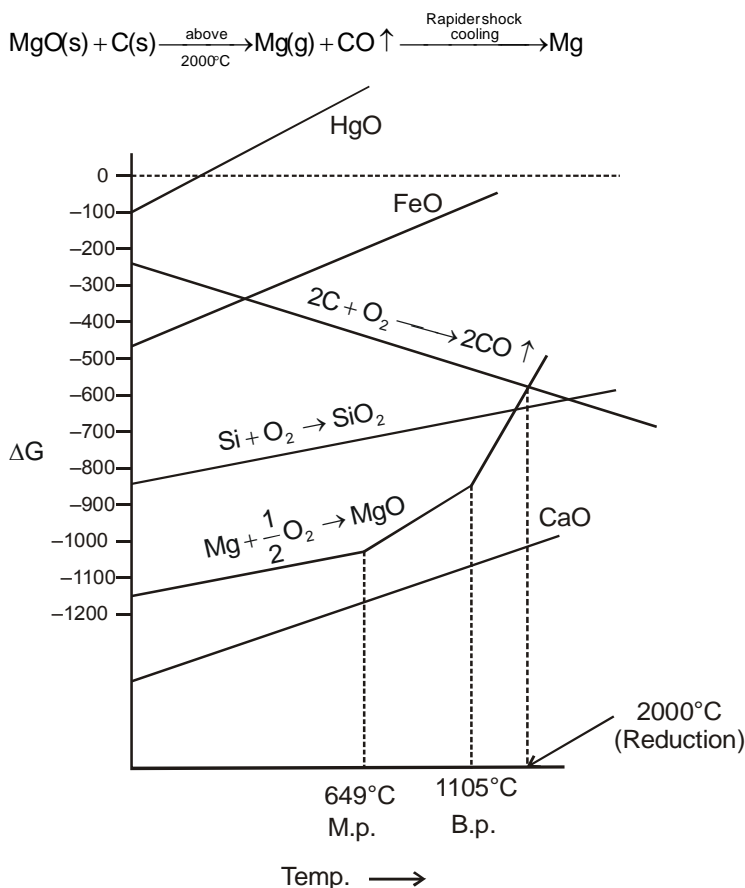
**MAGNESIUM**

**Sources / Ores :** Magnesite :  $\text{MgCO}_3$  ,  
Dolomite :  $\text{CaCO}_3 \cdot \text{MgCO}_3$   
Carnallite :  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$   
Epsom's salt :  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

**Extraction**

From Magnesite :

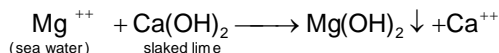
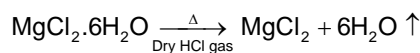
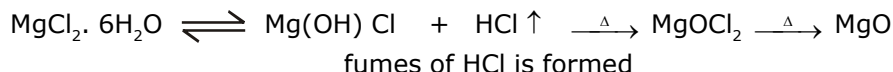
- Calcination :  $\text{MgCO}_3 \xrightarrow{\Delta} \text{MgO} + \text{CO}_2 \uparrow$
- Smelting or Carbon Reduction

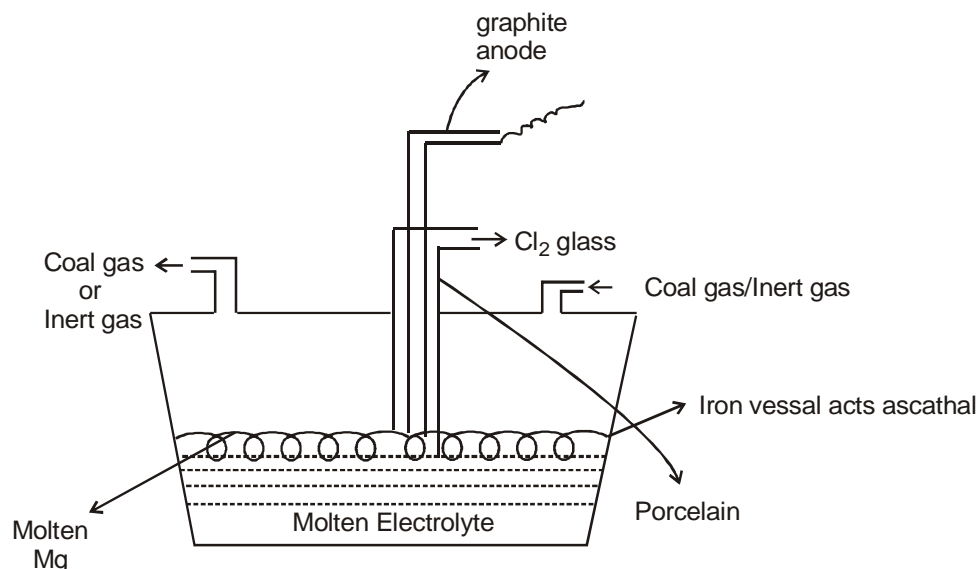


Extraction of Mg by Pidgeon Process ;

**Extraction of Mg by Electrolytic Reduction of  $\text{MgCl}_2$  : By Dow's Process**

It is completed in two steps

**Step I : Isolation of  $\text{MgCl}_2$  (Anhydrous  $\text{MgCl}_2$ ) from sea water****By Dow's sea water process**Conversion of  $\text{Mg(OH)}_2$  into  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ Conversion  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  into anhydrous  $\text{MgCl}_2$ If  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is heated in absence of dry HCl to make Anhydrous

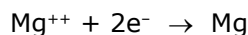
**Step II:** Electrolysis of fused  $\text{MgCl}_2$ 

Coal gas is continuously passed because Mg has great affinity towards  $\text{O}_2$ ,  $\text{N}_2$  etc. Impurities are of more electro positive metals (Mg has less electropositive than Na and Ca).

**Electrolyte :** 35%  $\text{MgCl}_2$  + 50%  $\text{NaCl}$  + 15%  $\text{CaCl}_2$

M.P. of the electrolyte :  $700^\circ\text{C}$  under this composition.

At cathode :



At Anode



impurities are of more electropositive metals (Mg has less electropositive than Na & Ca)

**ALUMINIUM**

**Ores :** Bauxite :  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$   
Cryolite :  $\text{Na}_3\text{AlF}_6$   
Corundum :  $\text{Al}_2\text{O}_3$

Extraction of Al

It completes in three steps :

Step I : concentration or Purification of Bauxite

Step II : Electrolytic Reduction of Alumina

Step III : Refining of Impure Aluminium

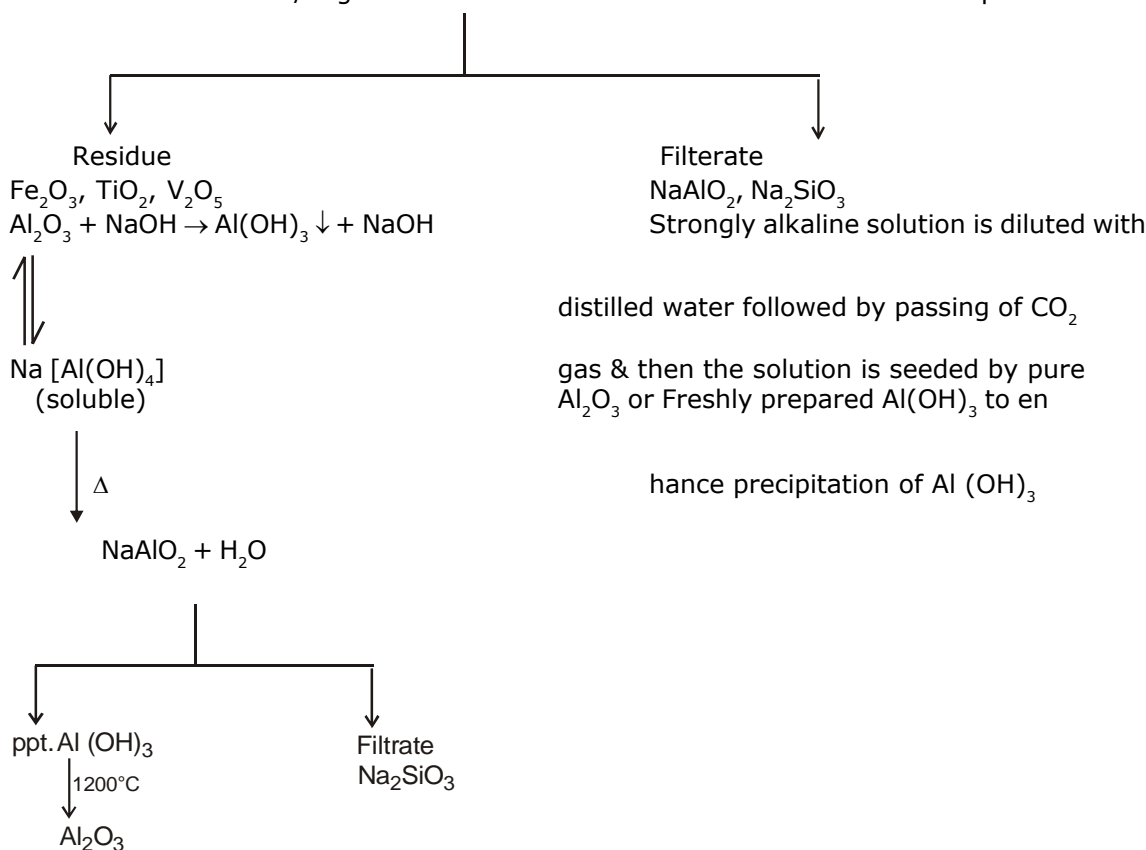
**Step I :** Concentration or purification of Bauxite :

**(A) By Bayer's Process :** It is used for the purification of red Bauxite by leaching with sodium hydroxide.

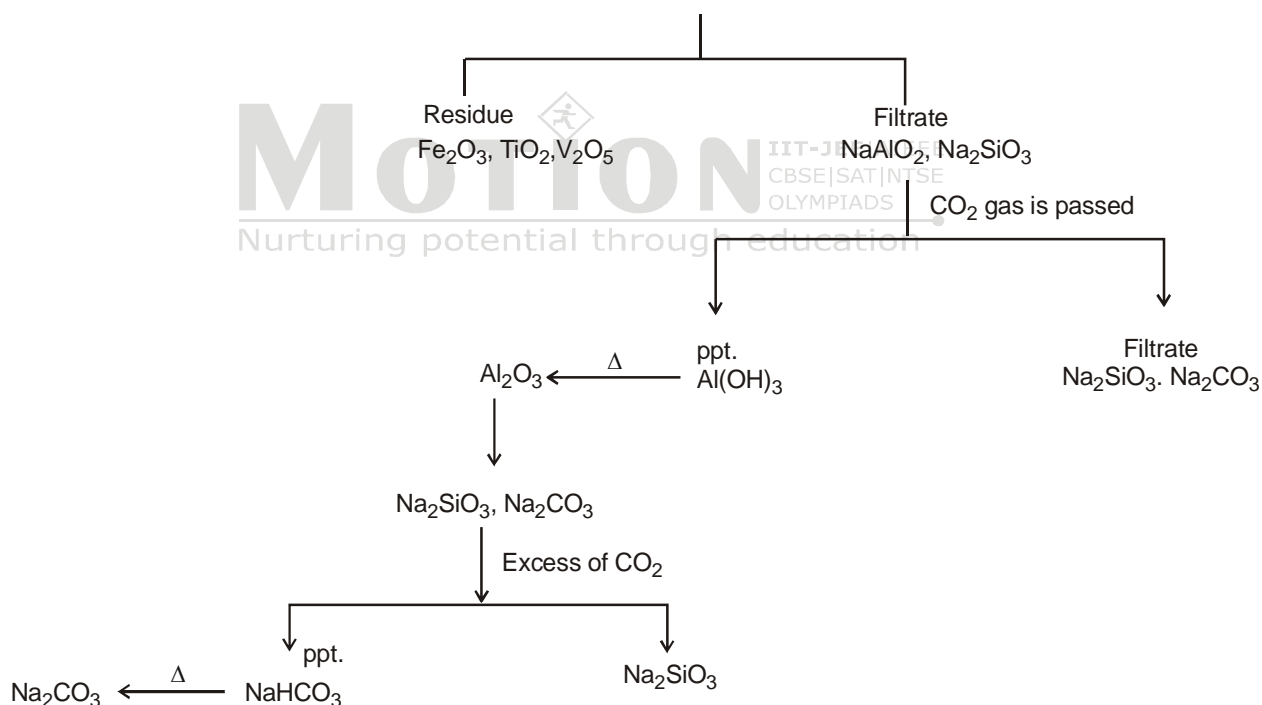
Red Bauxite contains :  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$  & 0.2 – 0.3 %  $\text{V}_2\text{O}_5$  due to the presence of  $\text{Fe}_2\text{O}_3$  change transfer phenomena takes place in  $\text{Fe}_2\text{O}_3$  Bauxite colour is red.



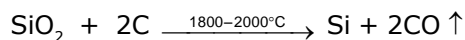
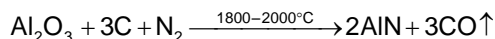
Red Bauxite is leached/ digested with conc. NaOH at 200 – 250°C at 35 atm pressure and filtered.



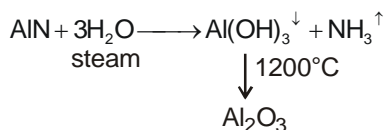
**(B) By Hall's Process :** - It is also used for purification of red Bauxite. Solid Red Bauxite is fused with solid sodium carbonate Na<sub>2</sub>CO<sub>3</sub> & then fused mass is extracted with water & filtered



- (C) **By Serpek's Method** : This is used for purification of white Bauxite (that has impurity mainly of silica). White Bauxite is mixed with coke & it is heated in presence of  $N_2$  gas in temperature range of  $1800^\circ - 2000^\circ C$



Now, AlN is treated with steam :



**Note** : Only Bayer's process comes under leaching because in leaching aq. reagent is used & in other two process it is fused.

### Step II : Electrolytic Reduction of pure Alumina by Hall Heroult's Process :

M.P. of Al :  $660^\circ C$

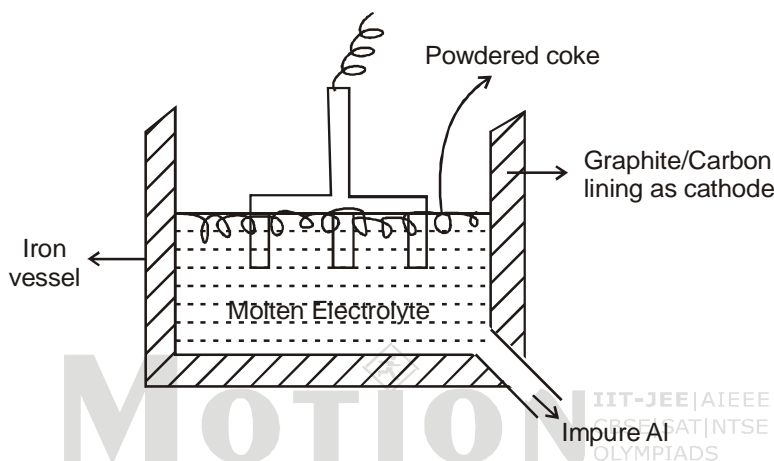
M.P. of  $Al_2O_3$  :  $2000^\circ C$

B.P. of Al :  $2467^\circ C$

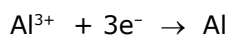
$Al_2O_3$  is not good conductor

Electrolyte :  $85\% Na_3AlF_6 + 5\% AlF_3 + 5\% CaF_2 + 5\% Al_2O_3$

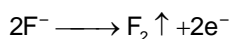
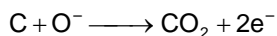
M.P. of electrolyte under this composition :  $950^\circ C$



At cathode

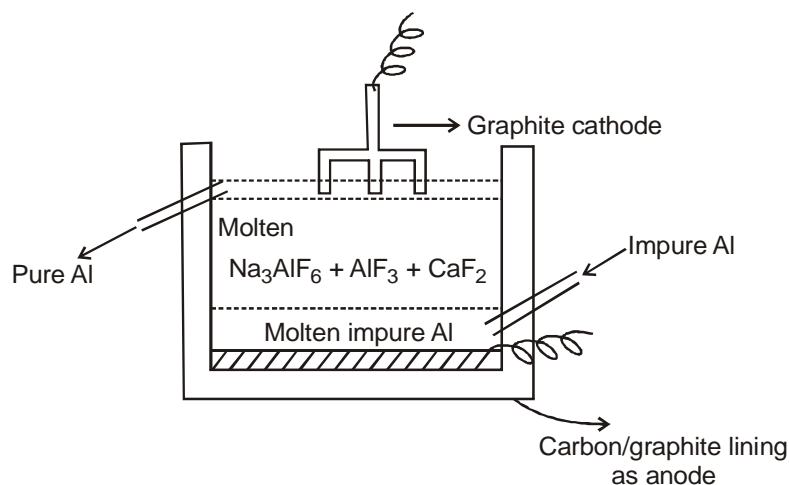


At Anode :



In place of cryolite, Lithium carbonate can be used.  $Li_2CO_3$  place following growths :

- It reduces m.p. of alumina & also increases its electrical conductivity.
- By its use fluorine & fluorocarbons are not evolved at anode.

**Step III : Refining of impure Aluminium By Hoop's Process :**

$$E^\circ_{\text{Al}/\text{Al}^{3+}} = +1.66 \text{ V}$$

Hoop's method is based on density. Molten impure Al has higher density so it is found at bottom level.

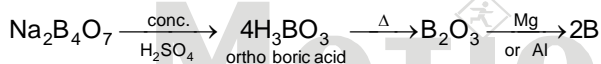
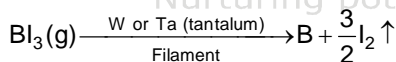
**BORON****Ores / Sources :**

Borax :  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

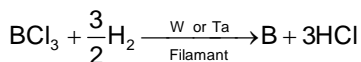
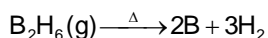
Colemanite :  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

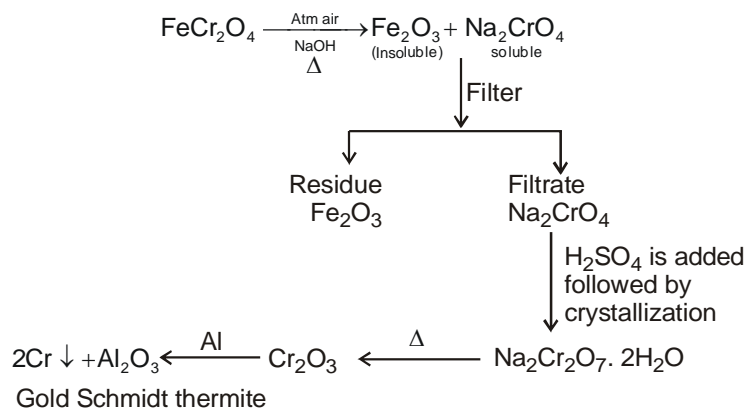
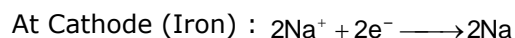
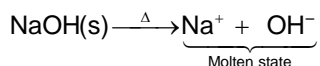
Panderinite :  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 3\text{H}_2\text{O}$

Boronatrocalcite :  $\text{CaB}_4\text{O}_7 \cdot \text{NaBO}_2 \cdot 8\text{H}_2\text{O}$

**Extraction****⇒ From Borax :****⇒ By Van Arkel Process :**

{ $\text{BI}_3$  is formed when orthoboric acid react with  $\text{HI}$ }

**⇒ By Reduction of  $\text{BCl}_3$** **⇒ By Thermal decomposition of  $\text{B}_2\text{H}_6$** **⇒ B is also isolated from  $\text{B}_4\text{C}$  (Boron carbide)**

**CHROMIUM****Ore :** Chromite :  $\text{FeCr}_2\text{O}_4$  ( $\text{FeO} + \text{Cr}_2\text{O}_3$ )**Extraction :****SODIUM**Isolation by electrolysis of fused  $\text{NaOH} \Rightarrow$  Castner's Process

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