

METALLURGY

Preface

Metallurgy having its importance from ancient days. After stone age primitive man entered into metal age 5000 years ago. So man is well acquainted with metals from very long ago.

This “Metallurgy” chapter consists of how to extract a metal from its ore by most economic method. This text also consists of chief ores of different metals and basic methods followed in Metallurgy.

At the last stage of this chapter you can predict whether a particular substance element can be able to reduce a compound to its metallic state or not, should have an knowledge about best economic processes to treat different types of ores.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develop a better understanding of the chapter and to have a better grasping level in the class.

Total number of Questions in Metallurgy are :	
In Chapter Examples	12
Solved Examples	09
Total no. of questions	21

1. INTRODUCTION ::

The process of extraction of metal from its ores in profitable manner is called metallurgy.

- (i) **Mineral** is a substance in which metal is present in either native state or combined state.
- (ii) **“Ore”** is the mineral from which the metal can be economically and conveniently extracted.
- (iii) **“Gangue or matrix”** is the non metallic impurities present in the ore.

2. COMMON STEPS INVOLVED IN METALLURGY ::

2.1 Crushing and grinding

Operation in which size reduction of large lumps to small pieces followed by finely ground material is done by the use of crushers and grinders.

2.2 Concentration (Dressing) of the ore

Operation in which the removal of impurities (gangue) from ore by the following methods.

2.2.1 Levigation or gravity separation

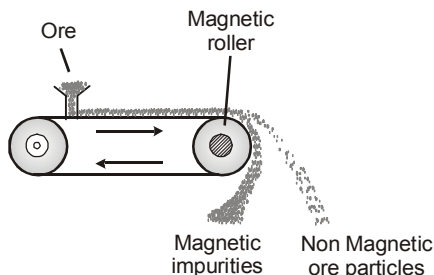
- (i) This method is based on the difference in densities of the ore gangue particles.
- (ii) The powdered ore with gangue particles is introduced in the running stream of water.
- (iii) Lighter impurity particles washed off with water and heavier ore particles settle down at the bottom.
- (iv) Usually employed for oxide and carbonate ores.

Eg. Generally oxides & carbonate ores are concentrated by this method.

2.2.2 Magnetic separation

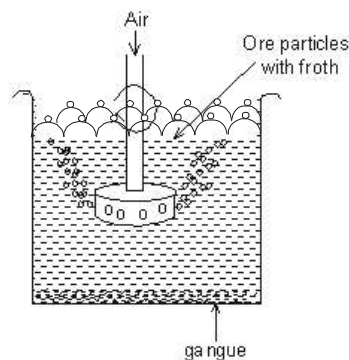
- (i) Ore and gangue are separated, if only one of them is having magnetic property.

Eg. This process is used in metallurgy of Fe.



2.2.3 Froath floatation process

- (i) It is employed for sulphide ores.
- (ii) It is based on the different wetting characteristics of the ore and gangue particles with water and oil.



- (iii) Usually ore particles are making as aerophilic & gangue particles as aerophobic by using different reagents.
- (iv) Ore particles raised to the surface along with air bubbles and collected at the surface where as gangue particles are wetted and settled down at the bottom of the tank.
- (v) Reagents used a frothing agents (pine oil), collectors (ethyl xanthate and potassium ethyl xanthate), Activators (copper sulphate) and depressors (sodium cyanide, alkali).

2.2.4 Leaching

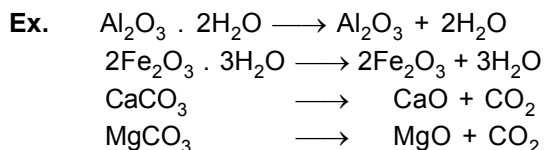
- (i) Chemical method of concentration.
- (ii) Selective dissolution of ore in strong reagents where as gangue particles are undissolved and gets separated. (Hydrometallurgy)
- (iii) Employed for concentrating ores of aluminium, silver, gold etc.

2.3 Working of the concentrated ore

2.3.1 Conversion of the concentrated ore into its oxide form

(a) Calcination :

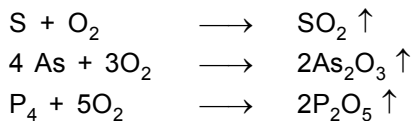
- (i) Ore is heated in absence of air to remove water or CO_2 from hydrated oxides or carbonates respectively.
- (ii) Process temperature is below the melting points of treated ores.
- (iii) During calcination moisture, volatile impurities are removed there by ore becomes porous.



(b) Roasting :

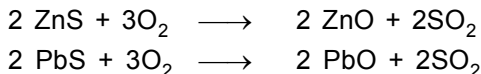
- (i) Ore is heated strongly with other substances, usually with oxygen.
- (ii) Employed for sulphide ores.

- (iii) Process temperature is below the melting points of treated ore.
- (iv) Chemical conversion of ore is takes place.
- (v) Some of the impurities removed as volatile substances.

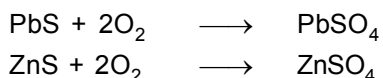


Example :

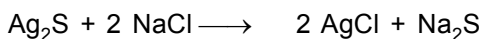
- (a) Conversion of metal sulphides into oxides.



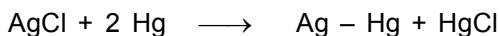
- (b) Metal sulphides are converted into sulphates.



- (c) Metal sulphides converted into chlorides.

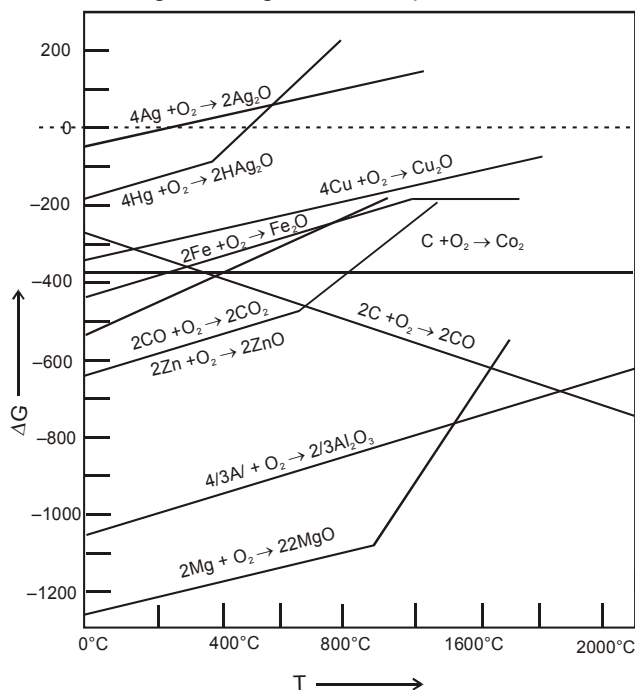


- (d) Conversion as amalgams.



Ellingham Diagram

The changes in Gibbs energy that occur when one mole of oxygen is used may be plotted against temperature for a number of reaction of metals to form their oxides. Such a graph is shown in Fig. and is called an **Ellingham diagram** for oxides. Similarly, we can plot Ellingham diagrams for sulphides and halides.



The Ellingham diagram for oxides show the following important features :

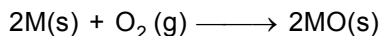
- (i) Ellingham diagram normally consist of plots of ΔG° vs T for the formation of oxides of elements, i.e. for the reaction.
- (ii) The graphs for metal oxide all slope upwards because the change in Gibbs energy becomes less negative with in crease in temperature.
- (iii) Each plot follows a straight line unless there is some change in phase.
- (iv) When the temperature is increased, a point will be reached when the line crosses $\Delta G = 0$ line. Below this temperature the $\Delta_f G^\circ$ of oxide is negative and hence the oxide is stable. Above this temperature $\Delta_f G^\circ$ of the oxide is positive and hence the oxide becomes unstable and decomposes on its own into metal and oxygen.

2.3.2 Conversion of the oxide to metallic form

The roasted or calcined ore is converted into metallic form through reduction by using different reducing techniques which will depends upon the nature of the ore, some of the methods are mentioned below

Thermodynamic Principles:

Consider a reaction such as formation of an oxide.



In this reaction, the randomness of the system decreases. because gases have more randomness than solids. Hence, ΔS for this reaction is negative. Thus, if temperature is increased then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in equation, ΔG becomes less negative. On the other hand, if ΔS is positive, on increasing the temperature the value of ΔG decreases and becomes more negative. For example, in the reaction, $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CO}(\text{g})$, ΔS is positive and ΔG decrease and becomes more negative as the T increase.

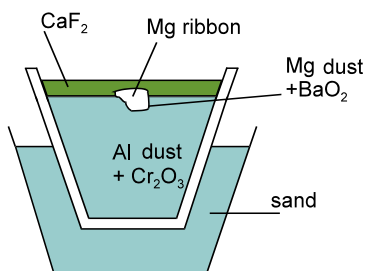
- (a) **Reduction by carbon (smelting)**

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced by strongly heating with coal or coke.

- (i) Reduction of the oxide with carbon at high temperature is known as smelting

- (ii) Flux is added during smelting, which reduces the melting point of impurities to form an easily fusible substance called as 'slag' and can be separated easily because of its lower density.
- (iii) Selection of flux depends upon nature of impurity present. Its impurity is acidic or basic flux is employed and vice versa.
- (iv) Smelting is usually carried out in blast furnaces or reverberatory furnace.

(b) Reduction by aluminium (Alumino-thermic reduction)

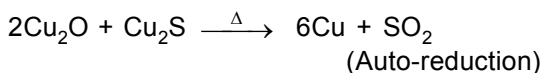
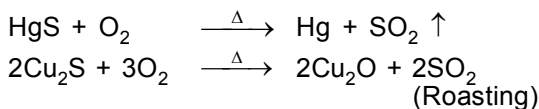


- (i) Aluminium acts as reducing agent due to its high electropositive nature.
- (ii) Oxides such as Cr_2O_3 , Mn_3O_4 are reduced by this method
- (iii) The process is also known as "Gold Schmidt thermite process".

(c) Reduction by heating in air (Auto-reduction)

- (i) Employed for metals of less active such as Hg, Cu and Pb
- (ii) Due to unstable nature in the oxide form at high temperature, no reducing agent is required for their reduction..

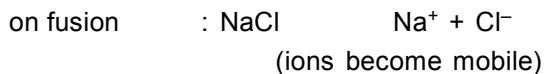
Example :



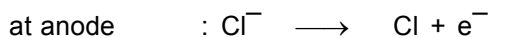
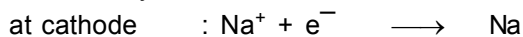
(d) Electrolytic reduction (Electro-metallurgy)

- (i) Employed for highly electropositive metals such as Na, K, Ca, Mg, Mg etc.
- (ii) These metals are extracted by the electrolysis of their oxides, hydroxides or chlorides in fused state.

Example :



on electrolysis :



(iii) Aluminium is obtained by the electrolysis of electrolyte which consists of mixture of alumina, cryolite and calcium fluoride (Hall-Herault process)

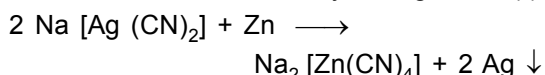
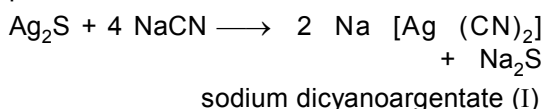
(e) Other method are

- (i) Reduction by carbon monoxide (employed for iron (iii) oxide)
- (ii) Reduction by water gas (employed for nickel oxide)
- (iii) Amalgamation method (employed for noble metals)

2.3.3 Hydrometallurgy (Reduction by precipitation)

- (i) Process in which more electropositive metal displace less electropositive metals from salt solution.
- (ii) First the concentrated ore is dissolved in strong reagent and remove insoluble precipitates.
- (iii) Now the metal is precipitated by addition of more electropositive metal.

Example : Silver sulphide dissolved in sodium cyanide which forms a soluble complex, then silver is precipitated by the addition of zinc powder.



Note : This type of precipitation process is called **cementation**.

2.4 Refining or purification

- (i) The metals after reduction process consists of number of impurities like Si, P, slag, oxides, other metals etc.
- (ii) Removal of all these impurities to get pure metal is called as refining.
- (iii) Methods of refining are as under.

2.4.1 Liquation

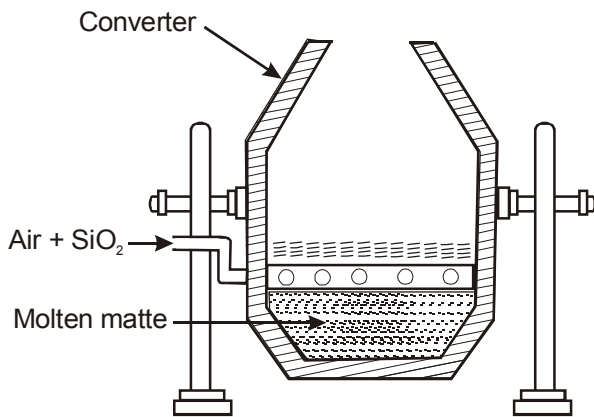
- (i) This is based on the principle of difference in melting points of metal and impurity.
- (ii) Employed for purification of low melting point metals like Pb, Sn etc.

2.4.2 Distillation process

- (i) This is based on difference in boiling points of metals and impurities.
- (ii) Employed for low boiling point metals like Zn, Hg etc.

2.4.3 Oxidation process

- (i) This is a selective oxidation method.
- (ii) Used for refining those metals in which the impurities have greater tendency to get oxidised than the metals itself.
- (iii) The impurities converted into oxide & skimmed off from the metal.
- (iv) Various oxidation processes used for different metals bear different names, e.g., poling, puddling, bessemerisation and cupellation (for Ag).

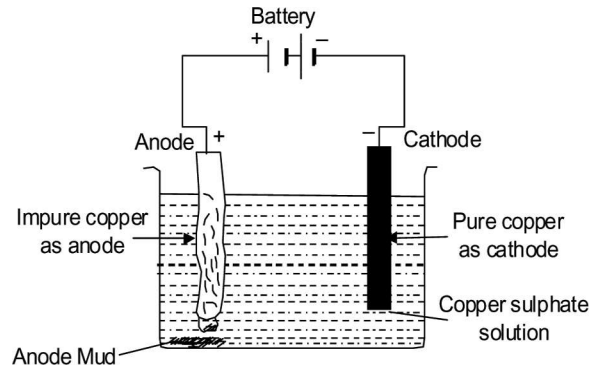


Bessemer converter of copper

2.4.4 Electrorefining

- (i) Employed for refining of highly electro positive metals like Al, Cu, Ag, Zn, Sn, Pb, Cr and Ni.
- (ii) Impure metal is made as anode, thin pure metal sheet is kept as cathode and the electrolyte comprising with soluble salt solution of the metal.
- (iii) On passing the electric current, pure metal from the anode dissolved and is deposited on the cathode.
- (iv) The soluble impurities goes into the solution (remains in the solution after the completion

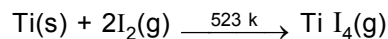
of refining) while the insoluble impurities settle down below the anode as "anode mud"



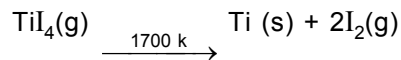
Electrolytic refining of copper

2.4.5 Van-Arkel process

- (i) Employed to get metal in very pure form of small quantities.
- (ii) In this method, the metal is converted into a volatile unstable compound (e.g. iodide), and impurities are not affected during compound formation.
- (iii) The compound thus obtained is decomposed to get the pure metal.
- (iv) Employed for purification of metals like titanium and zirconium

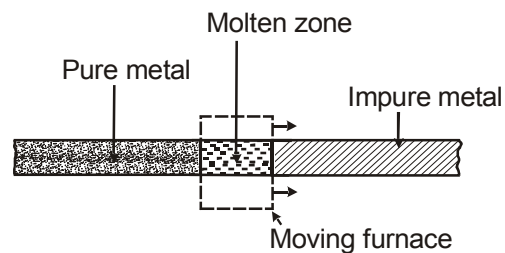


Impure



2.4.6 Zone refining

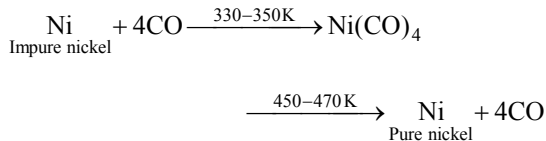
- (i) Employed for metals which requires in very high purity like semi conductors.
- (ii) The method is based on the principle that an impure metal on solidification will deposit crystals of pure metal and the impurities will remain behind in the molten part of the metal.
- (iii) Used to purify the elements such as silicon, germanium.



Zone refining

2.4.7 Mond's process

- (i) Nickel is purified by using CO gas. This involves the formation of nickel tetracarbonyl.



Example based on

Common Steps Involved in Metallurgy

- Ex.1** A substance which reacts with gangue to form fusible material is called –

- (A) Flux (B) Catalyst
(C) Ore (D) Slag

Sol. (A)

Flux combines with gangue to form a low melting substance called slag.

- Ex.2** Which of the following is not a concentration technique –

- (A) Levigation (B) Froth floatation
(C) Leaching (D) Calcination

Sol. (D)

Calcination is the process of extraction.

- Ex.3** The ores that are concentrated by floatation method are –

- (A) Carbonates (B) Sulphides
(C) Oxides (D) Phosphates

Sol. (B)

In floatation process, the ore particles should be aerophilic in preference to gangue particles. Sulphide ores having this character.

- Ex.4** Calcination is the process in which –

- (A) Heating the ore in presence of air
(B) Heating the ore in presence of sulphur
(C) Heating the ore in absence of air
(D) Heating the ore in presence of chlorine

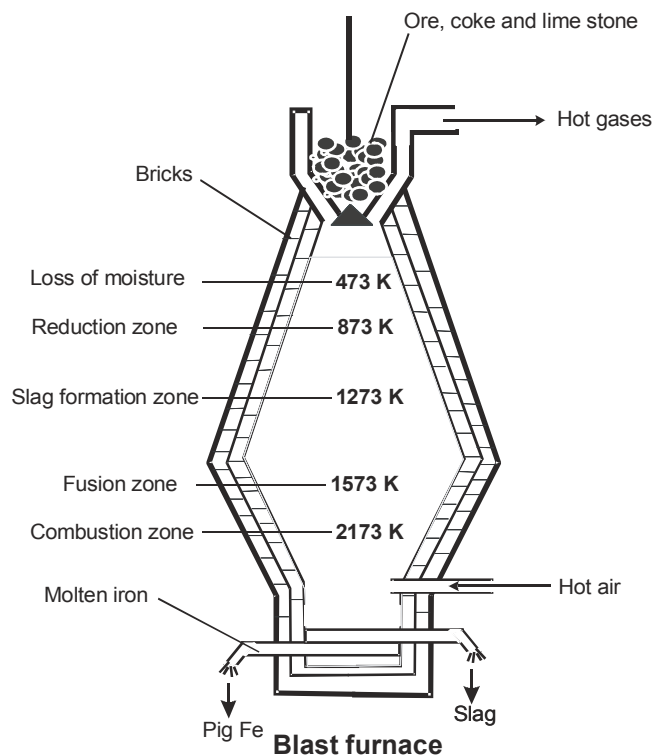
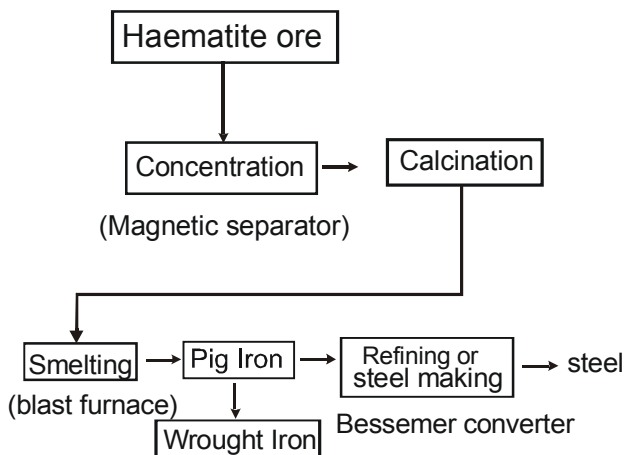
Sol. (C)

Calcination is the process in which moisture and volatile impurities are removed and process is carried in absence of air.

3. EXTRACTION OF IRON ::

- (a) **Ores :** Haematite – Fe_2O_3 Limonite – $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; Siderite FeCO_3 ; Magnetite – Fe_3O_4 , Pyrite- FeS_2 .

(b) Process:



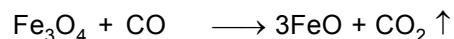
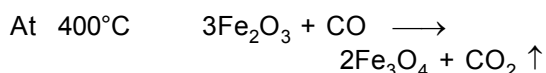
(c) Reactions :

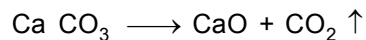
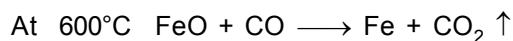
- (i) **Roasting :** FeO changes to Fe_2O_3 to prevent the loss of iron during smelting.



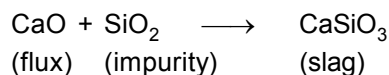
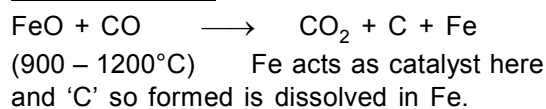
- (ii) **Smelting (In blast furnace) :**

In reduction zone : -

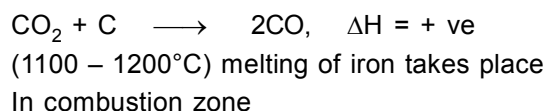




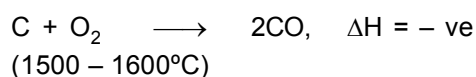
In central zone :



In fusion zone



In combustion zone



(d) **Pig Iron** : C \approx 3.1 – 4.5%, small amounts of Si, S, P ; hard and brittle, obtained from blast furnace

(e) **Wrought Iron** : C \approx 0.15 – 0.28%, purest form ; malleable, fibrous

(f) **Steel** : C \approx 0.15 – 1.5%, strength is high.

Example based on **Iron**

Ex.5 Magnetic separation is used for increasing concentration of the following –

- (A) Horn silver (B) Calcite
(C) Haematite (D) Magnesite

Sol. (C) Haematite ore is having magnetic property, can be separated by magnetic separation

Ex.6 In blast furnace, iron oxide is reduced by –

- (A) Silica (B) CO
(C) C (D) lime stone

Sol. (B) $\text{FeO} + \text{CO} \longrightarrow \text{Fe} + \text{CO}_2$

Ex.7 Steel consists of percentage of carbon –

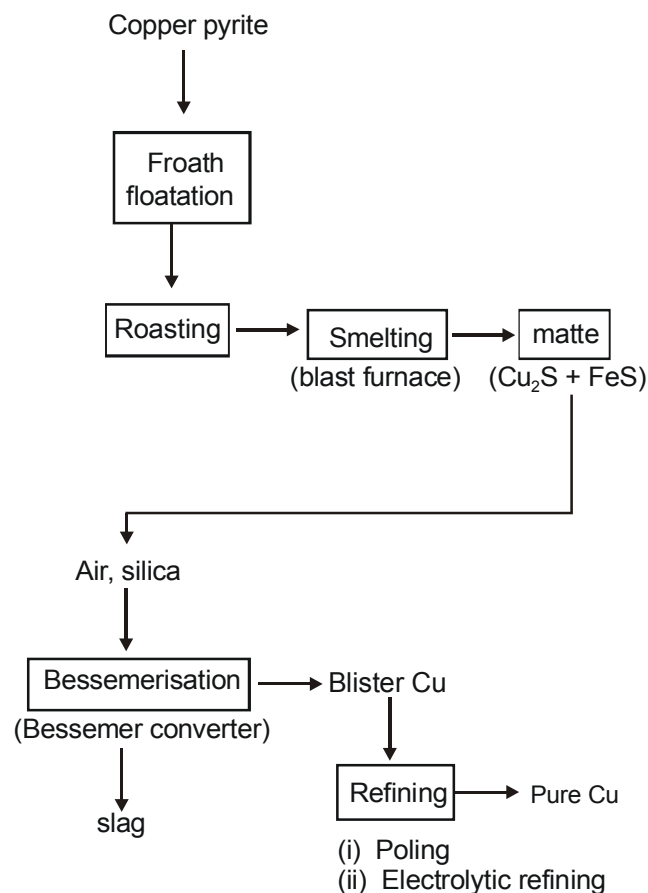
- (A) 3.1 – 4.5% (B) 2.2 – 3.1%
(C) 0.15 – 0.28% (D) 0.15 – 1.5%

Sol. (D)

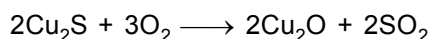
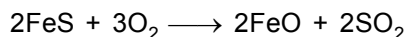
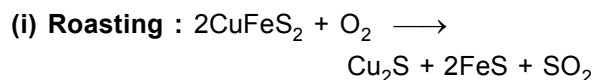
4. EXTRACTION OF COPPER ::

(a) **Ores** : Copper pyrites CuFeS_2 ; Cuprite or ruby copper Cu_2O ; Copper glance Cu_2S ; Malachite $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$; Azurite $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$.

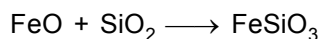
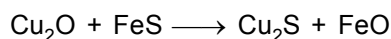
(b) **Process:**



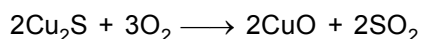
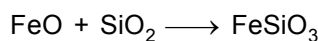
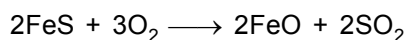
(c) **Reactions :**



(ii) **Smelting :**



(iii) **Bessemerisation :**



(iv) **Poling** : Molten Cu is stirred with poles of green wood to reduce any copper oxide in Copper

(v) **Electrolytic refining** : Anode – impure Cu ; cathode – pure Cu ; electrolyte $\text{CuSO}_4 + \text{H}_2\text{SO}_4$.

Note : Copper can be extracted by hydrometallurgical process also.

Example based on

Copper

Ex.8 Matte is obtained after this step –

- (A) Froath floatation (B) Roasting
(C) Smelting (D) Refining

Sol. (C) Matte is Cu_2S and FeS , obtained from base of furnace.

5. EXTRACTION OF ALUMINIUM ::

(a) **Ores** :

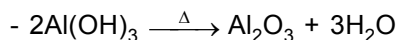
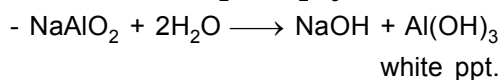
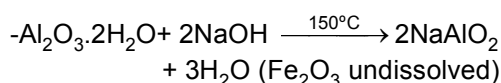
- (i) Oxides : Bauxite $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (chief) ;
Diaspore $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$; Corundum Al_2O_3 .
(ii) Silicates : Felspar KAlSi_3O_8 ; Mica
 $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; Kaolinite
 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
(iii) Fluorides : Cryolite Na_3AlF_6

(b) **Process** :

(i) **Purification of Bauxite** :

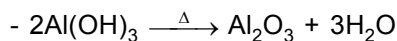
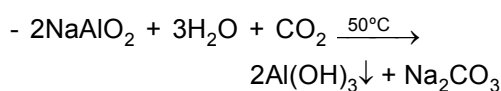
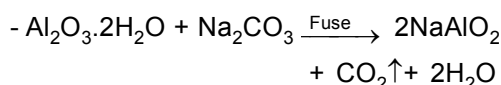
(x) **Baeyer's Method**

If Fe_2O_3 is major impurity - Red bauxite
- ore is roasted to convert ferrous oxide
to ferric oxide



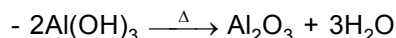
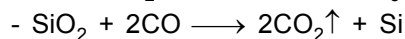
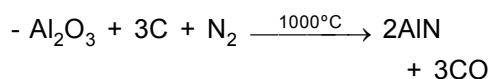
(y) **Halls' method**

If Fe_2O_3 is major impurity –Red bauxite
- bauxite ore is fused with Na_2CO_3



(z) **Serpeck's method** :

If SiO_2 is major impurity - white bauxite



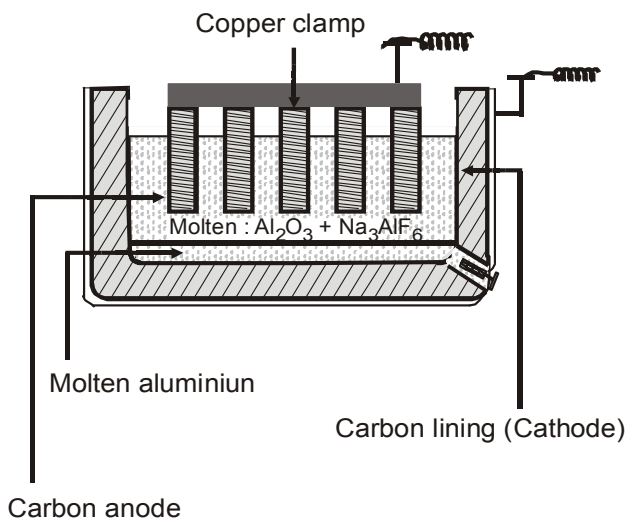
(ii) **Electrolysis of fused Alumina.**

Cathode : Iron-tank lined with carbon bricks

Anode : carbon

Electrolyte : Molten [Al_2O_3 (5%) Na_3AlF_6 (85%)
+ CaF_2 (5%) + AlF_3 (5%)]

O_2 is liberated at anode and Al collects at the bottom.

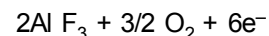


Hall Heroult process

(iii) Reactions : $\text{Na}_3\text{AlF}_6 \longrightarrow 3\text{NaF} + \text{AlF}_3$



At anode : $\text{Al}_2\text{O}_3 + 6\text{F}^- \rightarrow$



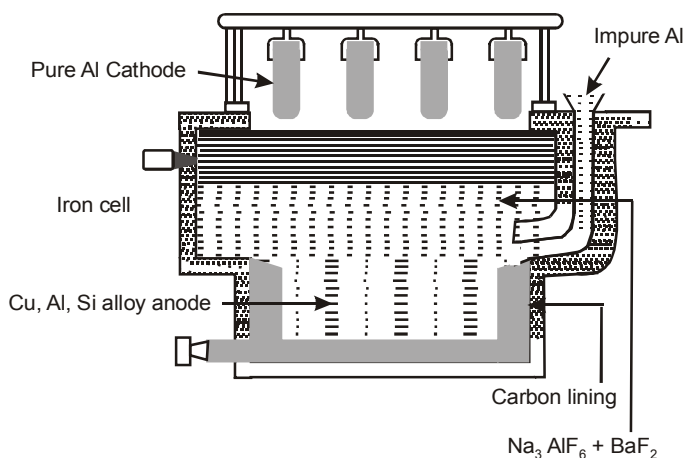
At cathode : $2\text{Al}^{3+} + 6\text{e}^- \longrightarrow 2\text{Al}$

(iv) **Electrolytic refining (Hoope's process)**,
three layers process.

Cathode : carbon electrodes

anode : Fe tank lined with carbon bricks

Electrolyte :



Hoope's process for purification of aluminium

Bottom layer : Impure aluminium consists of Cu, Si etc in molten state.

Middle layer : molten mixture of Fluorides of Na, Ba, Al and Al_2O_3

Top layer : pure molten aluminium.

On passing the current, Al is deposited at cathode from the middle layer and an equivalent amount of Al from the bottom layer moves into the middle layer leaving behind the impurities.

Example based on

Aluminium

Ex.9 Aluminium is obtained from Al_2O_3 by this method –

- (A) Thermal reduction
- (B) Hydro metallurgical method
- (C) Electrolytic reduction
- (D) Reduction by Iron.

Sol. (C) For all metals with high electropositive nature, electrolytic reduction is best method.

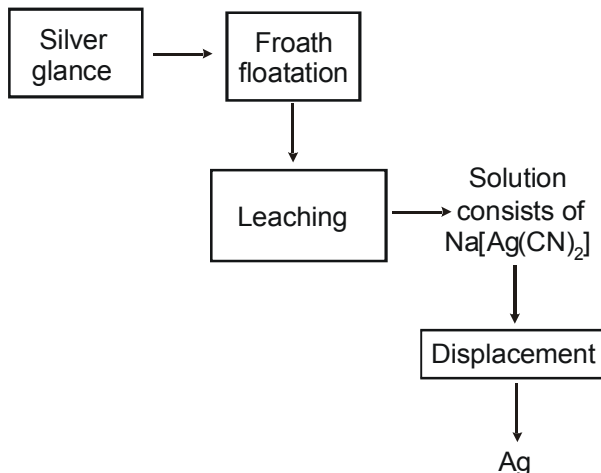
Ex.10 If Bauxite consists of SiO_2 as impurity, this process is employed –

- (A) Hall's process
- (B) Baeyer's process
- (C) Hoop's process
- (D) serpeck's process

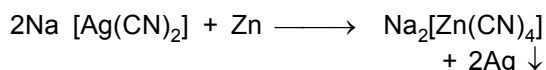
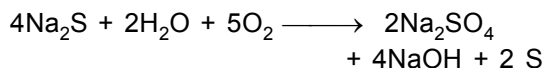
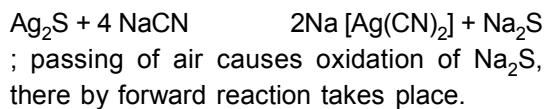
Sol. (D) Bayer & Hall's process are used when Fe_2O_3 is major impurity. Hoop's process is a refining process.

6. EXTRACTION OF SILVER ::

- (a) **Ores** : Silver glance or argentite Ag_2S , Ruby silver Ag_2S , Sb_2S_3 , Horn silver $AgCl$.
- (b) **Process** : Cyanidation or Mac-Arthur-Forrest cyanide process



(c) **Reactions (Leaching)** :



sodium argento cyanide sodium zinco cyanide

The precipitated silver is separated and purified by fusion with borax or KNO_3 to get pure silver.

Electrolytic refining : Anode : Impure Ag
 cathode : Pure Ag
 Electrolyte : $AgNO_3(aq.) + HNO_3$.

Example based on

Silver

Ex.11 Leaching is preferred for which sulphide are.

- (A) Galana
- (B) Argetide
- (C) Sphalerite
- (D) Cinnabar

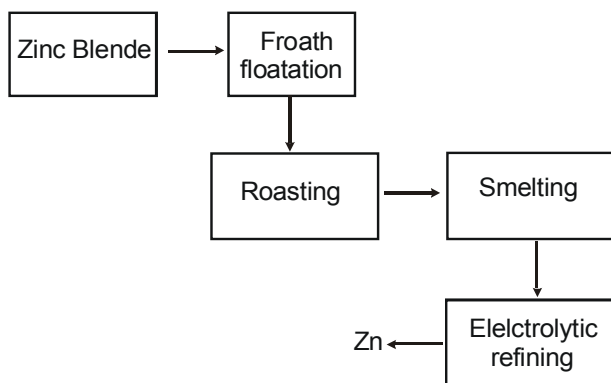
Sol. (B) Argentite is leached using NaCN as reagent

7. EXTRACTION OF ZINC ::

Occurrence : Zinc is usually found in the combined state although traces of the metal in the native state have been reported from Melbourne (Australia). Its chief ores are :

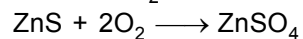
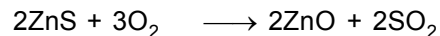
1. Zinc blende, ZnS.
2. Calamine or Sphalerite, ZnCO₃
3. Zincite, ZnO

1. **Extraction process** : It involves the following steps :

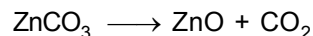


2. Roasting :

Reactions:

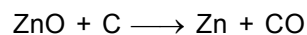


When the ore is calamine, it shall decompose into oxide with evolution of carbon dioxide (calcination is used).



For roasting, a reverberatory furnace may be used.

Smelting



Example based on

Zinc

Ex.12 Calamine is concentrated by :

- (A) Magnetic Separation
- (B) Froath floatation
- (C) Cynide process
- (D) Gravity separation

Sol. (D)

Carbonate ores are concentrated by Gravity separation.

SOLVED EXAMPLES

Ex.1 Which of the following is not used for extraction of Aluminium –

- (A) Van arkel process
- (B) Serpeck's process
- (C) Baeyer's process
- (D) Hall-Heroult's process

Sol. (A)

Van Arkel process is one the refining process to get very pure metal. In this process the impure metal is converted into volatile iodides, which are again dissociated to get pure metal.

Ex.2 Heating an ore in the absence of air below its melting point is called:

- (A) leaching
- (B) roasting
- (C) smelting
- (D) calcination

Sol. (D)

Roasting is heating in presence of air.

Ex.3 Carnallite is an ore of:

- (A) Sodium
- (B) Potassium
- (C) Manganese
- (D) Aluminium

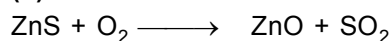
Sol. (B)

Carnalite is $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

Ex.4 Zinc blende on roasting in air gives –

- (A) Zinc carbonate
- (B) SO_2 and ZnO
- (C) ZnS and ZnSO_4
- (D) CO_2 and ZnO

Sol. (B)



Ex.5 Reagent used in cyanide process is –

- (A) NaOH
- (B) NaCN
- (C) Na_2CO_3
- (D) NaNO_3

Sol. (B)

It is used to concentrate gold & silver

Ex.6 In aluminothermite process, aluminium is used as:

- (A) Oxidising agent
- (B) Flux
- (C) Reducing agent
- (D) Solder

Sol. (C)

Al is used to reduce oxide of Cr & Mn.

Ex.7 Which of the following is not a concentration technique

- (A) Levigation
- (B) Froth floatation
- (C) Leaching
- (D) Calcination

Sol. (D)

In calcination, volatile impurities are removed by heating concentrated ore in Reverberatory furnace.

Ex.8 Cassiterite is an ore of:

- (A) Mn
- (B) Ni
- (C) Sb
- (D) Sn

Sol. (D)

Cassiterite is SnO_2

Ex.9 Cassiterite is concentrated by:

- (A) Levigation
- (B) Electromagnetic separation
- (C) Floatation
- (D) Liquefaction

Sol. (B)

It contains magnetic (wolframite) impurities.