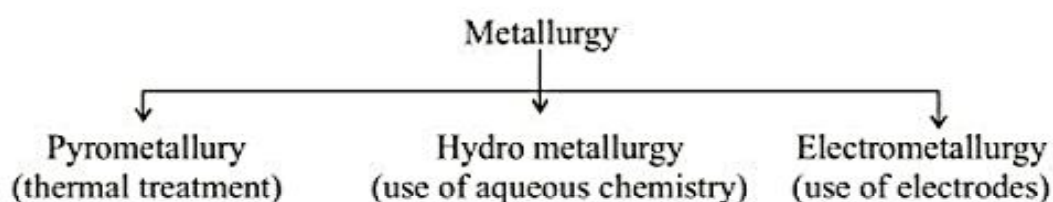


# METALLURGY

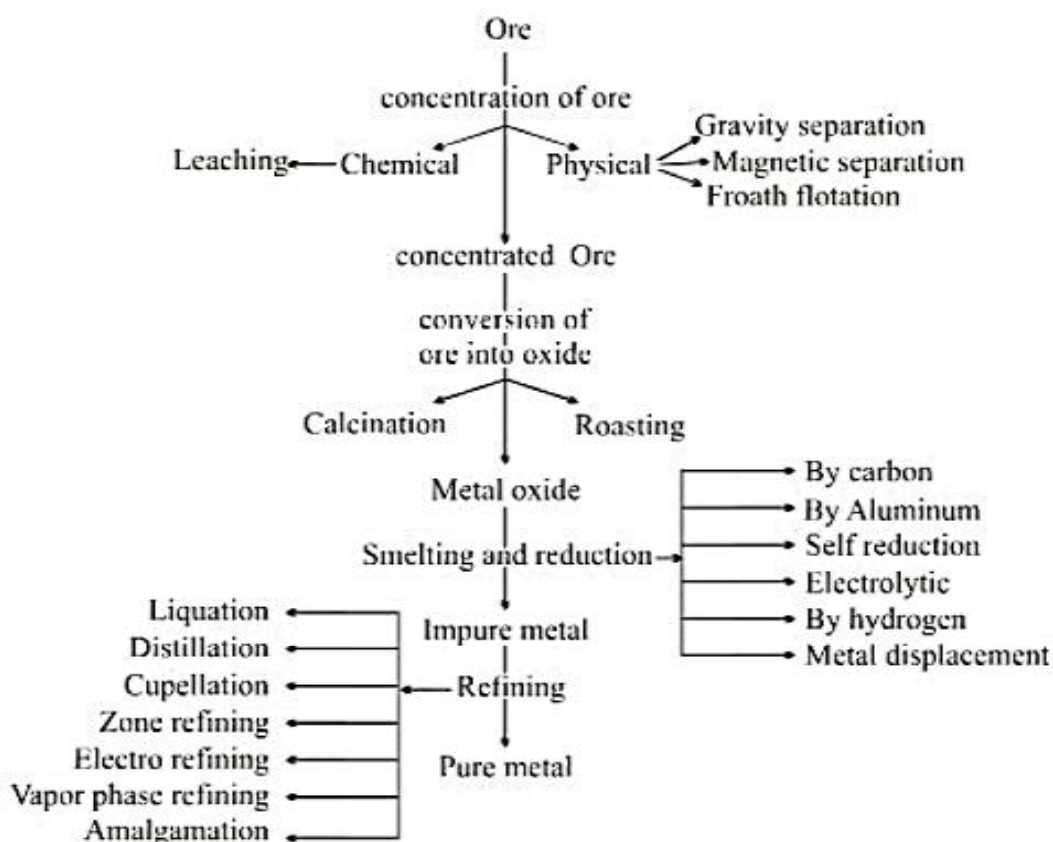
## INTRODUCTION

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 form which the metal can be economically and conveniently extracted.
- (iii) **"Gangue or matrix"** is the non metallic impurities present in the ore.



## Steps involved in metallurgy



## COMMON STEPS INVOLVED IN METALLURGY

- **Crushing and grinding (Pulverization)**  
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.  
**Handpicking** : To pick up selective pieces of ores.
- **Concentration (Dressing) of the ore**  
Operation in which the removal of impurities (gangue) from ore by the following methods.

### Levigation or gravity separation :

- This method is based on the difference in densities of the ore gangue particles.
- The powdered ore with gangue particles is introduced in the running stream of water.
- Lighter impurity particles washed off with water and heavier ore particles settle down at the bottom.  
Eg. Generally oxides & carbonate ores are concentrated by this method.

### Magnetic separation

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

Eg. In metallurgy of Fe .

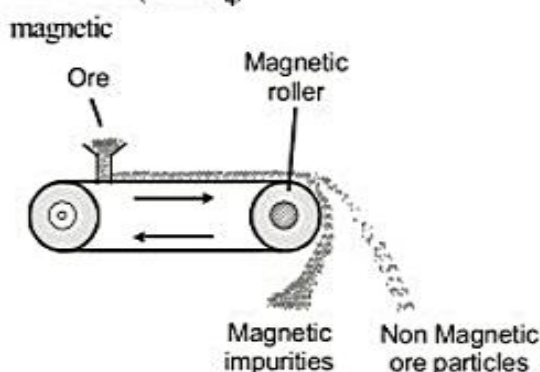
Ore  $\longrightarrow$  magnetic

impurity  $\longrightarrow$  non magnetic

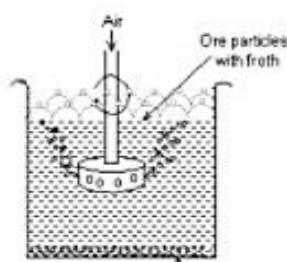
In metallurgy of Sn (tin stone)

Ore  $\longrightarrow$  non magnetic ( $\text{SnO}_2$ )

impurity  $\longrightarrow$  wolframite ( $\text{FeWO}_4$ )



- **Froath flotation process**
  - It is employed for sulphide ores.
  - 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 (sodium ethyl xanthate and potassium ethyl xanthate), Activators (copper sulphate) and depressors (sodium cyanide, alkali).

\* **Collectors :**

These compounds adsorb themselves on polar groups to grains of ores and thus derive them on the surface to pass on into the forth e.g. sodium ethyl xanthate and potassium ethyl xanthate.

\* **Activators and depressants :**

These compounds activate or depress the floating property of one of the components of the ore and thus help in the separation of different minerals present in the same ore. Copper sulphate is an example of activator, while sodium and potassium cyanides are the examples of depressants e.g. Galena (PbS) is usually associated with sphalerite (ZnS) and pyrites (FeS<sub>2</sub>). Floatation is carried out in presence of potassium ethyl xanthate (collector) and sodium cyanide and alkali (depressants). The later compounds depress the flotation property of ZnS and FeS<sub>2</sub> particles and hence only PbS particles go into the forth when air is blown in. After the removal of galena, the process is repeated by adding copper sulphate (activator) which activates the floating character of ZnS particles and thus this time ZnS comes with the froath. The acidification of remaining slurry leads to the flotation of FeS<sub>2</sub>.

• **Leaching**

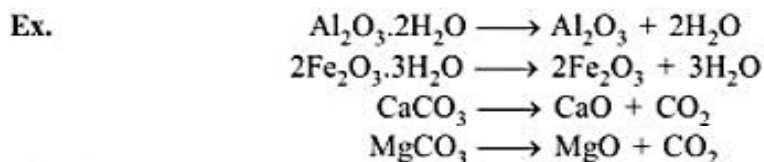
- (i) Chemical method of concentration.
- (ii) Selective dissolution of ore in strong reagents where as gangue particles are undissolved and gets separated. (Hydrometallurgy)
- (iii) Employed for concentrating ores of aluminium, silver, gold etc.

**Working of the concentrated ore**

• **Conversion of the concentrated ore into its oxide form**

(a) **Calcination :**

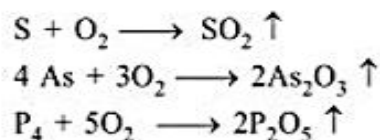
- (i) Ore is heated in absence of air to remove water or CO<sub>2</sub> from hydrated oxides or carbonates respectively.
- (ii) Process temperature is below the melting points of treated ores.
- (iii) During calcination moisture, volatile impurities are removed there by ore becomes porous.



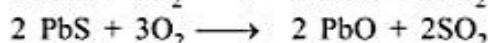
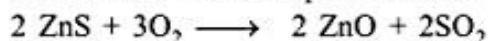
(b) **Roasting :**

- (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 :**

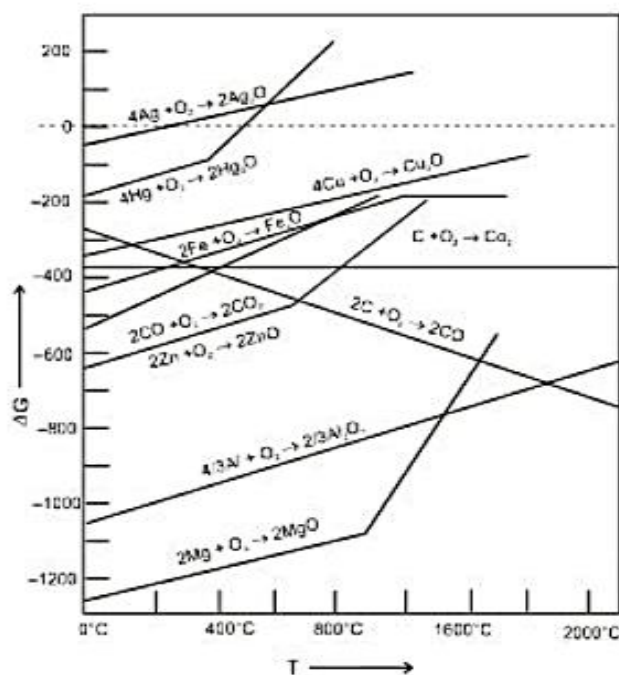
- (a) Conversion of metal sulphides into oxides.



- (b) Metal sulphides are converted into sulphates.

**Smelting**

- (i) 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.
- (ii) Selection of flux depends upon nature of impurity present. Its impurity is acidic or basic flux is employed and vice versa.
- (iii) Smelting is usually carried out in blast furnaces or reverberatory furnace.

**Ellingham Diagram**

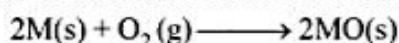
The changes in Gibbs energy that occur when one mole of oxygen is used may be plotted against temperature for a number of reactions of metals to form their oxides. Such a graph is shown in Figure below and is called an **Ellingham diagram** for oxides. Similarly, we can plot Ellingham diagrams for halides.

**The Ellingham diagram for oxides show the following important features :**

- (i) Ellingham diagram normally consist of plots of  $\Delta G^\circ$  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 increase 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.
- **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.

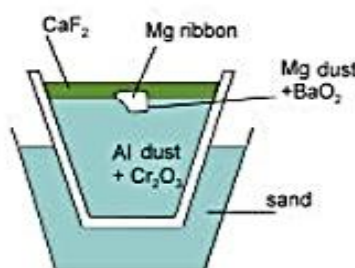


In this reaction, the random of the system decreases because gases have more random than solids. Hence,  $\Delta S$  for this reaction is negative. Thus, if temperature is increased then  $T\Delta S$  becomes more negative. Since  $T\Delta S$  is subtracted in equation,  $\Delta G$  becomes less negative. On the other hand, if  $\Delta S$  is positive, on increasing the temperature the value of  $\Delta G$  decreases and becomes more negative. For example, in the reaction,  $2C(s) + O_2(g) \longrightarrow 2CO(g)$ ,  $\Delta S$  is positive and  $\Delta G$  decrease and becomes more negative as the T increase.

**(a) Reduction by carbon**

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

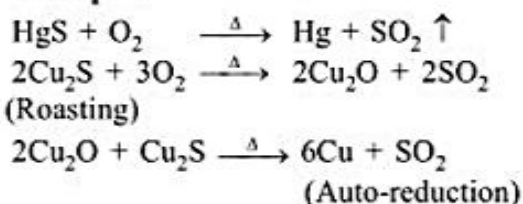
**(b) Reduction by aluminium (Alumino-thermic reduction)**



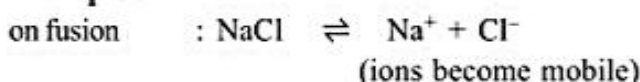
- (i) Aluminium acts as reducing agent due to its high electropositive nature.
- (ii) Oxides such as  $Cr_2O_3$ ,  $Mn_2O_3$  are reduced by this method
- (iii) The process is also known as “Gold Schmidt thermite process”.

**(c) Reduction by heating in air (Auto-reduction) /Self reduction**

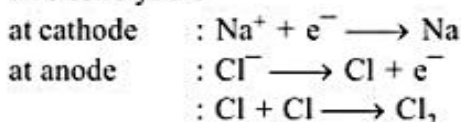
- (i) Employed for metals of less active such as Hg, Cu and Pb
- (ii) Due to unstable nature in the oxide form at high temperature, no reducing agent is required for their reduction..

**Example :****(d) Electrolytic reduction (Electro-metallurgy)**

- (i) Employed for highly electropositive metals such as Na, K, Ca, Mg 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)

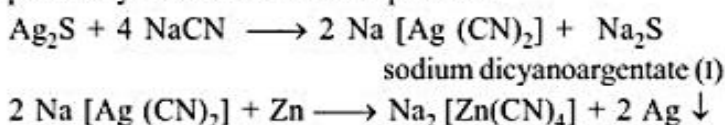
**(e) Other method are following :**

- (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)

- **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**.

**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.

- **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.

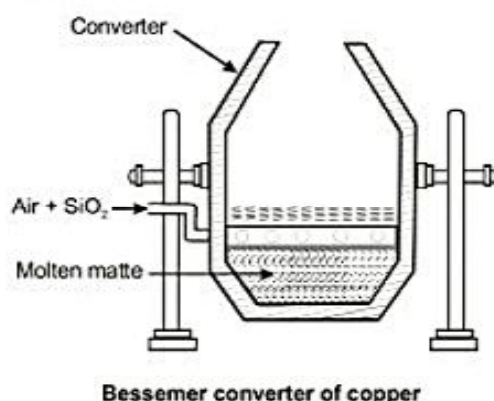


- **Distillation process**

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

- **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).

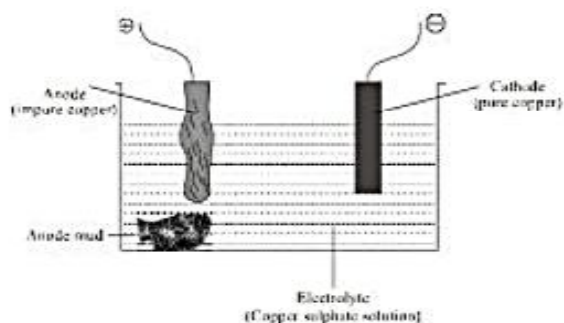


## CUPELLATION

The process in which a impure sample of metal (say Pb in Ag) is fused in a bone ash crucible (Cupel) on the hearth of furnace in the blast of air. The impurity (Pb) present is oxidized and blown away with air. Some PbO is absorbed by Cupel.

- **Electrorefining**

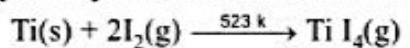
- (i) Employed for refining of highly electro positive metals like Al, Cu, Ag, Zn, Sn, Pb, Cr and Ni.
- (ii) Impure metal is made as anode, thin pure metal sheet is kept as cathode and the electrolysis comprising with soluble salt solution of the metal.
- (iii) On passing the electric current, pure metal 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**”



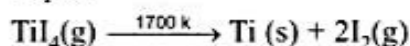
**Electrolytic refining of copper**

- **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

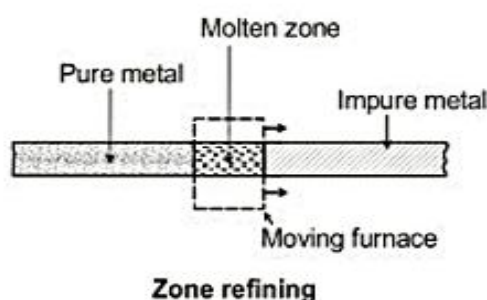


Impure



- **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.



**Amalgamation process :** Noble metals ores like Ag, Au, Pt in finely powdered state are mixed with water to form slurry. The slurry is then flown over Cu or brass plates coated with Hg arranged in slanting position. The metal particles forming amalgam with Hg are retained on these plates. The amalgam is scrapped off and then distilled in iron retorts where Hg distillates over leaving free metals. Hg vapours



- **Mond's process**

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





### Illustration

**Q.1** The ores that are concentrated by floatation method are –

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

**Ans.** (B)

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

**Q.2** 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

**Ans.** (C)

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

### Exercise

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

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

**Ans.** (A)

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

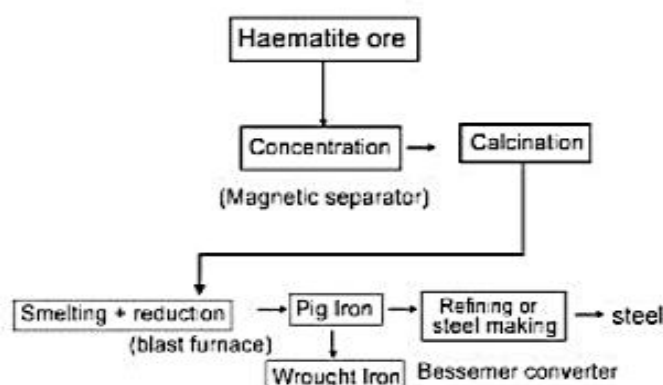
- (A) Levigation (B) Froth floatation (C) Leaching (D) Calcination

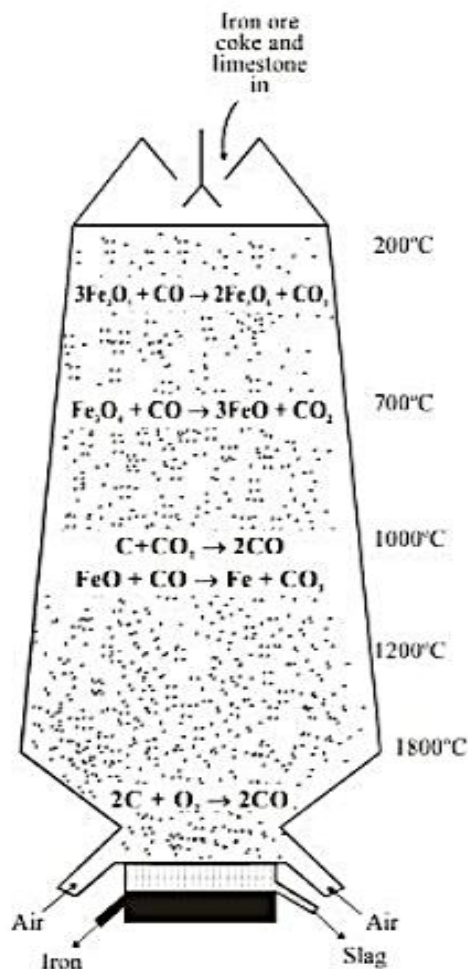
**Ans.** (D)

## EXTRACTION OF IRON

(a) **Ores :** Haematite –  $\text{Fe}_2\text{O}_3$  Limonite –  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; Siderite  $\text{FeCO}_3$ ; Magnetite –  $\text{Fe}_3\text{O}_4$ , Pyrite-  $\text{FeS}_2$ .

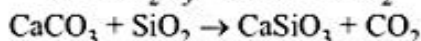
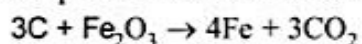
(b) **Process:**



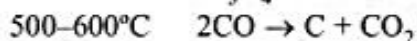
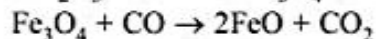
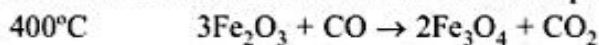


(c) **Reactions involved :**

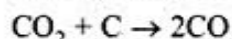
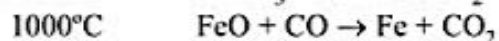
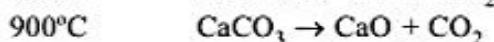
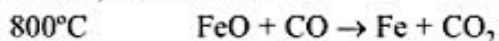
The overall process for the extraction of Fe is :



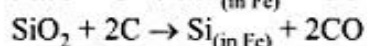
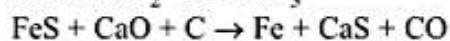
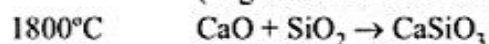
The reaction proceeds in several stages at different temperatures. Since the air passes through in a few seconds, The individual reactions do not reach equilibrium.



The C is deposited as soot and reduces FeO to Fe but it also reacts with the refractory lining of the furnace, and is harmful



(Together these two reactions appear to be  $\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}$ )



- (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

### Illustration

**Q.1** Magnetic separation is used for increasing concentration of the following –

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

**Ans.** (C)

**Sol.** Haematite ore is having magnetic property, can be separated by magnetic separation

**Q.2** In blast furnace, iron oxide is reduced by –

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

**Ans.** (B)

**Sol.**  $\text{FeO} + \text{CO} \longrightarrow \text{Fe} + \text{CO}_2$

### Exercise

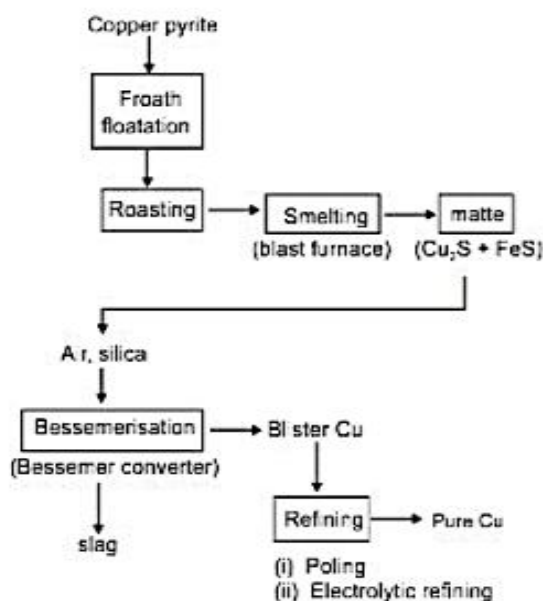
**Q.1** Steel consists of ..... percentage of carbon –

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

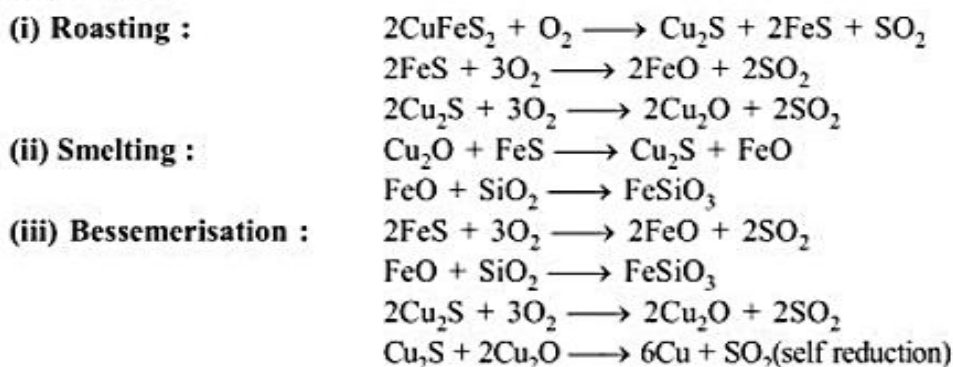
**Ans.** (D)

## EXTRACTION OF COPPER

- (a) **Ores** : Copper pyrites  $\text{CuFeS}_2$  ; Cuprite or ruby copper  $\text{Cu}_2\text{O}$  ; Copper glance  $\text{Cu}_2\text{S}$  ; 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 :**

**(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 :** Low grade copper can be extracted by hydrometallurgical process also.

**Illustration**

**Q.1** In electrorefining of copper, some gold is deposited

- (A) as anode mud      (B) as cathode mud      (C) at the cathode      (D) in the electrolyte

**Ans.** (A)

**Sol.** In electrorefining of copper, impure copper is made as anode and a pure copper strip is made as cathode. A soluble copper salt is taken as electrolyte. On passing current, impurities like Fe, Zn, Ni, and Co dissolve in the solution and Au, Ag, etc. settle down as anode mud.

**Exercise**

**Q.1** Matte is obtained after this step –

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

**Ans.** (C)

**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  $\text{Al}_2\text{O}_3$ .

(ii) Silicates : Felspar  $\text{KAlSi}_3\text{O}_8$ ; 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  $\text{Na}_3\text{AlF}_6$

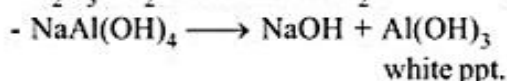
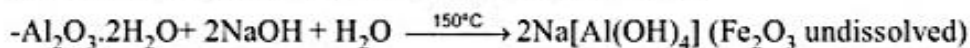
**(b) Process :**

(i) **Purification of Bauxite :**

(x) **Baeyer's Method**

If  $\text{Fe}_2\text{O}_3$  is major impurity - Red bauxite

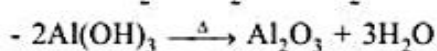
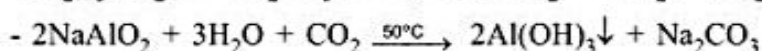
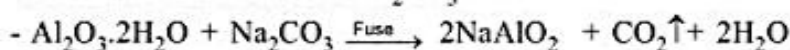
- ore is roasted to convert ferrous oxide to ferric oxide



(y) **Halls' method**

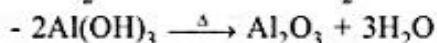
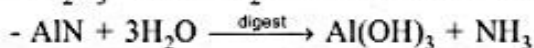
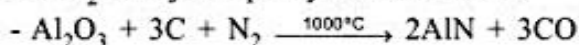
If  $\text{Fe}_2\text{O}_3$  is major impurity - Red bauxite

- bauxite ore is fused with  $\text{Na}_2\text{CO}_3$



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

(i) If  $\text{SiO}_2$  is major impurity - white bauxite



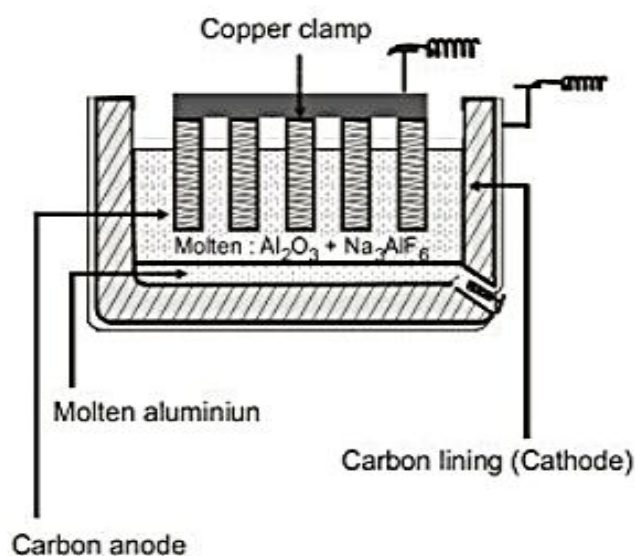
(ii) Electrolysis of fused Alumina.

Cathode : Iron-tank lined with carbon bricks

Anode : carbon

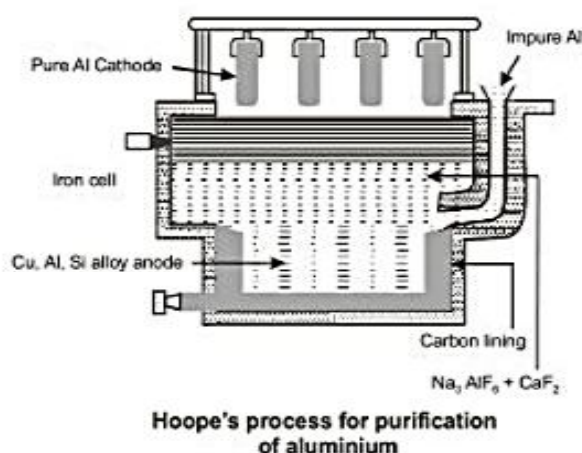
**Electrolyte :** Molten  $[\text{Al}_2\text{O}_3 (5\%) \text{ Na}_3\text{AlF}_6 (85\%) + \text{CaF}_2(5\%) + \text{AlF}_3(5\%) ]$

$\text{O}_2$  is liberated at anode and Al collects at the bottom.



**Hall Heroult process**

- (iii) Reactions :  $\text{Na}_3\text{AlF}_6 \longrightarrow 3\text{NaF} + \text{AlF}_3$   
 $\text{AlF}_3 \longrightarrow \text{Al}^{3+} + 3\text{F}^-$   
 At anode :  $\text{Al}_2\text{O}_3 + 6\text{F}^- \rightarrow 2\text{AlF}_3 + 3/2 \text{O}_2 + 6\text{e}^-$   
 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 :  $\text{Na}_3\text{AlF}_6 + \text{CaF}_2$



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

Middle layer : molten mixture of Fluorides of Na, Ba, Al and  $\text{Al}_2\text{O}_3$

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.

### Illustration

**Q.1** Aluminium is obtained from  $\text{Al}_2\text{O}_3$  by this method –

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

**Ans.** (C)

**Sol.** For all metals with high electropositive nature, electrolytic reduction is best method.

### Exercise

**Q.1** If Bauxite consists of  $\text{SiO}_2$  as impurity, this process is employed –

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

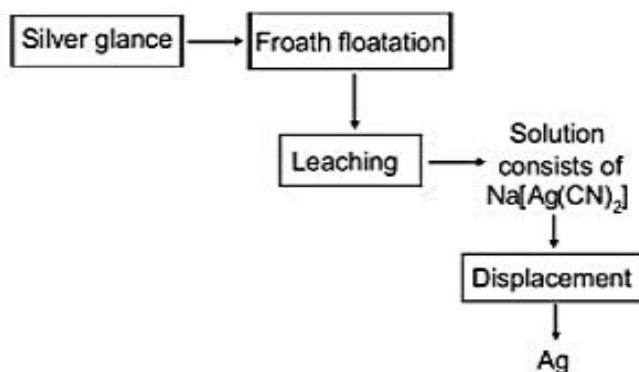
**Ans.** (D)



## EXTRACTION OF SILVER

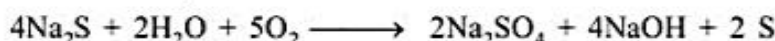
(a) **Ores :** Silver glance or argentite  $\text{Ag}_2\text{S}$ , Ruby silver  $\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ , Horn silver  $\text{AgCl}$ .

(b) **Process :** Cyanidation or Mac-Arthur-Forrest cyanide process



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

$\text{Ag}_2\text{S} + 4 \text{NaCN} \longrightarrow 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$ ; passing of air causes oxidation of  $\text{Na}_2\text{S}$ , thereby forward reaction takes place.



sodium argento cyanide

sodium zinc cyanide

The precipitated silver is separated and purified by fusion with borax or  $\text{KNO}_3$  to get pure silver.

Electrolytic refining: Anode : Impure Ag

cathode : Pure Ag

Electrolyte :  $\text{AgNO}_3(\text{aq.}) + \text{HNO}_3$ .

### Illustration

**Q.1** Which of the following processes is/are the examples of leaching:

(I) Mac Arthur forest process

(II) Hoop's process

(III) Baeyer's process

(IV) Allumino thermite process

Choose the correct code:

(A) I, II and III

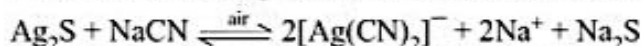
(B) I, III and IV

(C) I and III

(D) III only

**Ans.** (C)

**Sol.** (I) In Mac Arthur forest process, silver ore is leached out as  $[\text{Ag}(\text{CN})_2]^-$



(II) In Baeyer's process, alumina and  $\text{SiO}_2$  is leached out as  $[\text{Al}(\text{OH})_4]^-$  and  $\text{Na}_2\text{SiO}_3$  respectively.

(III) Hoop's process is used for purification of Aluminium.

**Exercise**

**Q.1** Leaching is preferred for which sulphide ore.

- (A) Galena (B) Argentite (C) Sphalerite (D) Cinnabar

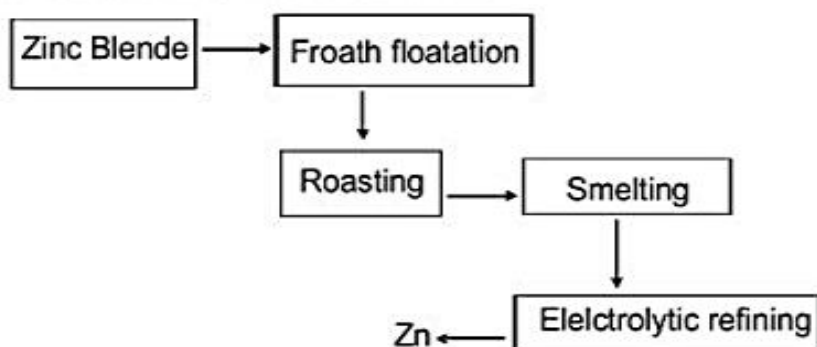
**Ans.** (B)

**EXTRACTION OF ZINC**

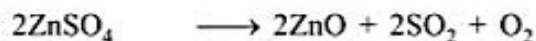
**Occurrence :** Zinc is usually found in the combined state although traces of the metal in the native state have been reported from Melbourne (Australia). Its chief ores are :

1. Zinc blende,  $\text{ZnS}$ .
2. Calamine or Sphalerite,  $\text{ZnCO}_3$
3. Zincite,  $\text{ZnO}$

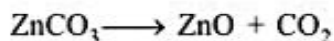
1. **Extraction process :** It involves the following steps :



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**

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**Illustration**

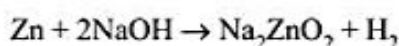

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**Q.1** Zn and Ag can be separated from each other by

- (A) distillation (B) heating with conc. NaOH  
(C) treating with dil.  $\text{HNO}_3$  (D) fractional crystallisation

**Ans.** (B, D)

**Sol.** Zinc is a volatile metal. Its boiling point is 1180K. It can be separated from silver by distillation. It can also be separated by heating with conc. NaOH solution in which Zn gets dissolved leaving Ag as such. The reaction is


**Exercise**


---

**Q.1** Calamine is concentrated by :

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

**Ans.** (D)

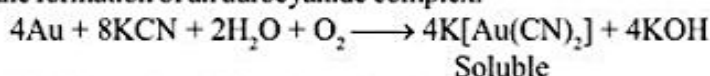
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**EXTRACTION OF GOLD**
**Occurrence of Gold :**

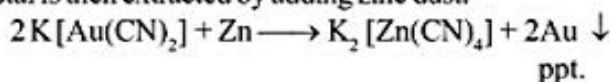
Gold is mainly found in native state either as vein good, placer gold or alluvial good. It is also present to a small extent in the combined state as sulphide, telluride and arsenosulphide. Some important ores of gold are :

(i) Calaverite,  $\text{AuTe}_2$  (ii) Sylvanite,  $\text{AuAgTe}_2$  and (iii) Bismuth aurite,  $\text{BiAu}_2$

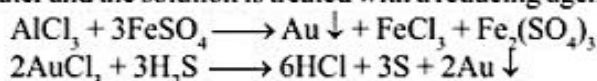
- (i) **Mac-Arthur-Forest Cyanide process :** The powdered gold ore, after concentration by Forth-floatation process, is roasted to remove easily oxidisable impurities of tellurium, arsenic and sulphur. The roasted ore is then treated with a dilute solution of KCN in presence of atmospheric oxygen when gold dissolves due to the formation of an aurocyanide complex.



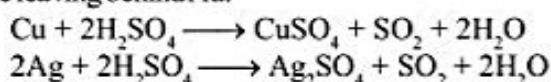
The metal is then extracted by adding zinc dust.



- (ii) **Plattner's chlorine process :** The roasted ore is moistened with water and placed in wooden vats with false perforated bottoms. It is saturated with current of chlorine, gold chloride thus formed is leached with water and the solution is treated with a reducing agent such as  $\text{FeSO}_4$  or  $\text{H}_2\text{S}$  to precipitate gold.



The impure gold thus obtained contains imparities of Ag an Cu. The removal of Ag and Cu forms gold is called parting. This is done by heating impure gold with conc.  $\text{H}_2\text{SO}_4$  (or  $\text{HNO}_3$ ) when Ag and Cu dissolve leaving behind Au.



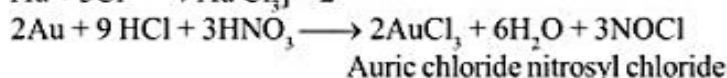
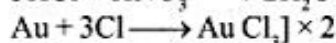


**Properties of gold :**

Gold is a yellow, soft and heavy metal. Gold and Ag are called noble metals since they are not attacked by atmospheric oxygen. However, Ag gets tarnished when exposed to air containing traces of  $\text{H}_2\text{S}$ . Gold is malleable, ductile and a good conductor of heat and electricity. Pure gold is soft. It is alloyed with Ag or Cu for making jewellery. Purity of gold is expressed in terms of carats. Pure gold is 24 carats. Gold '14 carats' means that it is an alloy of gold which contains 14 parts by weight of pure gold and 10 parts of copper per 24 parts by weight of the alloy. Thus the percentage of gold in "14 carats" of gold is =

$$\frac{100}{24} \times 14 = 58.3\%$$

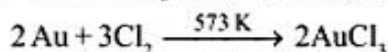
Most of the jewellery is made from 22 carat gold (91.66% pure gold). Gold is quite inert. It does not react with oxygen, water and acids but dissolves in aqua regia (3 parts concentrated  $\text{HCl}$  + 1 part concentrated  $\text{HNO}_3$ )

**Oxidation states of gold :**

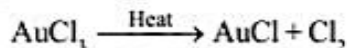
The principal oxidation states of gold are +1 and +3 though +1 state is more stable than +3

**Compounds of gold :**

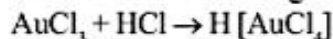
- (1) Auric chloride  $\text{AuCl}_3$ . It is prepared by passing dry  $\text{Cl}_2$  over finely divided gold powder at 573 K



It is a red coloured crystalline solid soluble in water and decomposes on heating to give gold (I) chloride and  $\text{Cl}_2$ .

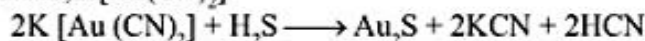


It dissolved in conc.  $\text{HCl}$  forming chloroauric acid



Chloroauric acid is used in photography for toning silver prints and as an antidote for snake poisoning.

- (2) Aurous sulphide,  $\text{Au}_2\text{S}$ . It is prepared when  $\text{H}_2\text{S}$  is passed through an acidified solution of potassium aurocyanide,  $\text{K}[\text{Au}(\text{CN})_2]$



It is dark brown solid, not attacked by dilute mineral acids and hence is probably the most stable gold (I) compound

**Illustration**

- Q.1** Which of the following metals can not be extracted by self reduction?

(A) Au                      (B) Hg                      (C) Cu                      (D) Pb

**Ans.** (A)

**Sol.** Hg, Cu and Pb metals can be extracted by self reduction from their respective sulphide ores.

**Exercise**

- Q.1** Which of the following ore of the metal(s) is / are concentrated by leaching method

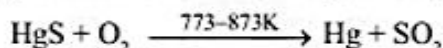
(A) Al                      (B) Fe                      (C) Au                      (D) Ag

**Ans.** (A, C, D)

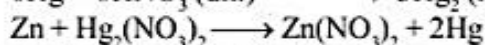
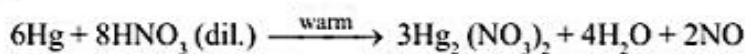
## EXTRACTION OF MERCURY

### Occurrence and extraction of mercury :

Cinnabar (HgS) is the only important ore of Hg. It is concentrated by froth floatation method and mercury is extracted from this ore by heating it in air at 773–873 K (auto reduction)



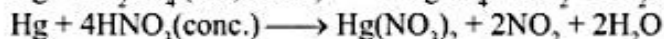
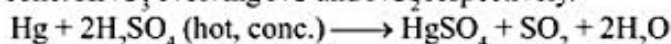
The mercury vapours thus obtained are condensed to give liquid metal. Hg thus obtained contains impurities of Zn, Sn and Pb. These are removed by treating the impure metal with dil.  $\text{HNO}_3$ . Mercurous nitrate,  $\text{Hg}_2(\text{NO}_3)_2$  thus formed reacts with metals present as impurities forming their nitrates which pass into solution leaving behind pure mercury. However, it is best purified by distillation under reduced pressure.



Similar reaction is given by Pb and Sn.

### Properties of mercury :

Mercury is less reactive than Zn. It is liquid at room temperature and has low thermal and electrical conductivity. Mercury forms dimeric mercury (II) ion,  $\text{Hg}_2^{+2}$  in which the two Hg atoms are bonded by a covalent bond. It is easily oxidised to  $\text{HgO}$  at about its boiling point. Hg does not react with dil.  $\text{HCl}$  or dil.  $\text{H}_2\text{SO}_4$  but reacts with hot concentrated  $\text{H}_2\text{SO}_4$  to form  $\text{HgSO}_4$ . It, however, reacts with both warm dil and conc.  $\text{HNO}_3$  evolving  $\text{NO}$  and  $\text{NO}_2$  respectively.



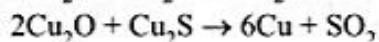
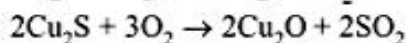
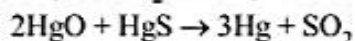
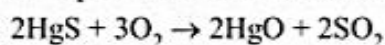
### Illustration

**Q.1** Auto reduction process is used in the extraction of

- (A) Cu and Hg      (B) Zn and Hg      (C) Cu and Mg      (D) Fe and Pb

**Ans.** (A)

**Sol.** Auto reduction takes place in the case of Cu and Hg. The reactions are as follows:



### Exercise

**Q.1** To obtain silver from silver amalgam it is heated in vessel which is made of

- (A) Cu      (B) Fe      (C) Ni      (D) Zn

**Ans.** (B)



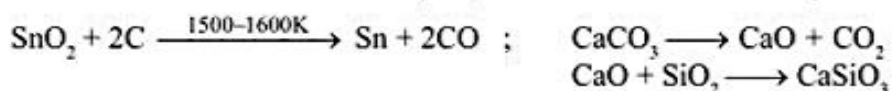
## EXTRACTION OF TIN

### Occurrence of tin :

Tin does not occur in nature in the native state. Its chief ore is cassiterite or tin stone ( $\text{SnO}_2$ ).

### Extraction of tin from tin stone :

The ore is crushed, washed and concentrated magnetically to remove magnetic impurities of tungstate of iron (wolframite,  $\text{FeWO}_4$ ) and manganese. The concentrated ore is roasted to remove sulphur and arsenic as their oxides. The roasted ore is then subjected to smelting i.e. ore is mixed with anthracite (coke) in the ratio 1 : 4 and little limestone (flux) and heated in a reverberatory furnace.

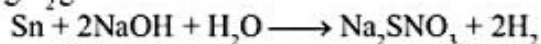


The molten metal is tapped out from the bottom of the furnace and cast into blocks. The tin thus obtained is called block tin and contains impurities of Fe, Pb and Cu etc. The crude metal is finally refined by either liquation, poling or electro-refining.

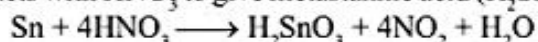
In electro refining, impure metal is made the anode while a sheet of pure metal acts as the cathode. The electrolyte consists of stannous sulphate  $\text{SnSO}_4$  containing little  $\text{H}_2\text{SO}_4$  and hydrofluosilicic acid ( $\text{H}_2\text{SiF}_6$ ). On passing current, tin dissolves from the anode and passes into the electrolyte while an equivalent amount of tin from the electrolyte gets deposited on the cathode.

### Properties of tin :

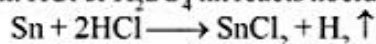
It is a soft white metal, malleable and ductile and can be rolled into sheets and foils. When heated in air, it forms  $\text{SnO}_2$ , with S it forms  $\text{SnS}_2$  and with  $\text{Cl}_2$  it gives  $\text{SnCl}_4$ . It dissolves in hot concentrated alkalis evolving  $\text{H}_2$  gas



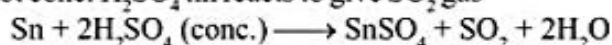
and reacts with  $\text{HNO}_3$  to give metastannic acid ( $\text{H}_2\text{SnO}_3$ )



With dil.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  tin reacts liberating  $\text{H}_2$  gas



With hot conc.  $\text{H}_2\text{SO}_4$  tin reacts to give  $\text{SO}_2$  gas



Tin is widely used for plating iron and brass vessels to resist corrosion. Tin foils are also used for wrapping cigarettes and making food containers.

### Illustration

**Q.1** A tin ore ( $\text{SnO}_2$ ) contains  $\text{FeCrO}_4$  as impurity. It can be concentrated by

- |                          |                        |
|--------------------------|------------------------|
| (A) magnetic separation  | (B) froth floatation   |
| (C) electrostatic method | (D) gravity separation |

**Ans.** (A)

**Sol.**  $\text{FeCrO}_4$  is magnetic material. Obviously, it can be separated from tin ore ( $\text{SnO}_2$ ) which is non-magnetic by magnetic separation method.



---

**Exercise**


---

**Q.1** Cassiterite is concentrated by:

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

**Ans.** (B)

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## EXTRACTION OF LEAD

### Occurrence of lead :

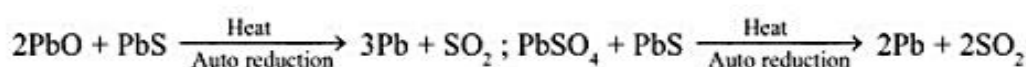
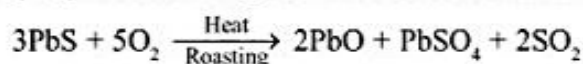
Lead does not occur in the free state. The important ores of lead are :

- (i) Galena (PbS)      (ii) Anglesite (PbSO<sub>4</sub>) and      (iii) Cerussite (PbCO<sub>3</sub>).

### Extraction of lead :

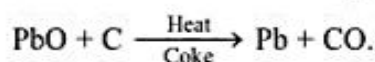
**(i) Self reduction process :**

Galena, after concentration by Froth-floatation process, is roasted in air to form PbO and PbSO<sub>4</sub>. The unchanged galena then brings about the reduction of PbO and PbSO<sub>4</sub> to Pb metal (auto reduction).



**(ii) Carbon reduction process :**

The roasted ore is reduced to metal by heating with coke.

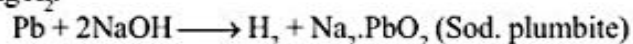


The metal obtained by above methods contain Ag, Cu, Fe, Sn and Sb as impurities. It is refined by either liquation, softening, desilverisation or electrolytic refining processes.

In electrolytic refining the electrolyte taken consists of a solution of lead fluorosilicate (PbSiF<sub>6</sub>) and hydrofluosilicic acid (H<sub>2</sub>SiF<sub>6</sub>) with a little gelatin.

### Properties of lead :

Lead is a bluish grey lustrous metal but when exposed to air, it acquires dull appearance due to the forming of a thin layer of Pb(OH)<sub>2</sub> and PbCO<sub>3</sub> on its surface. It dissolves in hot concentrated alkali evolving H<sub>2</sub>.



Other reactions with acids, S, Cl<sub>2</sub> are similar to those of Sn

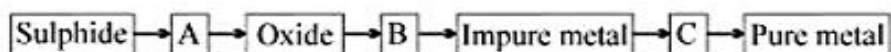
Lead forms two series of compounds i.e. Pb (II) and Pb(IV) compounds but Pb(II) compounds are more stable than Pb (IV) compounds. Pb (II) compounds are essentially ionic while Pb (IV) compounds are covalent in nature.

Lead used for making cable coverings, bullet shots, lead accumulators, tetraethyl lead (antiknocking agent) and a number of pigments such as red lead (Pb<sub>3</sub>O<sub>4</sub>); white lead [2Pb(OH)<sub>2</sub>.PbCO<sub>3</sub>], chrome yellow (PbCrO<sub>4</sub>) and chrome red (PbO.PbCrO<sub>4</sub>).

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**Illustration**

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**Q.1** Step C (refining) involved in purification of Pb metal

- (A) Distillation      (B) Bessemerization      (C) Cupelation      (D) Electrolytic refining

**Ans.** (D)

**Sol.** Sulphide ore  $\xrightarrow{\text{Roasting}}$  oxide  $\xrightarrow{\text{Auto Reduction}}$  Impure metal

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**Exercise**

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**Q.1** When ZnS and PbS minerals are present together, then NaCN is added to separate them in the froth floatation process as a depressant, because

- (A)  $\text{Pb}(\text{CN})_2$  is precipitated while no effect on ZnS  
(B) ZnS forms soluble complex  $\text{Na}_2[\text{Zn}(\text{CN})_4]$   
(C) PbS forms soluble complex  $\text{Na}_2[\text{Pb}(\text{CN})_4]$   
(D) They cannot be separated by adding NaCN.

**Ans.** (B)

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## SOLVED EXAMPLES

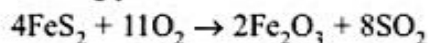
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**Q.1** Heating of pyrites in air for oxidation of sulphur is called

- (A) roasting                      (B) smelting                      (C) calcinator                      (D) slagging

**Ans.** (A)

**Sol.** Sulphide ores are strongly heated to convert them into oxides and this is called roasting.

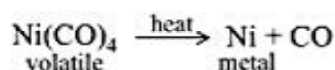


**Q.2** One of the following metals forms a volatile compound and this property is taken advantage of its extraction. The metal is

- (A) iron                      (B) nickel                      (C) cobalt                      (D) tungsten

**Ans.** (B)

**Sol.** Nickel combines with CO to form volatile  $\text{Ni}(\text{CO})_4$  (nickel carbonyl) which decomposes to give pure Ni metal and CO on heating.



**Q.3** 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

**Ans.** (A)

**Sol.** 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.

**Q.4** Heating an ore in the absence of air below its melting point is called:

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

**Ans.** (D)

**Sol.** Roasting is heating in presence of air.

**Q.5** Zinc blende on roasting in air gives –

- (A) Zinc carbonate    (B)  $\text{SO}_2$  and ZnO    (C) ZnS and  $\text{ZnSO}_4$     (D)  $\text{CO}_2$  and ZnO

**Ans.** (B)

**Sol.**  $\text{ZnS} + \text{O}_2 \longrightarrow \text{ZnO} + \text{SO}_2$

**Q.6** Reagent used in cyanide process is –

- (A) NaOH                      (B) NaCN                      (C)  $\text{Na}_2\text{CO}_3$                       (D)  $\text{NaNO}_3$

**Ans.** (B)

**Sol.** It is used to concentrate gold & silver

**Q.7** In alumino-thermite process, aluminium is used as:

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

**Ans.** (C)

**Sol.** Al is used to reduce oxide of Cr & Mn.

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**Q.8** Which of the following is not a concentration technique  
 (A) Levigation (B) Froth floatation (C) Leaching (D) Calcination

**Ans.** (D)

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

**Q.9** Cassiterite is an ore of :  
 (A) Mn (B) Ni (C) Sb (D) Sn

**Ans.** (D)

**Sol.** Cassiterite is  $\text{SnO}_2$

**Q.10** Cassiterite is concentrated by :  
 (A) Levigation (B) Electromagnetic separation  
 (C) Floatation (D) Liquefaction

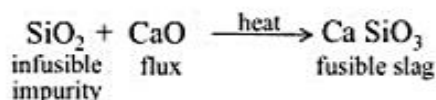
**Ans.** (B)

**Sol.** Its contain magnetic (wolframite) impurities.

**Q.11** In metallurgy, flux is a substance that is used to convert  
 (A) infusible impurities to fusible material (B) fusible impurities to infusible impurities  
 (C) soluble impurities to insoluble impurities (D) mineral into silicate

**Ans.** (A)

**Sol.** Flux converts infusible impurities to fusible material



**Q.12** Chromium is obtained by reducing purified chromite ore with  
 (A) red-hot coke (B) gaseous hydrogen (C) aluminium powder (D) carbon monoxide

**Ans.** (C)

**Sol.** Chromite ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is first converted into free  $\text{Cr}_2\text{O}_3$ . It is then reduced by Al to pure chromium metal.

