METALLURGY

Introduction

Metallurgy : The branch of chemistry which deals with the method of extraction of metals from their ores by profitable means.

Metal : The element which tends to form positive ion is called a metal.

Minerals : The various compounds of metals which occur in the earth's crust and are obtained by mining are called minerals. In earth crust order of abundance of elements is. O > Si > Al > Fe

A mineral may be single compound or a mixture.

Ore : The mineral from which a metal can be extracted **profitably** and **easily** is called an ore.

All ores are minerals but all minerals are not ores.

Gangue or matrix : The undesirable impurities present in an ore are called **gangue.**

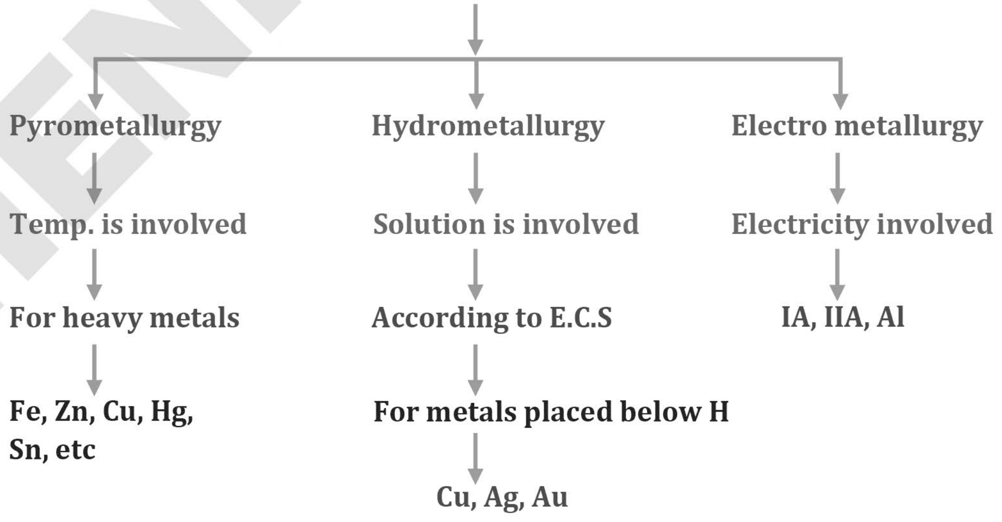
Type of Ores :

(I) **Combined Ore :** Metals placed above H in electrochemical series are generally reactive i.e. why they generally found in combined state.

- **(a)** **Halide ore / Sulphate ore / Oxy ore :** Metals are highly reactive
- **(b)** **Oxide ore :** Reactive metal (Al to Sn)
- **(c)** **Sulphide ore :** Metal placed near H or below H. (Pb, Hg, Cu, Ag)

(II) **Native Ore :** Metal placed below H in electrochemical series are generally found in native state. (Ag, Au, Cu, Pt etc.)

Types of metallurgy



Types of ores and their names

TYPES OF ORES	S.N.	FORMULA OF THE ORE	NAME
Oxide Ore	1.	ZnO (Philosopher's Wool)	Zincite
	2.	MnO_2	Pyrolusite
	3.	SnO_2	Cassiterite (Tin stone)
	4.	Cu_2O	Cuprite (Ruby Copper)
	5.	Fe_2O_3	Haematite
	6.	$Al_2O_3.2H_2O$	Bauxite
	7.	$FeO. Cr_2O_3$	Chromite
	8.	Fe_3O_4	Magnetite
	9.	$Fe_2O_3.3H_2O$	Limonite
	10.	TiO_2	Rutile
Sulphide Ore	1.	ZnS	Zinc Blende (Sphalerite)
	2.	HgS	Cinnabar
	3.	PbS	Galena
	4.	Ag_2S	Argentite or Silver glance
	5.	FeS_2	Iron pyrite (Fool's gold)
	6.	$CuFeS_2$	Copper pyrite (Chalcopyrites)
	7.	$Cu_2S.Ag_2S$	Copper silver glance
	8.	$Ag_2S.Sb_2S_3$	Pyrargyrite (Ruby silver)
	9.	Cu_2S (Copper glance)	Chalcocite
Halide Ore	1.	NaCl	Rock Salt
	2.	AgCl	Horn Silver
	3.	CaF_2	Flourspar
	4.	$AlF_3.3NaF$	Cryolite
	5.	$KCl.MgCl_2.6H_2O$	Carnalite
Carbonate Ore	1.	$MgCO_3$	Magnesite
	2.	$CaCO_3$	Lime stone
	3.	$MgCO_3.CaCO_3$	Dolomite
	4.	$ZnCO_3$ (Smithosonite)	Calamine
	5.	$PbCO_3$	Cerrusite
	6.	$FeCO_3$	Siderite
	7.	$CuCO_3. Cu(OH)_2$	Malachite green
	8.	$2CuCO_3.Cu(OH)_2$	Azurite
Sulphate Ore	1.	$CaSO_4.2H_2O$	Gypsum
	2.	$MgSO_4.7H_2O$	Epsomite Or Epsom salt
	3.	$K_2SO_4.Al_2(SO_4)_3.24H_2O$	Alum
Nitrate Ore	1.	$NaNO_3$	Chile- Salt Peter
	2.	KNO_3	Salt peter or Indian salt peter
Phosphate Ore	1.	$Ca_3(PO_4)_2$	Rock Phosphate

(A) concentration of the ore or benefaction or dressing of ore:

The removal of impurities from the ore is called its concentration or to increase the concentration of ore in ore sample. Two process – (1) **Physical** (2) **Chemical**

1. Physical Concentration :

(I) Gravity Separation (Levigation) : This method of concentration of the ore is based on the difference in the gravities of the ore and the gangue particles. Powdered ore is agitated with a running stream of water. The lighter gangue particles are taken away by water while heavier ore particles settle down.

Used for concentration of oxygenated ores.

(II) Froth Floatation Method

This method is mainly employed for the concentration of sulphide ores.

The method is based on the different wetting characteristics of the gangue and the sulphide ore with water and oil. The gangue particles are preferentially wetted by water and the ore particles by oil.

The crushed ore along with water is taken in a floatation cell. Various substances are added depending on the nature of the ore and a current of air is blown in. The substances added are –

(i) Frothers :– They generate a stable froth which rises to the top of the tank.

Example of frother is pine oil, Eucalyptus oil, fatty acids etc.

(ii) Collectors or floating agents :– They attach themselves by polar group to the granules of the ores which then become water repellent and pass on into the froth.

Example: sodium ethyl xanthate, pine oil and fatty acid.

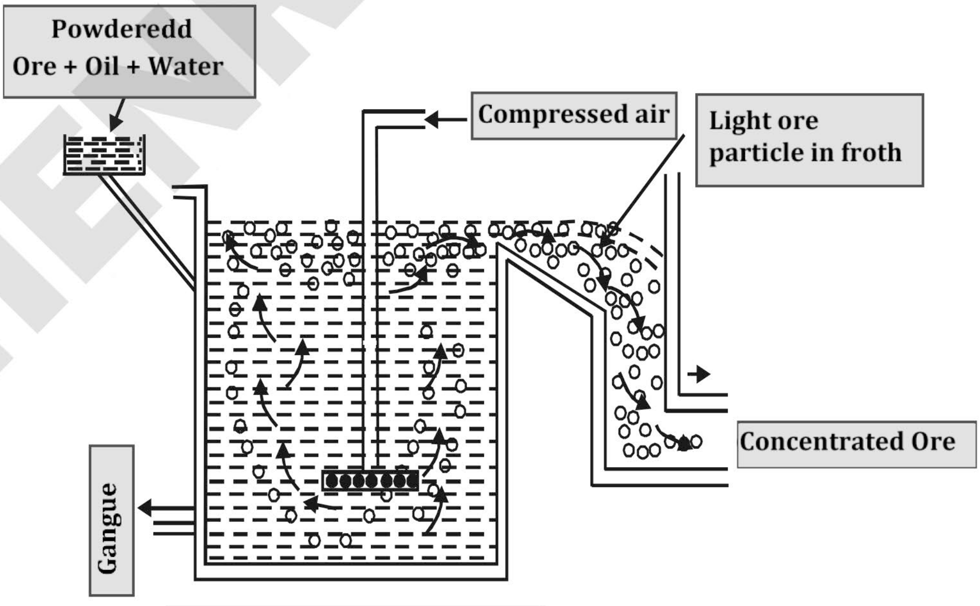
(iii) Froth stabilisers :- They stabilise froth.

Ex. Cresol, Aniline etc.

(iv) Depressants :– These reagents depress the floatation property and help in the separation of different sulphide ores present in a mixture.

for eg. in case of an ore containing ZnS and PbS the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

$$\mathrm{NaCN + (ZnS + PbS) \longrightarrow \underset{\text{(remain in the solution)}}{Na_2[Zn(CN)_4]} + \underset{\text{(comes to the froth}}{PbS}}$$

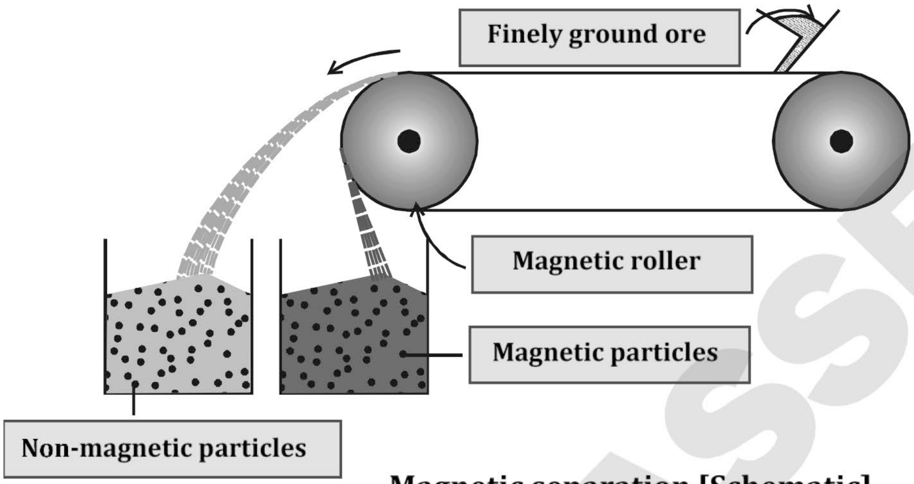


[Froth floatation process]

(III) Magnetic Separation :-

If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out (e.g. in case of iron ores)

e.g.
- SnO_2 which is non-magnetic having the impurities of $FeWO_4 + MnWO_4$ (Magnetic)
- $FeO.Cr_2O_3$ (Magnetic) having the impurities of SiO_2 (Non-magnetic)



Magnetic separation [Schematic]

2. **Chemical Concentration (Leaching)** : In this process we use suitable reagent which react with ore to form water soluble complex while impurities remain insoluble. Applicable for Al, Ag, Au.

(a) for Al

Red Bauxite $\longrightarrow Al_2O_3.2H_2O + Fe_2O_3/FeO$
(Major impurities)

White Bauxite $\longrightarrow Al_2O_3.2H_2O + SiO_2$
(Major impurities)

for red bauxite :

(i) Bayer's process : NaOH is used.

$$Al_2O_3 + NaOH \longrightarrow NaAlO_2 \xrightarrow{H_2O(excess)\&CO_2} Al(OH)_3\downarrow + NaOH$$

$$\underset{\text{(Basic)}}{Fe_2O_3/FeO} + NaOH \longrightarrow \text{insoluble}$$

(ii) Hall's process : Na_2CO_3 is used.

$$Al_2O_3 + Na_2CO_3 \longrightarrow 2NaAlO_2 \xrightarrow[CO_2]{HOH} Al(OH)_3\downarrow + Na_2CO_3$$

for white bauxite

(i) Serpeck's process : a mixture of $(C + N_2)$ is used

$$Al_2O_3 + N_2 \xrightarrow[-CO\uparrow]{1800°C} AlN \xrightarrow{H_2O} Al(OH)_3\downarrow + NH_3\uparrow$$

$$C + SiO_2 \longrightarrow CO_2\uparrow + Si\uparrow .$$

(b) for Ag and Au (Cyanide Process)

(I) for Ag $$Ag_2S + 4NaCN \xrightarrow{2O_2} 2Na[Ag(CN)_2] + Na_2SO_4$$

[in absence of O_2, reaction become reversible]

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

(II) for Au $$Au + KCN + H_2O \xrightarrow{O_2} K[Au(CN)_2] + KOH$$

$$K[Au(CN)_2] + KOH + Zn \longrightarrow K_2ZnO_2 + KCN + H_2O + Au\downarrow$$

(B) Calcination and Roasting (Conversion of ore into oxide form)

Concentrated ore must be converted into a form which is suitable for reduction, usually the ore is converted to oxide before reduction because oxides are easier to reduce.

(a) Calcination : Calcination is a process in which ore is heated at temperature below melting point, generally in the absence of air, to expel water from a hydrated or hydroxide ore and carbon dioxide from a carbonate ore.

e.g. $2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

$2Fe_2O_3.\ 3H_2O \xrightarrow{\Delta} 2Fe_2O_3 + 3H_2O$

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} CuO + CO_2 + H_2O$

Advantages of Calcination :–

(i) Moisture is removed.

(ii) Organic matter is destroyed

(iii) The ore become porous and easily workable

(b) Roasting : The removal of the excess sulphur contained in sulphide ores in the form of SO_2 by heating in an excess of air is called roasting.

The concentrated sulphide ore is heated in reverberatory furnace, below its melting point in the presence of an excess of air.

$2ZnS + 3O_2 \xrightarrow{\text{Roasting}} 2ZnO + 2SO_2\uparrow$

$PbS + O_2 \xrightarrow{\text{Roasting}} PbO + SO_2\uparrow$

Some important examples of roasting

Sulphide of Ag and Hg (Ag_2S, HgS) when roasted they give directly metal and oxygen because their oxides are unstable towards heat.

$$Ag_2S + O_2 \xrightarrow[-SO_2]{\Delta} \underset{\text{Unstable}}{Ag_2O} \xrightarrow[300°C]{\Delta} 2Ag + \frac{1}{2}O_2$$

$$HgS + O_2 \xrightarrow[-SO_2]{\Delta} \underset{\text{Unstable}}{HgO} \xrightarrow[400°C]{\Delta} Hg + \frac{1}{2}O_2$$

Oxides ores of iron Fe_2O_3 (heamatite), Fe_3O_4 (magnetite) has some amount of FeO and before reduction process these oxide ores of iron should undergo roasting so that FeO can be converted into Fe_2O_3 and it could not form slag with SiO_2 to prevent loss of Fe.

Advantages of Roasting :–

(i) Excess of sulphur is removed as volatile oxide.

$$\underset{\text{(air)}}{S + O_2} \rightarrow SO_2$$

(ii) Impurities of arsenic, antimony & phosphorous are removed as their volatile oxides.

$Sb_4 + 3O_2 \rightarrow 2Sb_2O_3\uparrow$

$As_4 + 3O_2 \rightarrow 2As_2O_3\uparrow$

$P_4 + 3O_2 \rightarrow 2P_2O_3\uparrow$

- For PbS, Cu_2S and HgS partial roasting is carried out because these sulphide ore easily converted into metal by self-reduction process.

(C) Reduction to the Metal :

The calcined or roasted ore is then reduced to the metallic state by either of the following method:

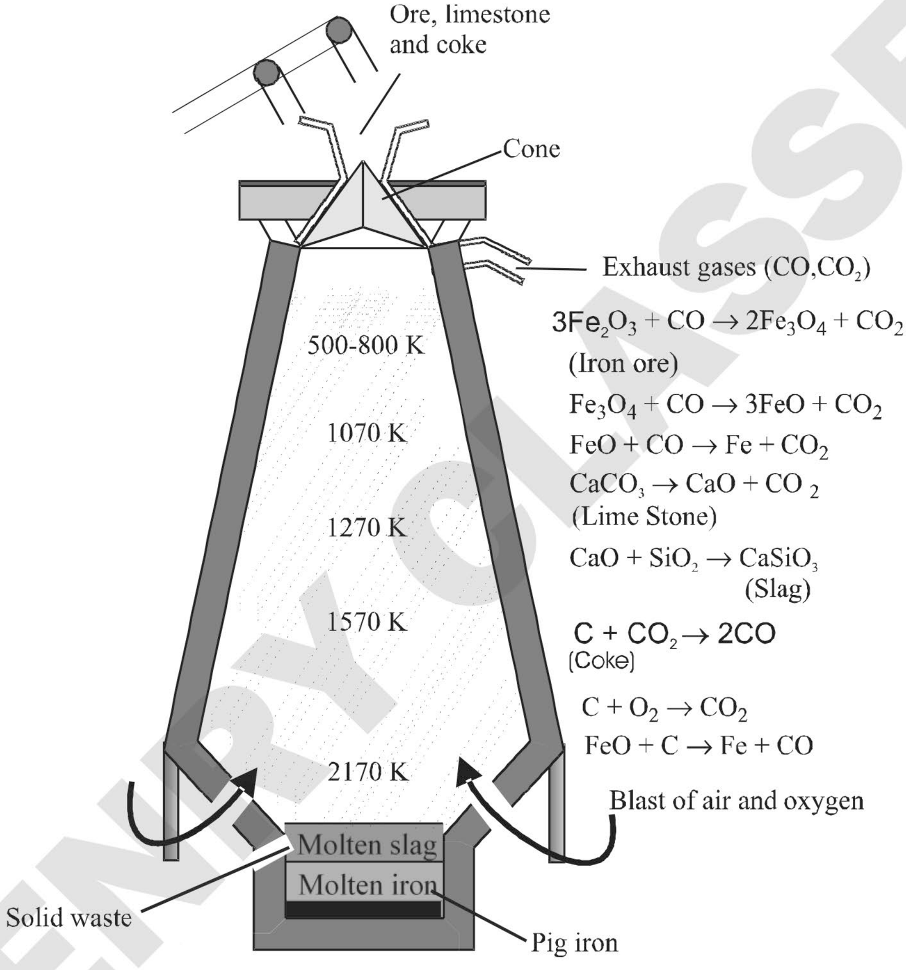
(I) Chemical reduction :

(i) Reduction by carbon (Smelting)

"Reduction of the oxide with carbon at high temperature is known as smelting".

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced to metal by strongly heating them with coal or coke, in the blast furnace.

Metal Oxide + Coke + flux → Metal + $CO_2\uparrow$ +Slag.



(Blast Furnace)

e.g.

$ZnO + C \longrightarrow Zn + CO\uparrow$

$PbO + C \longrightarrow Pb + CO\uparrow$

$SnO_2 + 2C \longrightarrow Sn + 2CO\uparrow$

$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO\uparrow$

These reactions are carried out at high temperature because at high temp. C is better reducing agent.

$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2\uparrow$

$PbO + CO \longrightarrow Pb + CO_2\uparrow$

$SnO_2 + 2CO \longrightarrow Sn + 2CO_2\uparrow$

These reactions are carried out at low temperature because at low temp. CO is better reducing agent.

FLUX : Substance used to convert non fusible impurities into fusible one.

Types of flux :-

(a) **Acidic Flux :** Substance used to remove basic impurities (metal oxide)

For example

$$\underset{\text{(basic impurity)}}{CaO} + \underset{\text{(acidic flux)}}{\underline{S}iO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

Acidic flux are non-metal oxide (SiO_2, P_2O_5 etc.)

(b) **Basic flux :** Substance used to remove acidic impurities (non-metal oxide)

For example

$$\underset{\text{(basic flux)}}{\underset{\downarrow}{CaO}} + \underset{\text{(acidic impurities)}}{\underset{\downarrow}{SiO_2}} \longrightarrow \underset{\text{(Slag)}}{\underset{\downarrow}{CaSiO_3}}$$

Basic flux are metal oxide. (CaO, MgO, etc.)

(c) **Neutral flux :** Substance used in electrolytic reduction to decrease the fusion temperature and to increase the conductivity of the mixture by providing free ions.

For example : $(\underset{\text{Cryolite}}{Na_3AlF_6} + \underset{\text{Flourspar}}{CaF_2}), CaCl_2$ etc.

Smelting in Cu-metallurgy

$$\begin{bmatrix} CuS + FeS \\ Cu_2O + FeO \end{bmatrix} + \underset{\downarrow}{\text{Coke}} + \underset{\text{(flux)}}{SiO_2} \xrightarrow[\text{furnace}]{\text{In blast}} \underset{\text{(Copper matte)}}{Cu_2S + FeS} + \text{slag } (FeSiO_3)$$

Only acts as fuel not as a reducing agent

[$MS + C \rightarrow M + CS_2$ $\Delta G = +ve$(non-spontaneous)]

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

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

(II) Self reduction

Compounds of certain metals are reduced to metal without using any additional reducing agent.

In this process metal sulphide ores are partially roasted to give some oxide. This oxide is now reduced to the metal by the remaining sulphide ore at elevated temperatures in the absence of air. The process is known as self-reduction. e.g. for sulphides of Cu, Pb, Hg etc.

Self reduction for Pb :-

$$\underset{\text{(Galena)}}{2PbS} + \underset{\text{(air)}}{3O_2} \xrightarrow{\text{Partial roasting}} 2PbO + 2SO_2\uparrow$$

$$PbS + 2PbO \xrightarrow[\text{Absence of air}]{\text{High temp}} 3Pb + SO_2\uparrow$$

Self-reduction for Cu (Bessemerisation)

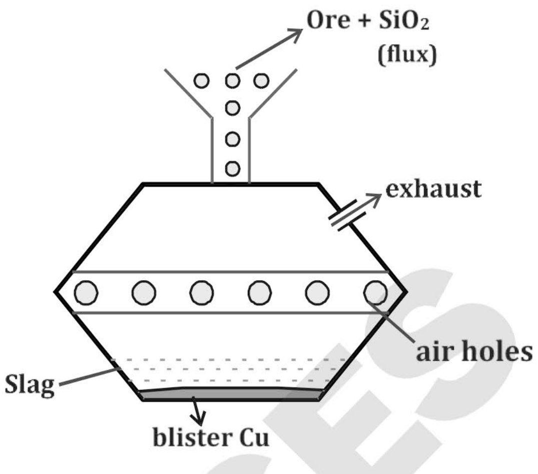
$$\underset{\text{(Copper matte)}}{Cu_2S + FeS} + \underset{\text{(flux)}}{SiO_2} \longrightarrow \text{Blister copper + slag}$$

$$FeS + O_2 \longrightarrow FeO + SO_2\uparrow$$

$FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)
(gangue) (flux)

$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2\uparrow$
(Blister copper)



[Bessemer convertor]

Note :
The solidified copper obtained has blistered appearance due to evolution of SO_2 and so it is called blister Copper.

Thermal Decomposition :

$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$

$2HgO \xrightarrow{\Delta} 2Hg + O_2$

(III) Alumino thermite process or thermite welding process : In this process those metal oxide (oxides of Mn, Ti, Cr, Fe) will be reduced which required high temperature and at high temperature carbon react with metal to from metal carbide.

In this process we use aluminium as a reducing agent due to :-

(i) Al has greater affinity towards oxygen as it forms most stable oxide (Al_2O_3)

(ii) This reaction is highly exothermic in nature and once it start it will continue till all the metal oxide is reduced into metal.

For Cr, Mn, Fe : (a) $Cr_2O_3 + Al \longrightarrow Al_2O_3 + 2Cr$
(b) $Fe_2O_3 + Al \longrightarrow Al_2O_3 + 2Fe$

Note : **Reaction (b) is used in welding of railway tracks.**

(IV) Electrolytic reduction

This process is mainly used for the extraction of highly electropositive metals. I A, II A & Al
Electrolysis is carried out in a large cell and a small amount of another suitable electrolyte is added which:

(i) Lowers the melting point of the main electrolyte

(ii) Enhances conductivity of molten mixture

(iii) Reduces corrosion troubles

e.g. Manufacture of metallic sodium (Down's process)

Molten NaCl containing $CaCl_2$ is electrolysed between graphite anode and iron cathode. The various reactions that take place are :

On Fusion : $NaCl \rightleftharpoons Na^+ + Cl^-$

On Electrolysis : At Cathode :– $Na^+ + e^- \rightarrow Na$
At Anode :– $2Cl^- \rightarrow Cl_2(g) + 2e^-$

(D) Refining of Metals

Metals obtained by the reduction of its compound still contains some impurities and have to be refined. Depending upon the nature of the metal and impurities, the following methods are used for purification of the metals.

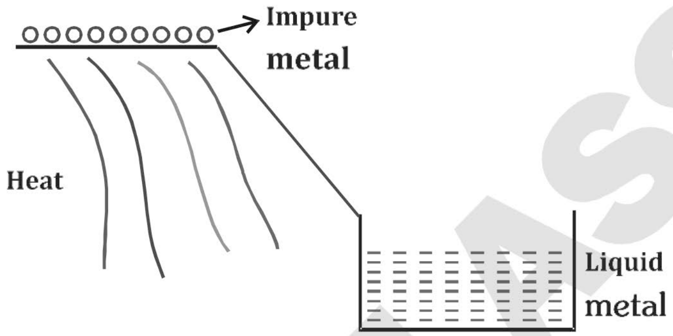
(I) Physical Process :

(i) Liquation : This method is used for the refining of metals having low melting point and are associated with high melting impurities.

Ex. **Pb, Sn, Sb** and **Bi**.

The impure metal is heated on the sloping hearth of a furnace.

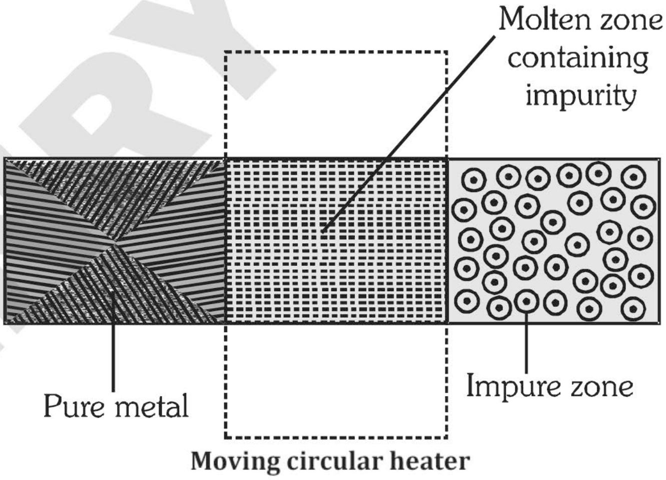
The pure metal flows down leaving behind the non- fusible impurities on the hearth.



(ii) Distillation : Metals having low boiling point are refined by this method. e.g. **Zn, Cd, Hg**

(iii) Zone refining : Metals of very high purity are obtained by zone refining. This refining method is based on the fact that impurities tend to remain dissolved in molten metal.

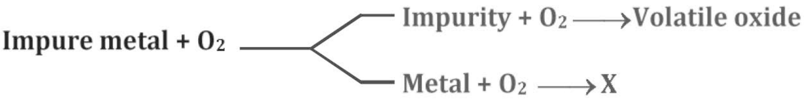
Ge, Si and Ga used as semiconductors are refined in this manner.



(II) Chemical Process :

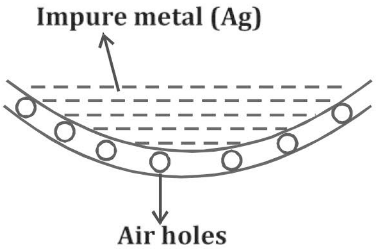
(i) Cupellation : This process is used to purify silver containing the impurities of Pb.

This process is used when impurity have greater affinity towards $\mathbf{O_2}$ while metal does not have.



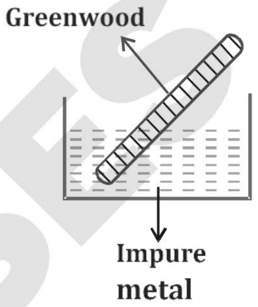
Impure metal + O_2 → Impurity + $O_2 \longrightarrow$ Volatile oxide

Impure metal + O_2 → Metal + $O_2 \longrightarrow X$



(ii) Poling : Used to purify **Cu, Pb**.

This process is used for the metal having the impurity of their own oxide. In this process a green wooden pole is heated with molten metal, which provide hydrocarbon (i.e. CH_4) and it reduces impurity of metal oxide to metal.



$$\mathbf{\underset{\text{Impurity}}{2Cu_2O} + CH_4 \longrightarrow 4Cu + CO_2 + 2H_2\uparrow}$$

(III) Electro–refining of Metals

Metals such as **Cu, Ag, Zn, Sn, Pb, Al, Ni, Cr** are refined by this method.

Anode of electrolytic cell is made from impure metal, while cathode is thin plate of pure metal. Electrolyte is the solution of a salt of the metal.

On passing the electric current pure metal from the anode dissolves and gets deposited at the cathode.

The soluble impurities go into the solution while insoluble or less electropositive impurities settle down below the anode as **anode mud**. For Example

- ***Electrorefining of Copper***
  Anode : Blister copper (98%)
  Cathode : Pure copper
  Electrolyte : An aqueous solution of $CuSO_4$ (15%) + 5% dil. H_2SO_4
- ***Electrorefining of Silver***
  Anode : Impure silver
  Cathode : Pure silver
  Electrolyte : aq. solution of $AgNO_3$ + 1% dil. HNO_3
- ***Electrorefining of Al (Hoope's process)***
  Anode : Impure Al,
  Cathode : Pure Al
  Electrolyte : A mixture of $Na_3AlF_6 + CaF_2$

(IV) Vapour Phase Refining (Thermal decomposition)

In this method the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal.

Two requirements are -

(i) The metal should form a volatile compound with available reagent.

(ii) The volatile compound should be easily decomposable, so that recovery is easy.

(i) Van Arkel method :

- Used for Ti and Zr

useful for removing all the oxygen and nitrogen impurities from metals like Zr and Ti.

$$Ti(s) + 2I_2\,(g) \xrightarrow{523k} TiI_4\,(g)$$

Impure

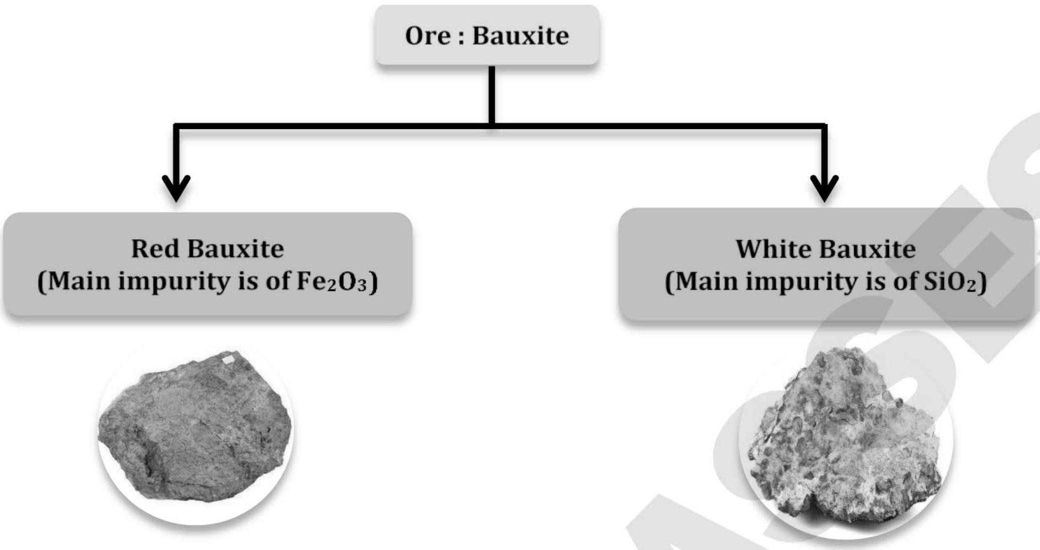
$$TiI_4\,(g) \xrightarrow{1800k} Ti(s)\ (pure) + 2I_2\,(g)$$

(ii) Mond's process :

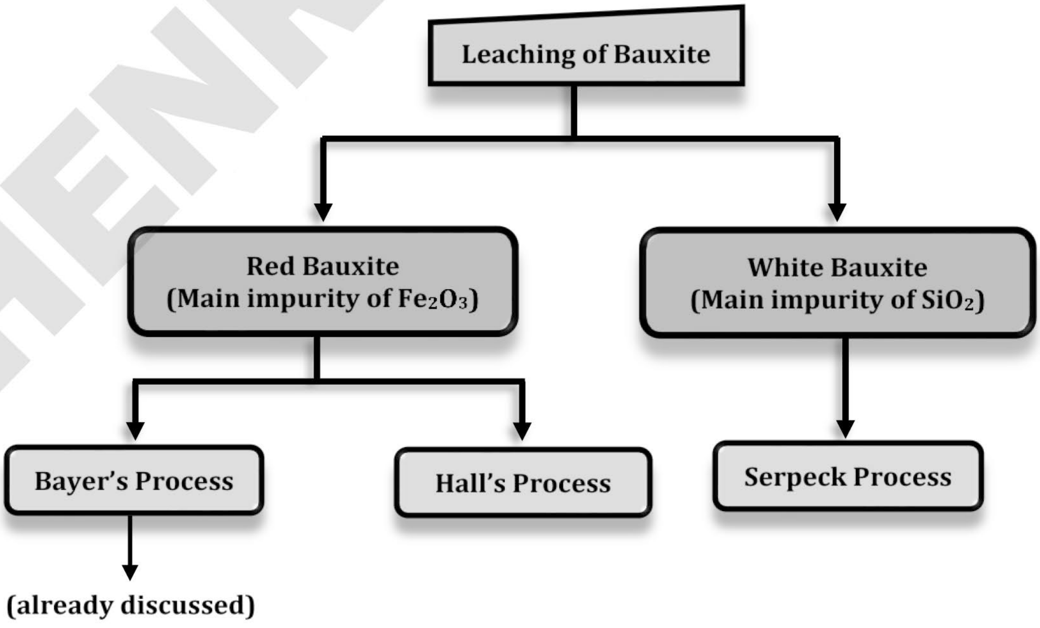
(i) Nickel is purified by using CO gas. This involves the formation of Nickel Tetracarbonyl.

$$Ni_{(Impure)} + 4CO \xrightarrow[350K]{330K} [Ni(CO)_4] \xrightarrow[470K]{450K} Ni_{(pure)} + 4CO\uparrow$$

Extraction of Aluminium :



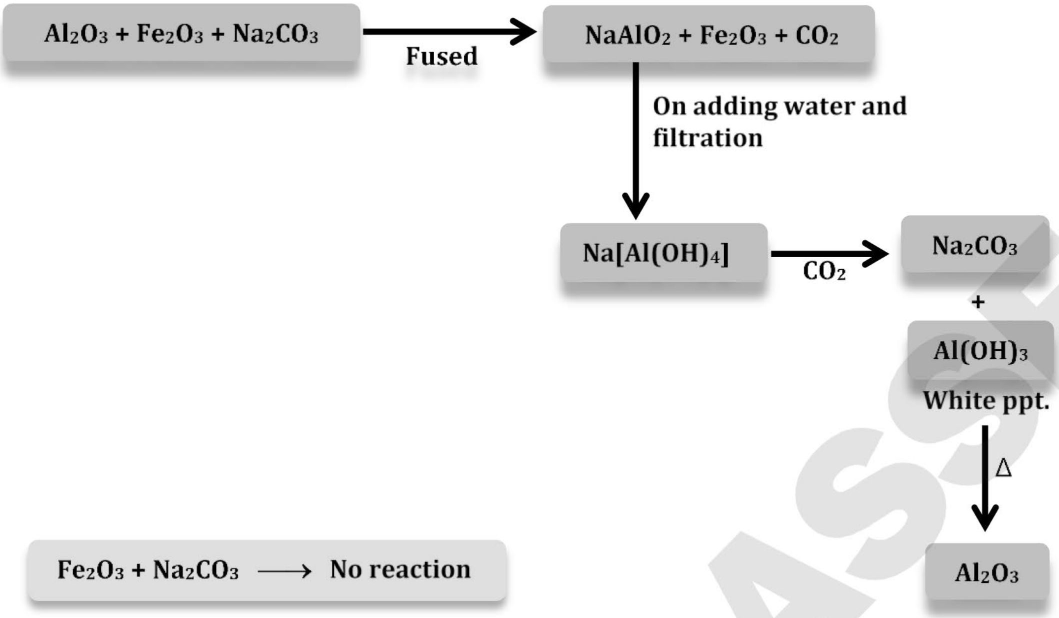
Main ore : Bauxite : $Al_2O_3.2H_2O$



ii. Hall's Process

Red Bauxite : $Al_2O_3.2H_2O$

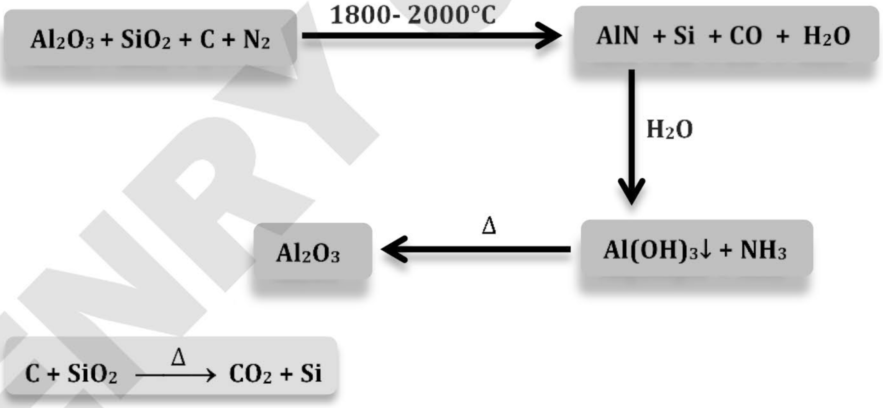
Main Impurity : Fe_2O_3 (Basic)



iii. Serpeck Process

White Bauxite : $Al_2O_3.2H_2O$

Main Impurity : SiO_2 (Acidic)



Hall Heroult Process :

This process is used for extraction of Al from alumina. The extraction of Al from Al_2O_3 is quite difficult because

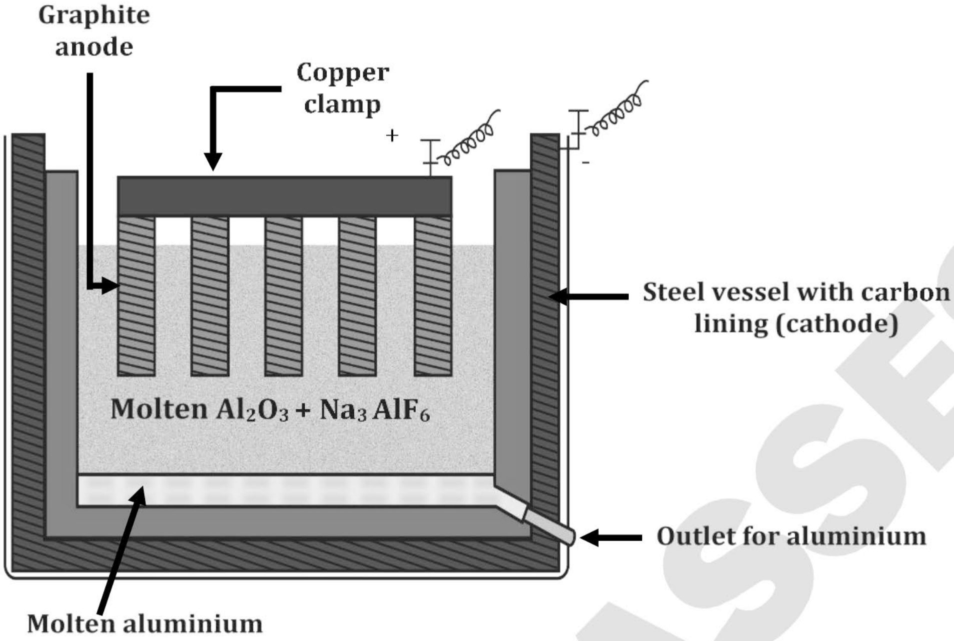
(i) Fusion temperature of Alumina is quite high (2050°C). Even more than boiling point of Al (1150°C).

(ii) It is a bad conductor of electricity. To overcome these difficulties we mix some amount of neutral flux (Na_3AlF_6 (Cryolite) + CaF_2(Flourspar)). Neutral flux provides free ions to the mixture which decreases the fusion temperature of Alumina from 2050°C to 950°C.

Purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2

→ lowers the melting point of Alumina and increases conductivity.

Steel cathode and graphite anode are used.



Reaction involved in Hall Heroult Process :

$$Al_2O_3 + \underset{\text{Cryolite}}{Na_3AlF_6} + \underset{\text{Flourspar}}{CaF_2} \longrightarrow Al^{3+} + Na^{+} + Ca^{2+} + O^{2-} + F^{-}$$

The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2.

$$C_{(s)} + O_2 \rightarrow CO_{(g)}$$
$$C_{(s)} + 2O_2 \rightarrow CO_{2\,(g)}$$

This way for each kg of Aluminium produced, about 0.5 kg of carbon anode is burnt away.

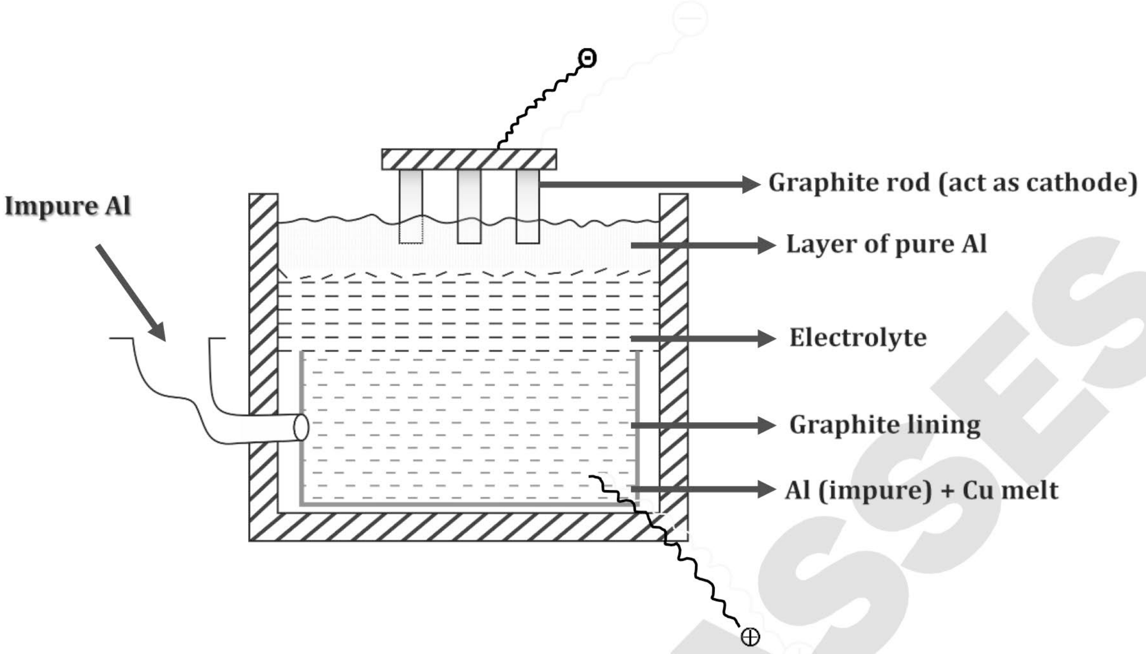
Electrolysis

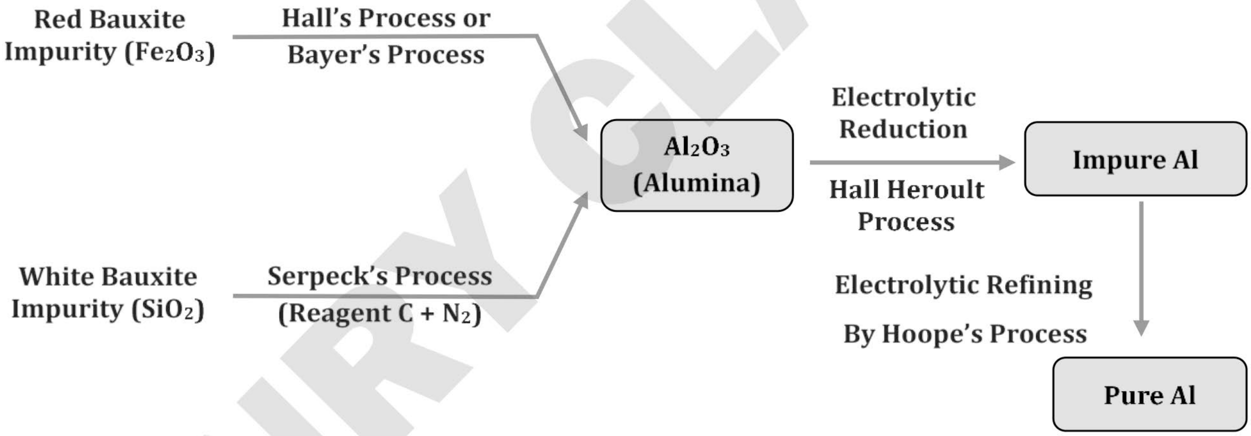
At Cathode : $Al^{3+} + 3e^{-} \rightarrow Al$ (Reduction)

At Anode : $2F^{-} \rightarrow F_2 + 2e^{-}$ (Oxidation)

$$3F_2 + Al_2O_3 \rightarrow 2AlF_3 + \frac{3}{2}O_2$$

Electro-Refining of Impure Al : (By Hoope's Process)





Extraction of Cu from copper pyrites ($CuFeS_2$)

Concentration of $CuFeS_2$: Froth flotation

$$2CuFeS_2 \longrightarrow Cu_2S + FeS + FeS_2$$

Partial roasting : $CuFeS_2 \xrightarrow[\text{limited}]{O_2} Cu_2S + FeO + SO_2$

Smelting : In Blast furnace

$$\left(\begin{array}{ccccc} \text{Roasted ore} & + & \text{C} & + & SiO_2 \\ & & \text{Used as} & & \\ & & \text{Fuel} & & \end{array} \right)$$

Smelting :

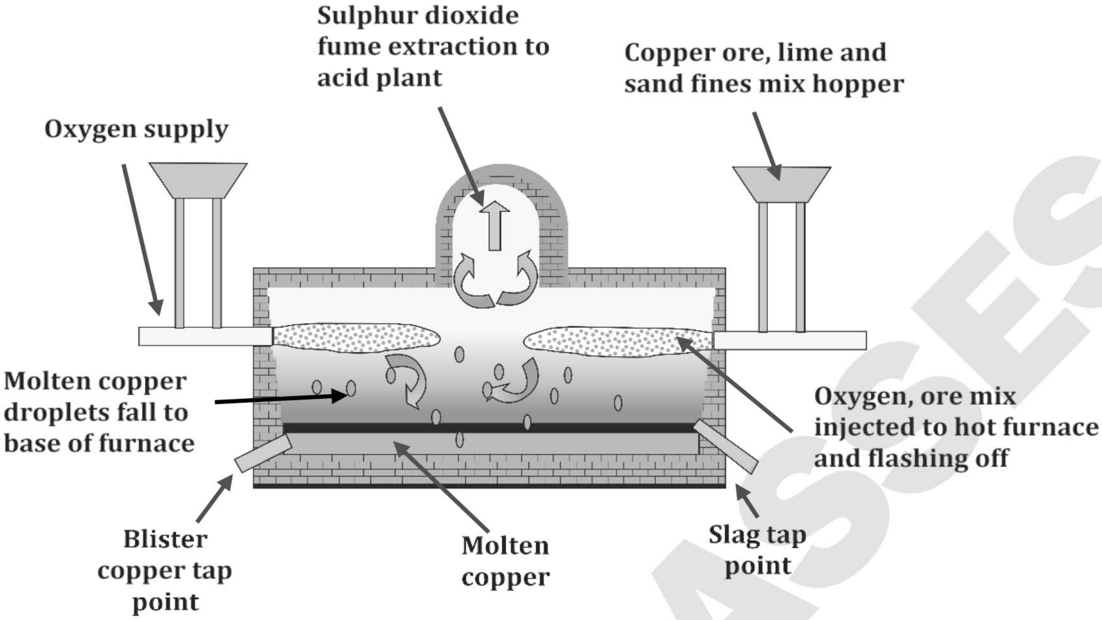
$FeS + O_2 \rightarrow FeO + SO_2\uparrow$

$FeO + SiO_2 \rightarrow FeSiO_3$ (Slag)

$Cu_2S + O_2 \rightarrow Cu_2O + SO_2$

$Cu_2O + FeS \rightarrow Cu_2S + FeO$

- Cu_2S remains almost unaffected during smelting.
- After smelting process, Copper matte (Cu_2S (98%) + FeS (2%)) is produced

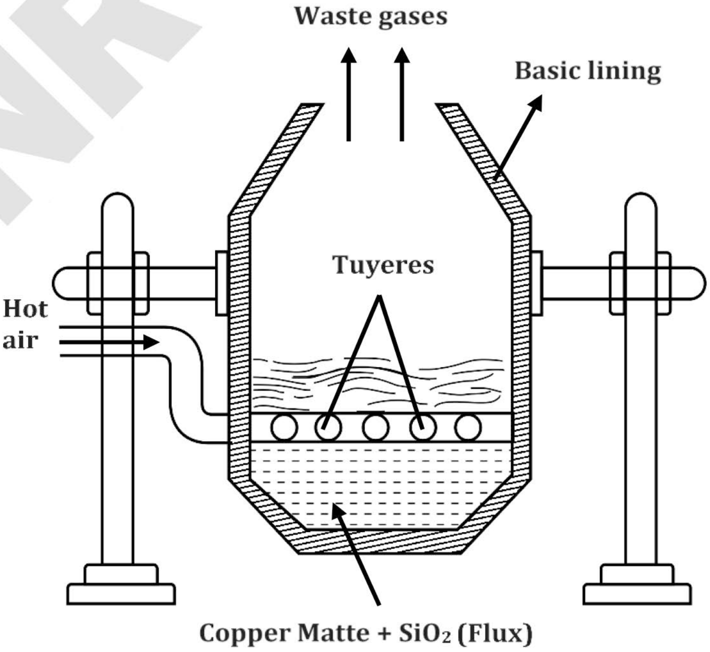


Bessemerization :

- Copper matte is then charged into silica lined convertor.
- Some silica is also added
- Hot air blast is blown
- Cu_2S/Cu_2O react to the metallic copper

$$FeS + O_2 \longrightarrow FeO + SO_2\uparrow$$

$$FeO + \underset{\text{Acidic Flux}}{SiO_2} \longrightarrow FeSiO_3\,(Slag)$$



Self Reduction :

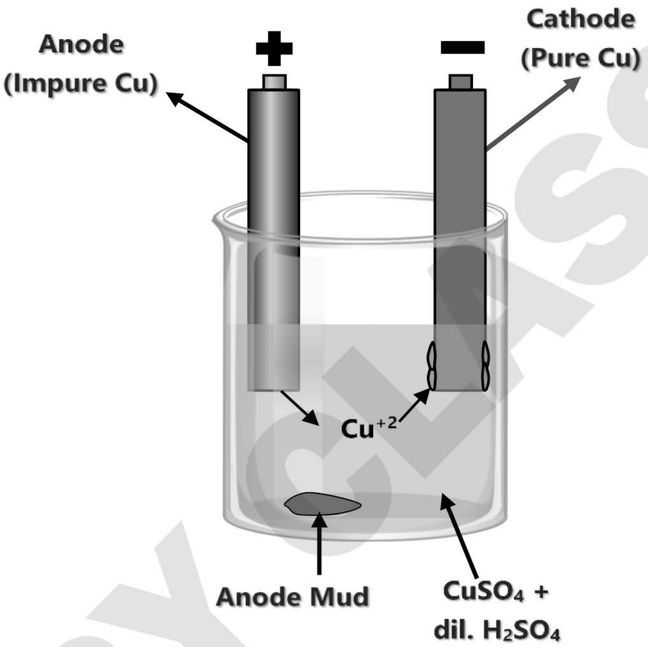
$Cu_2S + \underset{\text{limited}}{O_2} \longrightarrow Cu_2O + SO_2$ $\qquad$ $Cu_2S + Cu_2O \longrightarrow 6Cu + SO_2\uparrow$

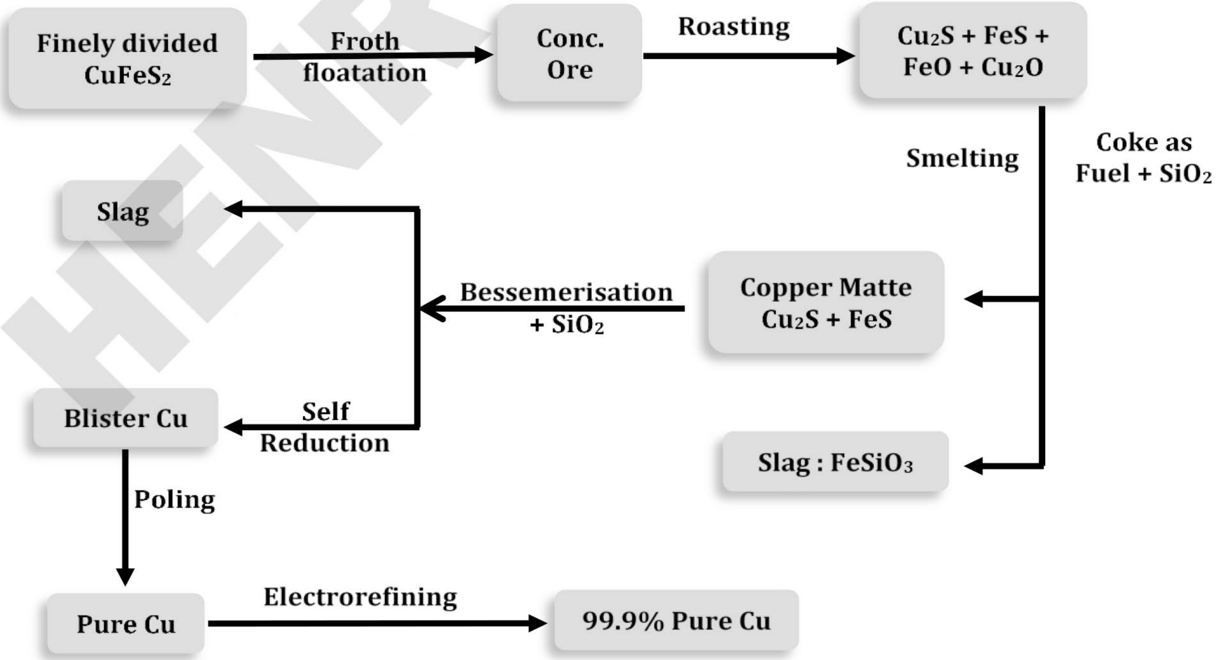
Blister Copper (98% pure)

Due to the evolution of SO_2

Electro Refining of impure Copper

- Anode : Cu (Impure)
- Cathode : Cu (Pure)
- Electrolyte : $CuSO_4(aq.) + dil.\ H_2SO_4$
- Anode mud : Ag, Au, Pt etc.

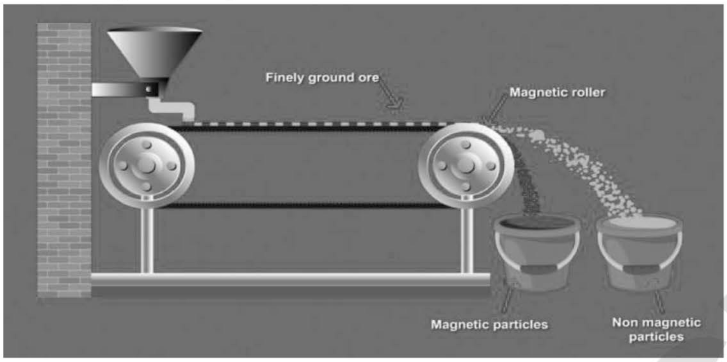




Extraction of iron from Fe_2O_3 :

(1) Concentration of ore :

By Gravity separation & Magnetic separation



(2) Calcination/Roasting :

It removes moisture and other volatile impurities

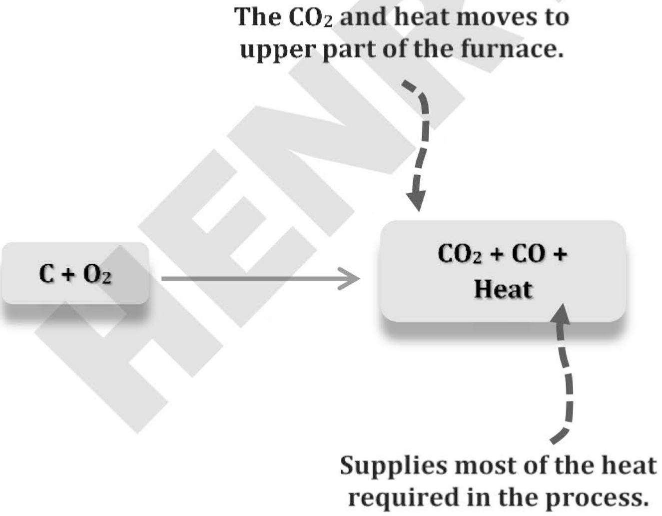
It also decomposes carbonates

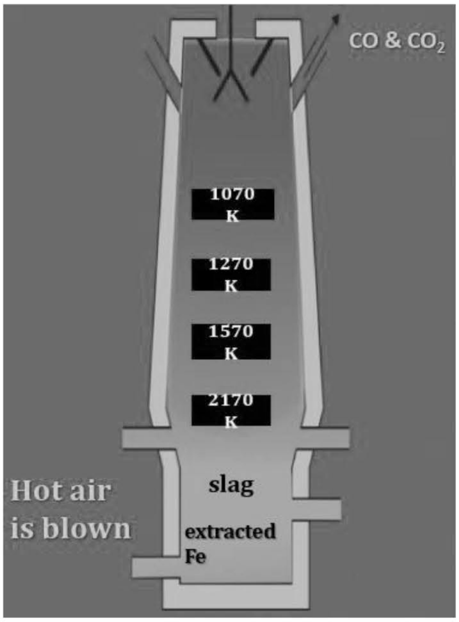
$$\begin{tikzcd} FeCO_3 \arrow[r, "\Delta"] & FeO + CO_2 \arrow[d, "\Delta \quad O_2"] & \\ & {} \arrow[r] & Fe_2O_3 \end{tikzcd}$$

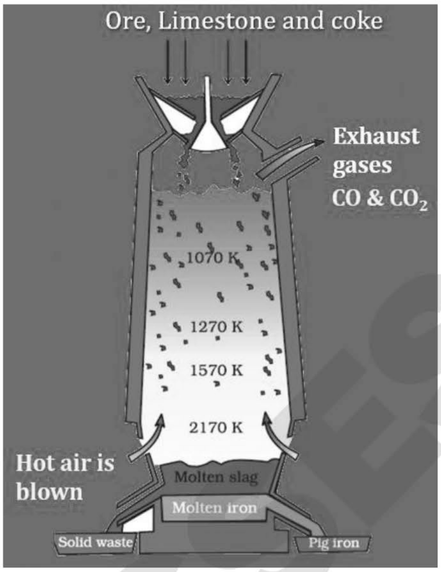
Carbon reduction (Smelting) in blast furnace :

Feed : $Fe_2O_3 + C + CaCO_3$

Combustion Zone : Coke is burnt







Reduction Zone :

Upper part/lower temperature range (500–800K)

$Fe_2O_3 + CO \xrightarrow{\Delta} Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \xrightarrow{\Delta} FeO + CO_2$

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

Slag Formation Zone :

Higher temperature range (900 – 1500 K) middle part in the blast furnace

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

SiO_2	+	CaO	$\longrightarrow$	$CaSiO_3$
Acidic Impurity		**Basic flux**		**Fusible Slag**

The slag is in molten state and separates out from iron.

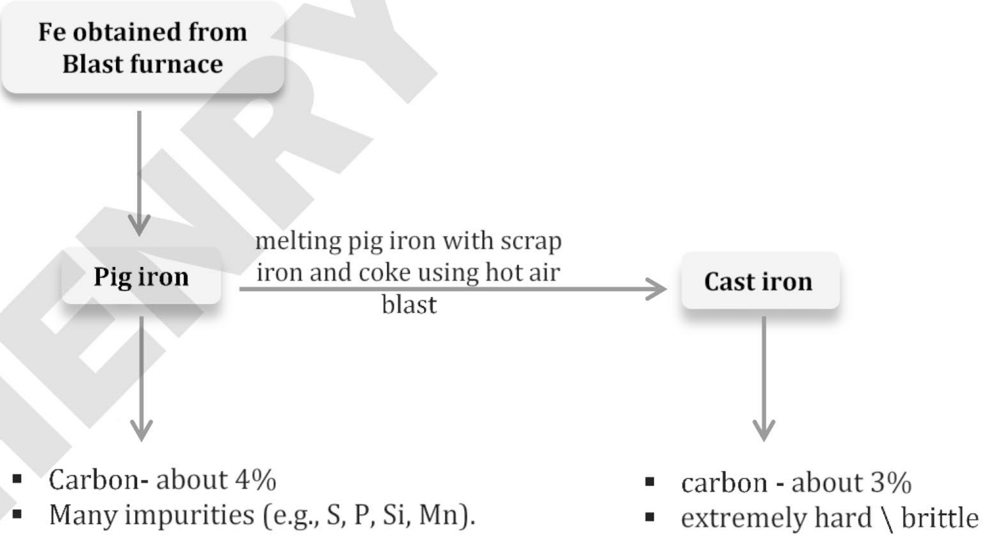
Iron oxide + 3C $\longrightarrow$ 2Fe + 3CO↑

Slag Formation Zone :

- After Smelting molten metal is obtained.
- Slag being lighter is deposited at surface of molten metal.
- Slag stops further oxidation of molten metal.

Fusion Zone :

- Iron obtained at the bottom of furnace is called pig iron.
- All the solid metal is obtained in fused form.



- Carbon- about 4%
- Many impurities (e.g., S, P, Si, Mn).

- carbon - about 3%
- extremely hard \ brittle

Manufacturing of wrought iron from the cast iron

Puddling Process :

- Wrought iron or malleable iron is the purest form of commercial iron
- It is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite.
- This haematite oxidises carbon to carbon monoxide:

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

- Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag.
- The metal is removed and freed from the slag by passing through rollers.
- Iron obtained from puddling furnace is called wrought iron (purest form of iron)
- Wrought iron contain 0.1 to 0.25% impurity of 'C'.

Manufacturing Steel from the Cast Iron :

Purification of Iron : In Bessemerisation process, impurities present in pig iron are oxidised by air.

Bessemerisation process

Purification of Iron :

$Mn / Si + O_2 \xrightarrow{\Delta} MnO / SiO_2$

$MnO + SiO_2 \xrightarrow{\Delta} MnSiO_3$

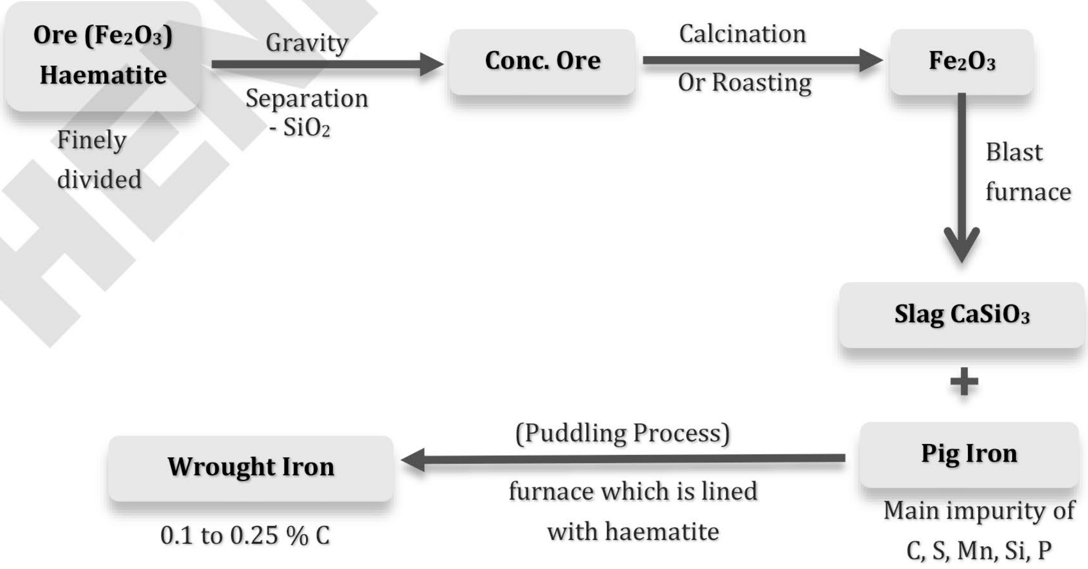
$SiO_2 + CaO \xrightarrow{\Delta} CaSiO_3$

$P_4 + O_2 \xrightarrow{\Delta} P_4O_{10}$

$P_4O_{10} + CaO \xrightarrow{\Delta} Ca_3(PO_4)_2$ **Thomas slag**

We add Mn, Cr and C in this extracted iron and remelt it, this form of iron is called Steel.

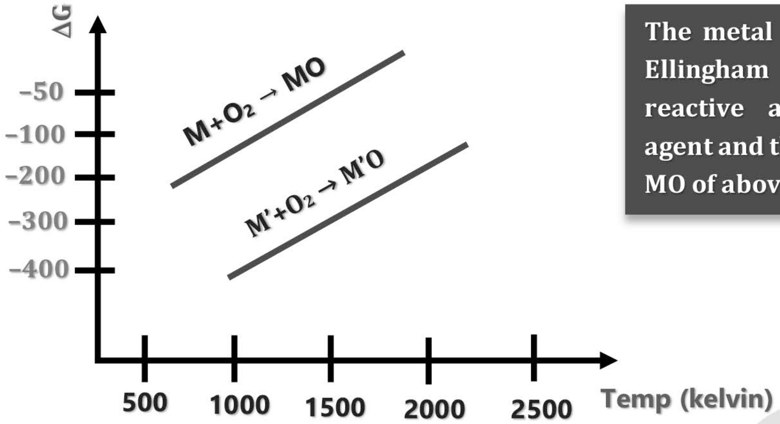
Steel contain 0.25 to 1% impurity of carbon.



Thermodynamics of reduction processes (Ellingham diagram)

In these diagrams, graph between ΔG and T is plotted for processes like oxidation of metals.

$M_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow MO_{(s)}$



The metal on lower line on the Ellingham diagram is more reactive and better reducing agent and thus easily reduces the MO of above line.

Thermodynamics of reduction processes (Ellingham diagram)

It is explanation of the feasibility of pyrometallurgical process by using Gibbs equation :

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

If **$\Delta G = -$ ve** Process is stable or spontaneous

$\Delta G = +$ ve Then process is unstable or non-spontaneous

When pyrometallurgical process contains more than one type of reaction then spontaneity of reaction can be explained by Ellingham diagram. Ellingham diagram contains plot.

ΔG vs T :