Metallurgy

The branch of chemistry deals with the method of extraction of metals from their ores.

Most abundent metal in earth crust is AA.

(1)	(2)	(3)	(4)
Minerals	**Ores**	**Flux**	**Gangue or Matrix**
Elements or other substances obtained from earth crust	Minerals from which metal can be extracted easily + profitably	Compounds which are used to remove non volatile impurities • acidic flux (used to remove basic impurities) • basic flux (used to remove acidic impurities)	Impurity present in ores

All ores are mineral but all minerals are not an ores

Types of Metallurgy

(1) Pyro metallurgy

(2) Hydro metallurgy

(3) Electro metallurgy

Different steps are used in pyro metallurgy

(a) Crushing & grinding of ore

(b) Concentration of ore

It is done by different methods

(1) Froth floatation method used for sulphide ore

(2) Froth floation method (water soluble impurities remove)

(3) Gravity separation method (Heavy/light impurities remove)

(4) Magnetic separation method (Magnetic/non-magnetic impurities remove)

(5) Leaching method (In this method chemicals are used which react with pure metal)

(c) Calcination (done in absence or controlled air)

(d) Roasting (Done in exess of air) (sulphide ore convert to oxide ore and SO_2, P_2O_5, As_2O_5 evolve out)

(e) Main advantage of roasting is to convert sulphide or into oxide ore because oxide ore easily reduced than sulphide.

(f) Smelting (non volatile impurities remove)

(g) Bessemerisation

(h) Purification of metal (by Electrolysis)

Hydro metallurgy

Cyanidation method

(a) Crushing ore

(b) Concentration of ore

(c) Complex formation

(d) Metal displacement

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[Extration of Ag from Ag$_2$S]

(a) Curshing of ore

(b) Ore reacts with excess of NaCN in presence of excess of air.

$Ag_2S + 4NaCN + 2O_2 \rightleftharpoons 2Na[Ag(CN)_2] + Na_2SO_4$

Use of oxygen is to convert reversible reaction into irreversible

(c) Displacement of Ag by Zn

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

Here Zn acts as reducing agent.

(A) **Concentration of the ore or dressing or benefaction**

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** :

(i) **Gravity separation (Levigation) :** This method of concentration of the ore is based on the difference in the specific 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. Ex. Oxygenated ore

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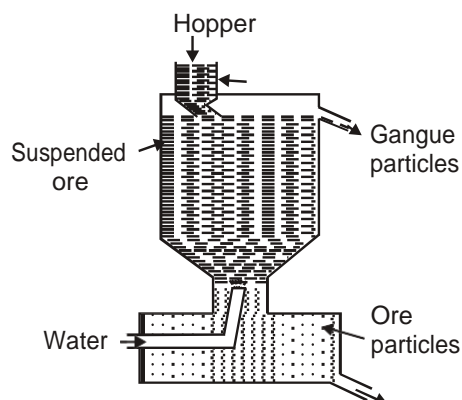
Concentrated
ore
Hydraulic classifier

(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 preferentially wetted by water and the ore 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 usually of three types.

(a) **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.

(b) **Collectors or floating agents :–** These 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.

(c) **Froth stabilisers** : To stabilise froth.

Ex. Cresol, Aniline etc.

(d) **Depressants :–** These reagents activate or depress the floatation property and help in the separation of different sulphide ores present in a mixture.
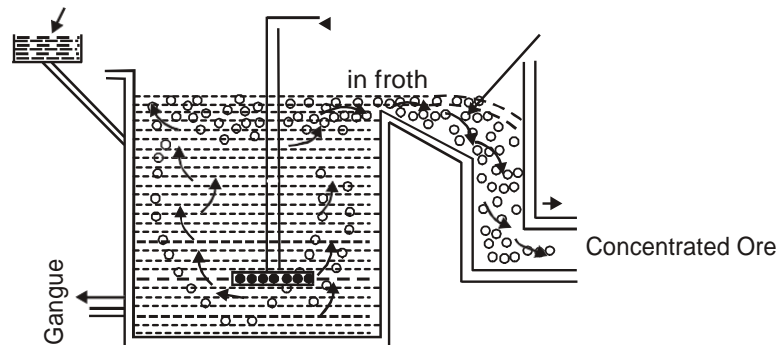
e.g. NaCN.

Impurity of ZnS in PbS ore removed by NaCN

NaCN+ [PbS + ZnS] →Na$_2$[Zn(CN)$_4$] + PbS → form froth

Powdered Ore + Oil + Water

Compressed air

Light ore particle

in froth

Concentrated Ore

Gangue

[Froth floatation process]

• Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants'.

• For example, 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 go along with the froth.
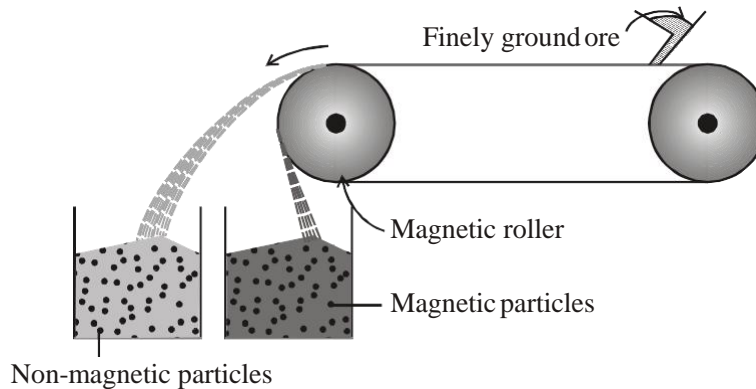
(iii) **Magnetic separation:-**

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)

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• SnO having the impurities of FeWO$_4$ + MnWO$_4$ (Wolframite)

• FeO.Cr$_2$O$_3$ having the impurities of SiO$_2$

Finely ground ore

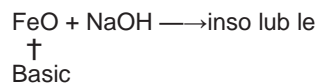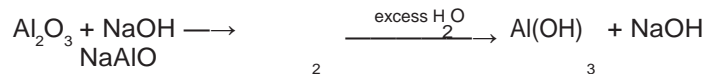Magnetic roller

Magnetic particles

Non-magnetic particles

2. **CHEMICAL SEPARATION (LEACHING)** : In this process we use suitable agent which react with ore to form water soluble complex while impurities remain insoluble. Applicable for Al, Ag, Au.
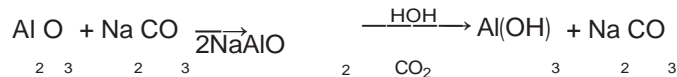
(a) **Aluminium :** $\begin{cases} \text{Re d Bauxite} \rightarrow Al_2O_3 .2H_2O + Fe_2O_3 \text{ (Major impurity)} \\ \text{White Bauxite} \rightarrow Al_2O_3 2H_2O + SiO_2 \text{ (Major impurity)} \end{cases}$

(I) **RED BAUXITE :** Two processes

(i) **Baeyer's process :** NaOH is used.

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

$$FeO + NaOH \longrightarrow \text{inso lub le}$$
$$\dagger$$
Basic

(ii) **Hall's process :** Na$_2$CO$_3$ is used.

$$Al_2O_3 + Na_2CO_3 \xrightarrow{2NaAlO_2} \xrightarrow{HOH \atop CO_2} Al(OH)_3 + Na_2CO_3$$

(II) **WHITE BAUXITE :** One process.

Serpeck's process : (C+N$_2$) is used

$$Al_2O_3 + N_2 \xrightarrow[-CO \uparrow]{1800°C} AlN \xrightarrow[\rightarrow]{H_2O} Al(OH)_3 + NH_3 \uparrow \text{ [not in NCERT]}$$

$$C + SiO_2 \longrightarrow CO \uparrow + SiT .$$
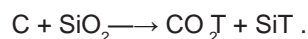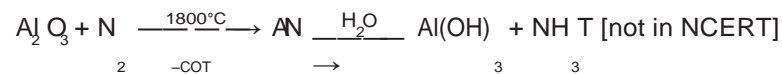
(b) **Ag and Au (CYANIDE PROCESS)**

(I) **Ag** $Ag_2S + 4NaCN \xrightarrow{2O_2} 2Na[Ag(CN)_2] + Na_2SO_4$ [in absence of O$_2$, reaction become reversible]

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

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

$K[Au(CN)_2] + KOH + Zn \longrightarrow K_2ZnO_2 + KCN + H_2O + Au \dagger$
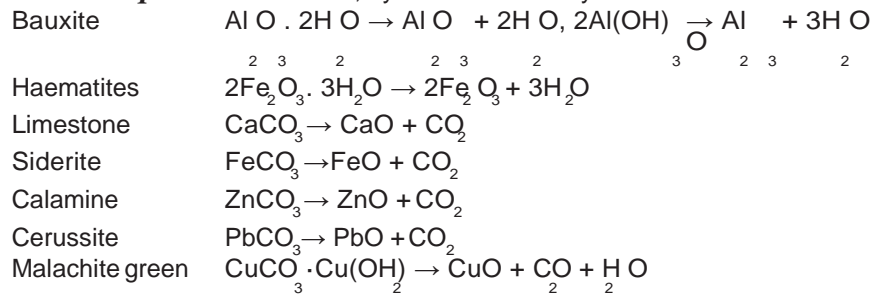
(B) **Conversion of concentrated ore into oxide form**

Calcination and roasting

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

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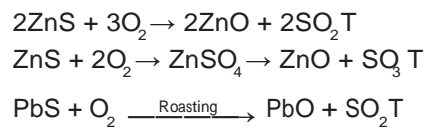*For Example*: All carbonates, hydrated ore and hydroxide ore

Bauxite $\quad\quad Al_2O_3 \cdot 2H_2O \rightarrow Al_2O_3 + 2H_2O$, $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

Haematites $\quad\quad 2Fe_2O_3 \cdot 3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$

Limestone $\quad\quad CaCO_3 \rightarrow CaO + CO_2$

Siderite $\quad\quad FeCO_3 \rightarrow FeO + CO_2$

Calamine $\quad\quad ZnCO_3 \rightarrow ZnO + CO_2$

Cerussite $\quad\quad PbCO_3 \rightarrow PbO + CO_2$

Malachite green $\quad CuCO_3 \cdot Cu(OH)_2 \rightarrow CuO + CO_2 + H_2O$

Advantages of Calcination :–

(i) Moisture is removed.

(ii) Organic matter is destroyed

(iii) The hydroxide and carbonates ores are converted into their oxides.
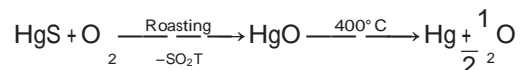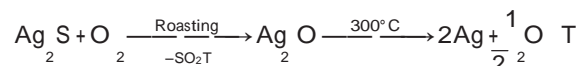
(iv) The ore become porous and easily workable

(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 with or without the addition of an external substance.
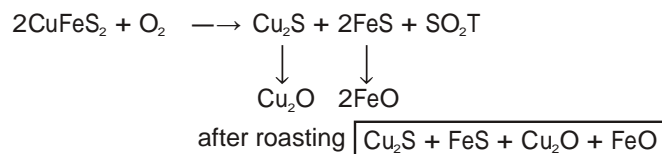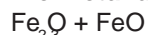
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \uparrow$$

$$ZnS + 2O_2 \rightarrow ZnSO_4 \rightarrow ZnO + SO_3 \uparrow$$

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

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Thermal reduction

Some less stable metal oxide further decompose into metal and oxygen.

$$Ag_2S + O_2 \xrightarrow[-SO_2\uparrow]{Roasting} Ag_2O \xrightarrow{300°C} 2Ag + \frac{1}{2}O_2 \uparrow$$

$$HgS + O_2 \xrightarrow[-SO_2\uparrow]{Roasting} HgO \xrightarrow{400°C} Hg + \frac{1}{2}O_2$$

Partial roasting

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2\uparrow$$

$$\downarrow \qquad \downarrow$$

$$Cu_2O \quad 2FeO$$

after roasting $\boxed{Cu_2S + FeS + Cu_2O + FeO}$

Roasting in Fe metallurgy

$$Fe_2O_3 + FeO$$

Haematite

$$Fe_3O_4 = Fe_2O_3 + FeO$$
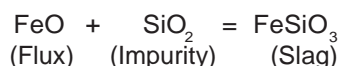
Magnetite

$$FeCO_3 \xrightarrow{A} FeO + CO_2\uparrow$$
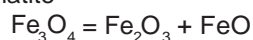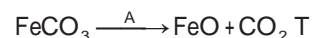
Siderite

Roasting → to prevent wastage of Fe as slag in reduction step

$$2FeO + \frac{1}{2}O_2 \rightarrow Fe_2O_3 \quad \text{(It does not form slag)}$$

In reduction step $\quad FeO + SiO_2 = FeSiO_3$

$\qquad\qquad\qquad$ (Flux) (Impurity) (Slag)
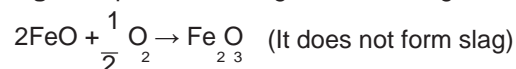
Advantages of Roasting :–

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

$$S + O_2 \rightarrow SO_2\uparrow$$
$$\text{(air)}$$
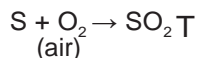
(ii) The metal sulphide is converted into metal oxide.

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

$$Sb_4 + 3O_2 \rightarrow 2Sb_2O_3\uparrow$$
$$As_4 + 3O_2 \rightarrow 2As_2O_3\uparrow$$
$$P_4 + 3O_2 \rightarrow 2P_2O_3\uparrow$$
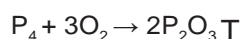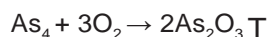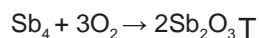
• For PbS, CuS and HgS partial roasting is carried out because these sulphide ore easily convert into metal by auto reduction process.

Reduction of metal oxide to metal

Different methods are used to convert metal oxide to metal

(a) Reduction by Carbon - Oxide of less reactive metal can be convert to metal on strongly heating with coke.

Eg. $PbO + C \longrightarrow Pb + CO$

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

$\qquad ZnO + C \longrightarrow Zn + CO$
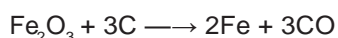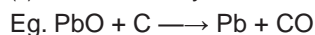
Note :- Some metal oxides like $AA_2O_3\, Cr_2O_3$, Mn_3O_4, MnO_2 are not reduced by coke.

Note :- CO is better reducer but not for Zn.

(b) Self reduction

Compounds of certain metals are reduced to metal without using any additional reducing agent. ores of Cu, Pb, Hg etc.

Their 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.

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Self reduction for Cu (*Extraction of Cu from copper glance.*)

$$2Cu_2O + Cu_2S \xrightarrow{\ \ A\ \ } 6\ Cu + SO_2$$

(c) *Metal displacement method*

In this method, a water soluble compound is obtained from the ore. The aqueous solution of the compound is reacted with a more electropositive metal which displaces, the metal from the solution.
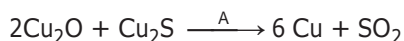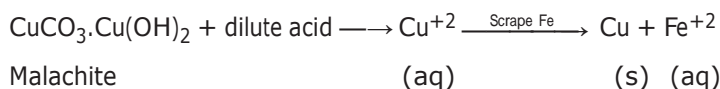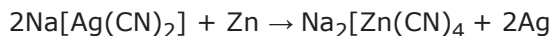
Ex. (i) Extraction of Cu fro low grade (lean) ore

$$CuCO_3.Cu(OH)_2 + \text{dilute acid} \longrightarrow Cu^{+2} \xrightarrow{\ \text{Scrape Fe}\ } Cu + Fe^{+2}$$

Malachite   (aq)   (s)   (aq)

Ex. (ii) Separation of Ag by Complex formation (Cyanide process).

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

(d) *Electrolytic reduction*

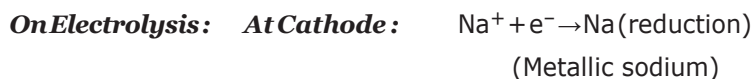This process is mainly used for the extraction of ***highly electropositive metals.***

Electrolysis is carried out in large cells and a small amount of another suitable electrolyte is added which:

(i) Lowers the melting point of the main electrolyte

(ii) Enhances its conductivity

(iii) Reduces corrosion troubles

Ex. Na, K, Mg, Ca, Al, etc.

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

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

On Fusion : $NaCl \rightleftharpoons Na^+ + Cl^-$ (Ions become mobile)

On Electrolysis :   ***At Cathode :*** $Na^+ + e^- \rightarrow Na$ (reduction)

                           (Metallic sodium)

               At Anode : $2Cl^- \rightarrow Cl_2 (g) + 2e^-$

Note : 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 boilling point of Al (1150°C).

(ii) It is a bad conductor of electricity.

To overcome these difficulties we mix some amount of neutral flux $[Na_3AlF_6 + CaF_2]$. Neutral flux provide free ions to the solution which decreases the fusion temperature of Alumina from 2050°C to 950°C.

(e) *Alumino thermite process :*
In this process those metal oxide 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 starts it will continue till all the metal oxide reduces to metal.

For Cr, Mn, Fe :

$$Cr_2O_3 + Al \longrightarrow Al_2O_3 + 2Cr$$
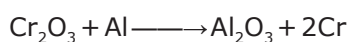
$$Fe_2O_3 + Al \longrightarrow Al_2O_3 + 2Fe$$

Commercial use of this method is in aluminothermite weldings.

Note :- (Fe_2O_3 : Al) mixture in 3 : 1 is used.

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REFINING OF METALS

Depending upon the nature of the metal and impurities, the following methods are used for purification of the metals.

(1) Distillation

Metals having low boiling point are refined by this method, for example, zinc, cadmium and mercury.

(2) 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, Bi and Hg.

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

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

(3) Electro–refining of Metals

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

Anode mud - Deposition of noble metals like Au Y Pt below anode.

Anode - made of impure metal

Cathode - made of pure metal

Electro refining of Copper

Anode : Blister copper (98%)

Cathode : Pure copper

Electrolyte : An aqueous solution of $CuSO_4$ (15%) + 5% dil H_2SO_4

Electro refining of Pb (Bett's process)

Anode : Impure lead.

Cathode : Pure lead.

Electrolyte : A mixture of $PbSiF_6$ and H_2SiF_6

(4) Zone refining or fractional crystallisation

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 than solid.

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

Molten zone containing impurity

Pure metal

Impure zone

Moving circular heater
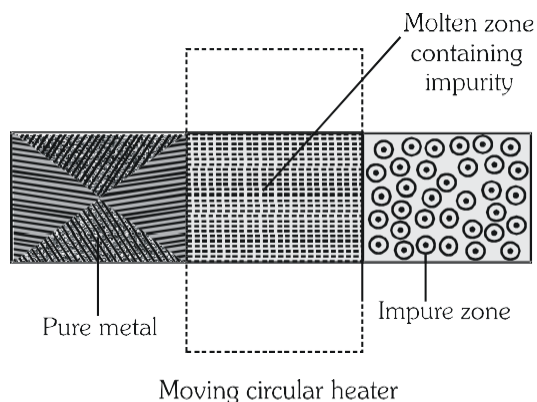
(5) Vapour phase refining

(i) Van - Arkel process

- Employed for purification of metals like *titanium(Ti)* and *zirconium(Zr)*.

$$Ti(s) + 2I_2 (g) \xrightarrow{523 \text{ k}} Ti\,I_4(g)$$

Impure

$$TiI_4(g) \xrightarrow{1700 \text{ k}} Ti(s) + 2I_2(g)$$

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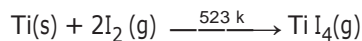
(ii) Mond's process

Nickel is purified by using CO gas. This involves the formation of nickel tetracarbonyl.

$$Ni_{(Impure)} + 4CO \xrightarrow[T]{A} [Ni(CO)_4] \xrightarrow[higher\,T]{A} Ni_{(pure)} + 4CO \uparrow$$

(6) Some chemical processes

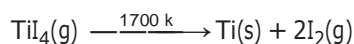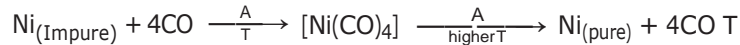**(i) Cupellation :** This process is used to purify silver containing the impurities of Pb.

This process is used when impurity have greater affinity towards O_2 while metal does not have.

$$\text{Impure metal} + O_2 \Big\langle \begin{array}{l} \text{Impurity} + O_2 \longrightarrow \text{Volatile oxide} \\ \text{Metal} + O_2 \longrightarrow X \end{array}$$

(ii) Polling : Used to purify Cu, Pb.

This process is used for the metal having the impurity of their own oxide. In this process a wooden pole is heated with molten metal, which provide C and H to metal oxide which reduces impurity of metal oxide to metal .

$$CuO + H_2 \longrightarrow Cu + H_2O \uparrow$$
$$CuO + C \longrightarrow Cu + CO \uparrow$$

(iii) Bessemerisation : Impure metal is heated in a furnace and a blast of compressed air is blown which oxidises the impurity into their oxides and that can be removed in the form of slag .

$$2Mn + O_2 \longrightarrow 2MnO$$
$$Si + O_2 \longrightarrow SiO_2$$
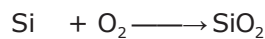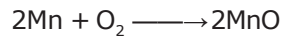
THERMODYNAMICS OF REDUCTION PROCESSES (ELLINGHAM DIAGRAM)

It is explanation of the feasibility of pyrometallurgical process by using gibbs equation $\boxed{AG = AH - TAS}$

If   AG = – ve   Process is stable or Spontaneous

AG = + ve or Less – ve then process is Unstable or non-Spontaneous

When pyrometallurgical process contains more than one type of reaction then spontanity of reaction can be explain by Ellingham diagram. Ellingham diagram contains plot $\boxed{AG \; vs \; T}$.

(I)

AG = –Ve

$$Ca \quad + \quad \boxed{MgO \mid Al_2O_3 \mid Cr_2O_3} \longrightarrow CaO \quad + \quad \boxed{Mg \mid Al \mid Cr}$$

AG = +Ve

$$Cr \quad + \quad \boxed{CaO \mid MgO \mid Al_2O_3} \longrightarrow Cr_2O_3 \quad + \quad \boxed{Al \mid Mg \mid Ca}$$
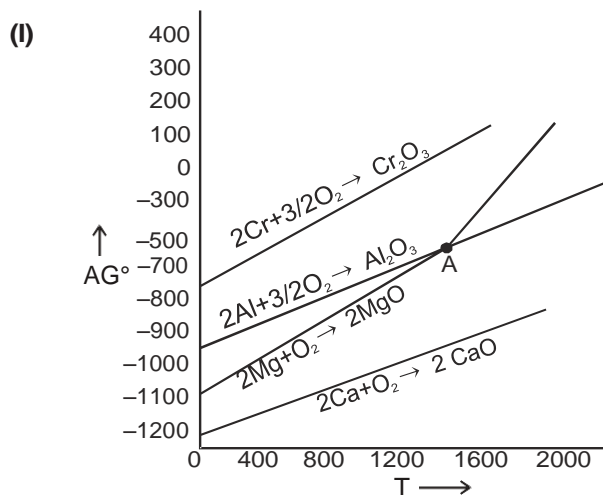
According to Ellingham diagram, the below metal can reduce the oxide of metal above it in the curve, as affinity of metal below for oxygen is more.

Example   Al Metal can reduce Cr_2O but can not reduce MgO & CaO.

At very high T after 'A' Point Al' metal can reduce MgO because Formation of MgO contains less – ve AG.

(II)

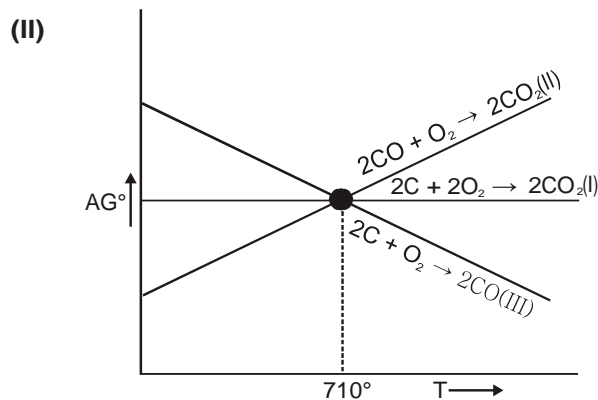According to diagram at high T (710°C or above 710°C) Oxidation of C contains more – ve AG so at high T 'C' is good Reducing agent.

At Low T (below 710°C) Oxidation of CO contains more –ve AG so at Low T, CO is good Reducing agent.

• **Types of Iron**

    Pig iron→Cast iron→Steel iron→ Wrought iron

(i) Cast iron and pig iron

It is most impure form of Iron and contains the highest proportion of carbon (2.5 - 4 %) along with traces of S, P, Mn and Si. Cast iron contain 2.5 to 4.3 & pig contain 2.5 to 5%.

(ii) Wrought iron (Fibrous iron) or malleable iron

It is the purest form of iron and contains minimum amount of carbon (0.12 - 0.25%) and less than 5% of other impurities.

(iii) Steel

It is the most important form of iron and finds extensive applications. As far as carbon content (impurity) is concerned it is mid-way between cast iron and wrought iron, it contains 0.25- 2% carbon. Thus all the three forms of iron differ in their carbon contents, both iron and steel are obtained from cast iron.

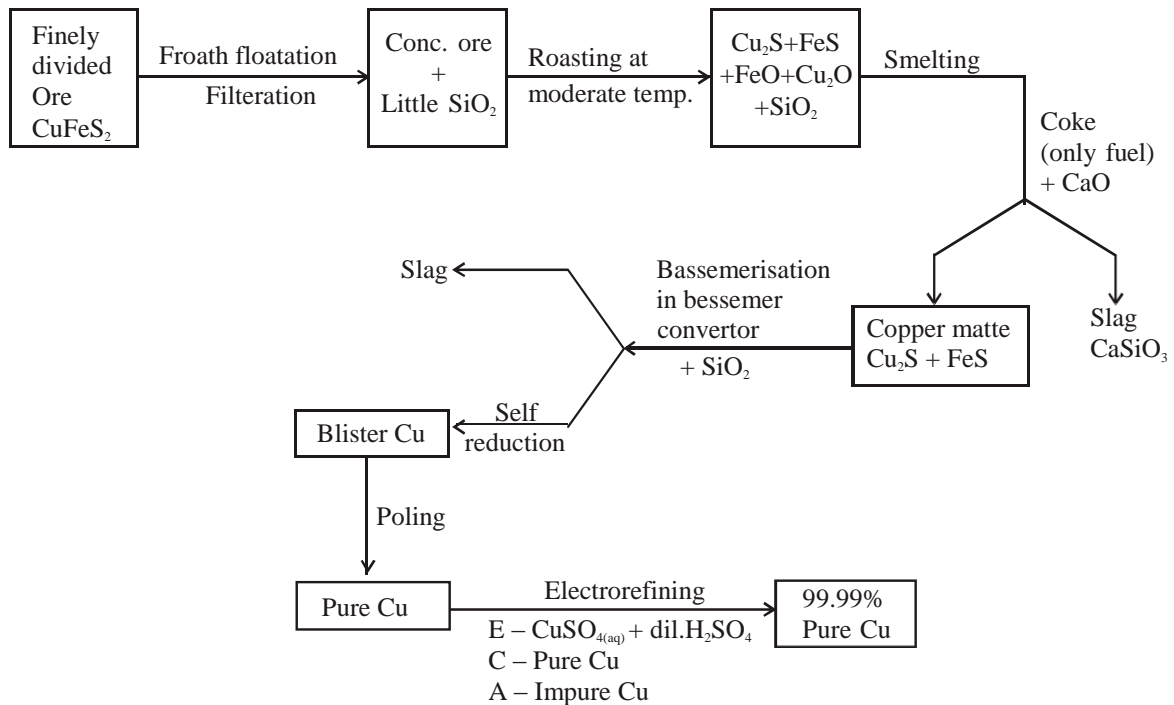Order of M.P. :- Wrought iron > Steel > Cast iron or Pig iron

◆

Heat Treatment of Steel

(a) *Quenching or hardening:* Steel is heated to red hot temp. and is then cooled suddenly by plunging into either cold water or oil. It makes steel hard and brittle.

(b) *Annealing:* The steel is heated to red hot temp. and then cooled slowly. It makes steel soft.

(c) *Tempering:* If quenched steel is heated to temp. between 500 to 575 K and then cooled slowly, it becomes quite hard but brittleness disappears. The process is called tempering.
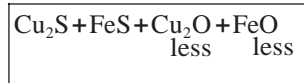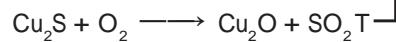
Extraction of Cu

Ore - $CuFeS_2$ copper pyrites

Finely divided Ore $CuFeS_2$ →(Froath floatation / Filteration)→ Conc. ore + Little SiO_2 →(Roasting at moderate temp.)→ $Cu_2S+FeS +FeO+Cu_2O +SiO_2$ →(Smelting)→ Coke (only fuel) + CaO → Copper matte $Cu_2S + FeS$ and Slag $CaSiO_3$

Copper matte →(Bassemerisation in bessemer convertor + SiO_2)→ Slag, and → Self reduction → Blister Cu

Blister Cu →(Poling)→ Pure Cu →(Electrorefining, E – $CuSO_{4(aq)}$ + dil.H_2SO_4, C – Pure Cu, A – Impure Cu)→ 99.99% Pure Cu

Reaction involved :

(a) Roasting step

$$CuFeS_2 + O_2 \longrightarrow Cu_2S + FeS + SO_2 \uparrow$$

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

$$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2 \uparrow$$

Very less

$$Cu_2S+FeS+\underset{less}{Cu_2O}+\underset{less}{FeO}$$
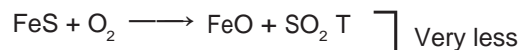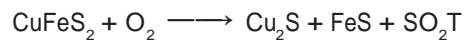
(b) Smelting step :-

Cu_2S remain unaffected again becoz carbon reduction occurs only for oxide and not for sulphide.

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

Slag → FeS + Cu$_2$O → FeO + Cu$_2$S

$\boxed{Cu_2S + FeS}$ copper Matte
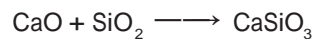
(c) Bassemer convertor reaction :-

$$FeS + O_2 \longrightarrow FeO + SO_2 \uparrow \qquad FeO + SiO_2 \longrightarrow FeSiO_3 \text{ slag}$$

$$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2 \uparrow \qquad Cu_2O + O_2 \longrightarrow Cu + SO_2 \uparrow$$
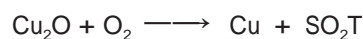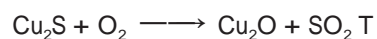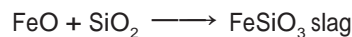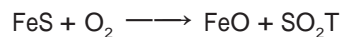
Blister Cu

◆

Extraction of Aluminium

Short chart of Al from $Al_2O_3.2H_2O$ (Bauxite)

(a) ⟶ (b) ⟶ (c)

- (A) Calcination
- (B) Roasting for [FeO] impurity
- (C) Leaching ⟶ Beayer's / Hall's / Serpeck's
- (D) Calcination

(e) Electrolytic refining ⟵ (d) Electrolytic reduction ⟵ (D) Calcination
(Hoop's process)
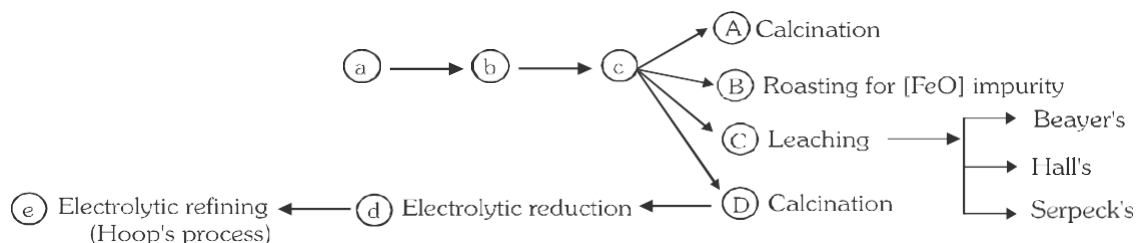
BAUXITE

†

Concentration of Bauxite ore

(a) **Baeyer's process :** (Used for red bauxite in which main impurity is iron oxide)

Bauxite ore $\xrightarrow{Roasted}$ as to convert FeO into Fe_2O_3

Roasted ore + NaOH $\xrightarrow[8\ atm]{150°C}$ $NaAlO_2$ $\xrightarrow{Hydrolysis}$ $Al(OH)_3$ + NaOH

solution   in presence ppt. of little $Al(OH)_3$
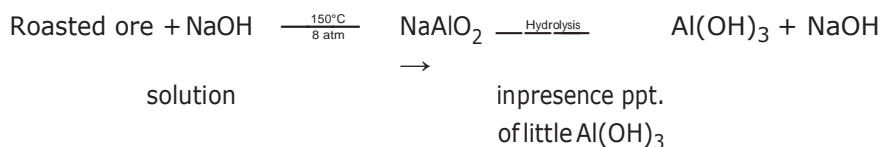
(b) **Hall's Process :** (Red bauxite)

Bauxite ore + Na_2CO_3 $\xrightarrow{Fused}$ $NaAlO_2$
† extracted with water
Solution
† warmed 50° – 60°C
CO_2 is circulated
†
$Al(OH)_3$ + Na_2CO_3
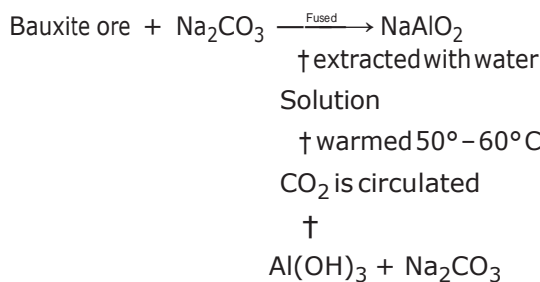
(c) **Serpeck's process :** (Used for white bauxite in which main impurity is silica)

Bauxite ore + coke $\xrightarrow{1800°C}$ AlN $\xrightarrow{H_2O}$ $Al(OH)_3$ + NH_3
+   ppt.
(Nitrogen) N_2 C + SiO_2 (gangue) $\rightarrow CO_2$A + Si †

†

CALCINATION

$Al(OH)_3$ $\xrightarrow{1500°C}$ Al_2O_3

†
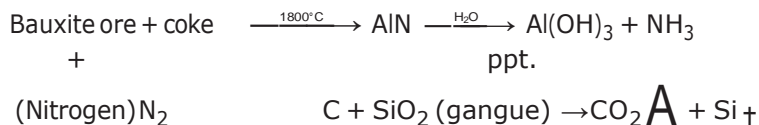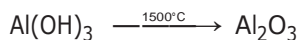
Electrolytic Reduction

Electrolyte Al_2O_3 dissolved in Na_3AlF_6 and CaF_2

Cathode–Carbon lining   **Anode** – Graphite rods

Al_2O_3 $\xrightarrow[950°C]{Electrolysis}$ Al + O_2
99.8% pure

‡
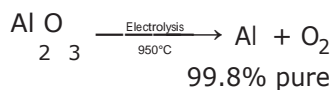
Electrolytic Refining
(Hoop's process)
Pure Al (99.98 % pure)

◆

Extraction of Fe

```
┌─────────────────────┐                    ┌──────────────┐  Calcination  ┌──────────┐
│ Finely divided ore  │                    │  Conc. ore   │     and       │ Fe₂O₃+   │  Carbon reduction
│ magnetite Fe₃O₄     │ Gravity separation │      +       │  Roasting     │ little SiO₂│
│ haematite Fe₂O₃     │ ───────────────▶   │  Little SiO₂ │ ───────────▶  │          │
│ limonite Fe₂O₃.3H₂O │      –SiO₂         │              │               │          │
│ Siderite FeCO₃      │                    └──────────────┘               └──────────┘
└─────────────────────┘
```

Fe_2O_3 + little SiO_2 → Carbon reduction

Blast Furnace — Ore (8) part +Coke (4) part +CaCO₃(1) part

(Pudding process) Molten iron taken in a furnace which is lined with Haematite

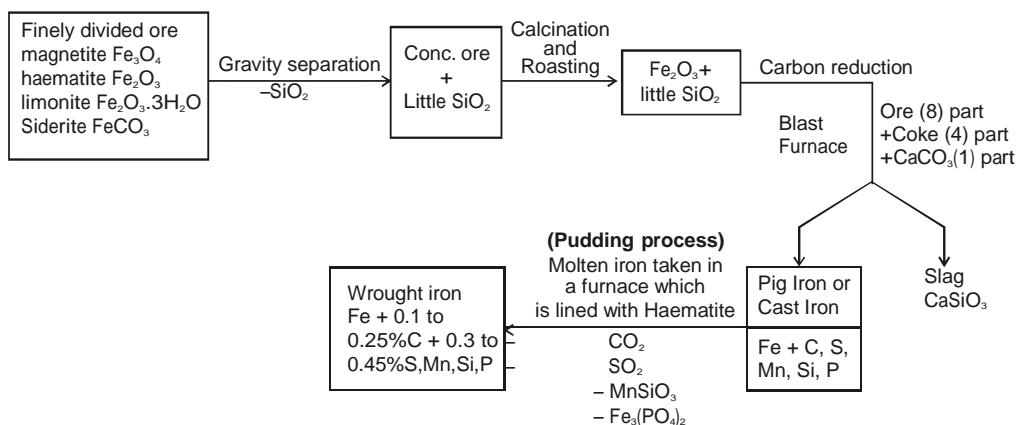| Wrought iron Fe + 0.1 to 0.25%C + 0.3 to 0.45%S,Mn,Si,P | CO_2 SO_2 – $MnSiO_3$ – $Fe_3(PO_4)_2$ | Pig Iron or Cast Iron | Fe + C, S, Mn, Si, P | Slag CaSiO₃ |

Reaction involved :

(1) Roasting step :-

$$Fe_3O_4 \xrightarrow{A} FeO + Fe_2O_3$$

$$FeCO_3 \xrightarrow{A} FeO + CO_2 \uparrow$$

$$FeO + O_2 \xrightarrow{A} Fe_2O_3$$

$$Fe_2O_3.3H_2O \xrightarrow{A} Fe_2O_3 + 3H_2O \uparrow$$
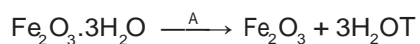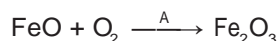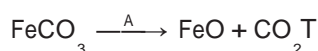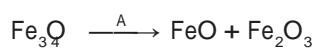
FeO reacts with SiO_2 to give $FeSiO_3$ as slag.

Hence to prevent the formation of $FeSiO_3$.

FeO is converted into Fe_2O_3 which does not react with SiO_2 due to high L.E.

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.

Ore, limestone and coke

Cone

Exhaust gases (CO,CO₂)

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$ (Iron ore)

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

$FeO + CO \rightarrow Fe + CO_2$

$CaCO_3 \rightarrow CaO + CO_2$ (Lime Stone)

$CaO + SiO_2 \rightarrow CaSiO_3$ (Slag)

$C + CO_2 \rightarrow 2CO$ (Coke)

$C + O_2 \rightarrow CO_2$

$FeO + C \rightarrow Fe + CO$

Blast of air and oxygen

500-800 K
1070 K
1270 K
1570 K
2170 K

Molten slag
Molten iron

Solid waste
Pig iron

(Blast Furnace)

◆

eg. 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.

◆