METALLURGY

Basic Terms – Mineral, ore, matrix, refractors, fluse, slag

Types of ores –

Metallurgical operations

- Powder formation (grinding)
- Concentration of ores
  - Hydraulic washing
  - Magnetic separation
  - Froth flotation process
  - → Physical process
  - Leaching → chemical process
- Isolation Process
  - oxide formation (i) Co (ii) Roasting
  - Reduction process
- Purification Process
  - Physical
    - Zone Refining
    - Distillation
    - chromatography
  - chemical
    - ☆ Vapour Phase Refining
    - Pudding Process
    - Parting Process
    - Polling process

Steel formation

2 Que. in Mains, 1-2 Que in Advance

BASIC TERMS USED

MINERAL

Substance containing mineral, obtained from nature.

ORE

Those minerals from which extractions of minerals is easier and cheaper.
All ores are minerals & vice-versa.

GANGUE / MATRIX

A undesirable substance present in ore is known as **gangue**.

REFRACTORIES

High melting pt. substance which do not change to its shape or size under high temperature.
These are electrically and thermally insulated.

E.g Basic Refractories – CaO MgO Al_2O_3
Acidic Refractories – P_2O_5, SiO_2
Neutral Refractories – Graphite, C-Bricks

FLUX

Those additional substance which are used to remove impurities present in ore.

Flux + gangue = slag

These substances are also used to decrease melting pt. of electrolyte and to increase electrical conductance.

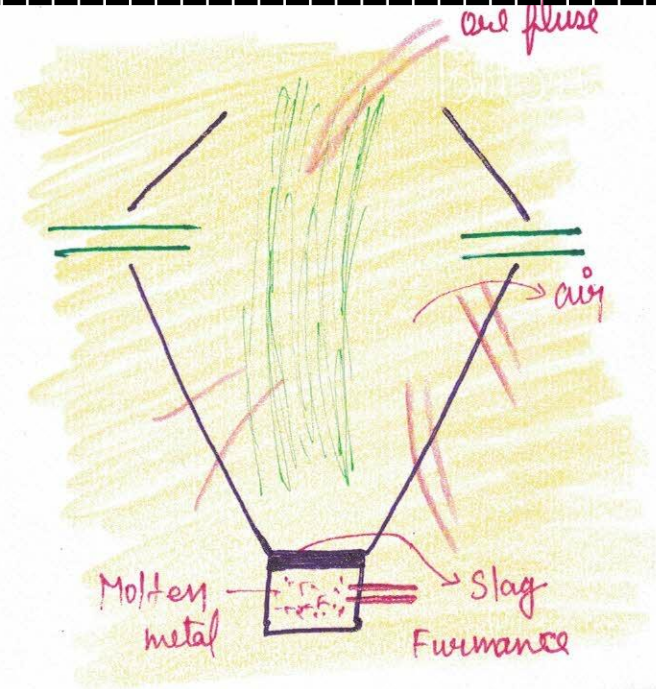
E.g In separation of Al from Al_2O_3, flux used in CaF_2 cryolite [Na_3AlF_6]

Mn_2O_3 (m.p formation = 2050°C) Al (b.p = 1800°C)

After flux is added → (mp = 920°C)

SLAG

Fusible mass which float on the surface of molten metal, because it has less density than molten metal.



It removes air contact from molten metal for further oxidation.

$CaSiO_3$ (slag) – cement industry

$Ca(PO_4)_2$ (slag) – fertilise industry

↳ [Thomas slag]

TYPES OF ORES

(i) Native ores Ag Au Pt

(ii) Combined Ore.

Oxide ores

- Hermetite – Fe_2O_3
- Bauxite – $Al_2O_3 \cdot 2H_2O$
- Cassisterite – SnO_2
- Cupesite – Cu_2O
- Zincite – ZnO

Carbonate ores

- Limestone – $CaCO_3$
- Dolomite – $CaCO_3 \cdot MgCO_3$
- Calamine – $ZnCO_3$
- Siderite – $FeCO_3$
- Cerrusite – $PbCO_3$
- Malachite – $CuCO_3 \cdot Cu(OH)_2$

Sulphide ores

- Galena – PbS
- Cinnabar – HgS
- Iron pyrite – FeS_2
- Copper glance – Cu_2S
- Copper pyrite – $CuFeS_2$ (chalcopyrites)
- Zinc blende – ZnS
- Argentite – Ag_2S

Phosphatus ores

Hydroxy apatite $3Ca_3(PO_4)_2 . Ca(OH)_2$

Chloro apatite $3Ca_3(PO_4)_2 . CaCl_2$

METALLURGICAL OPERATIONS

Scientific techniques by which extraction of metal is being carried out.

Metallurgical of any ore has following 4 steps -

i. Crending of ore
ii. Concentration
iii. Isolation of metal
iv. Refining / Purificate

v. Crending of ore
Carried out by using ball mill.

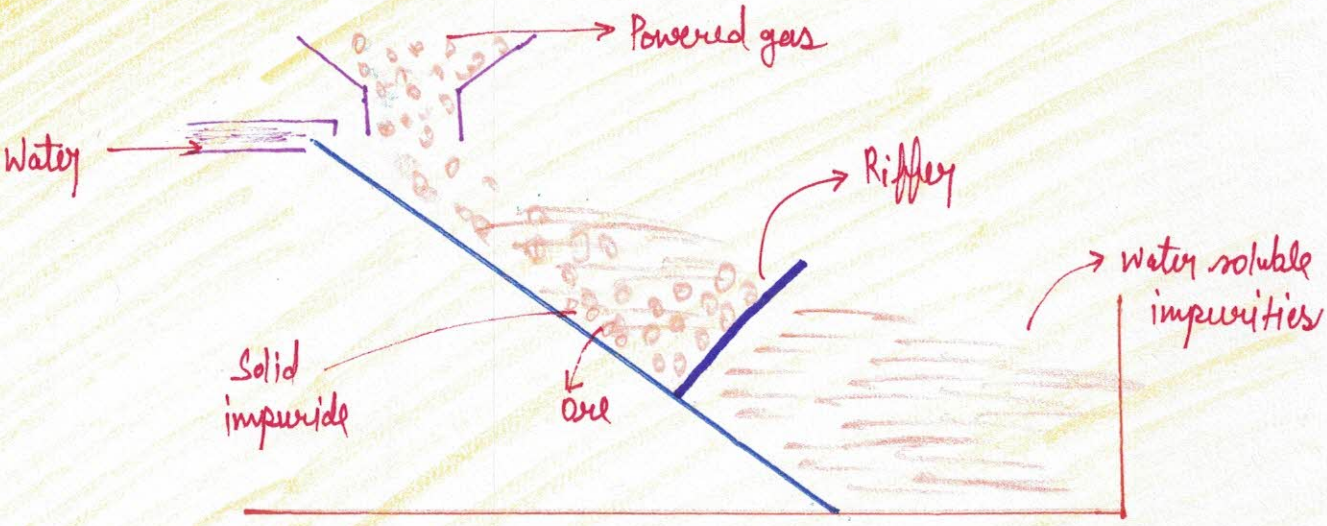
vi. Concentration of ore
Impurity present with powered ore is removed in this step.

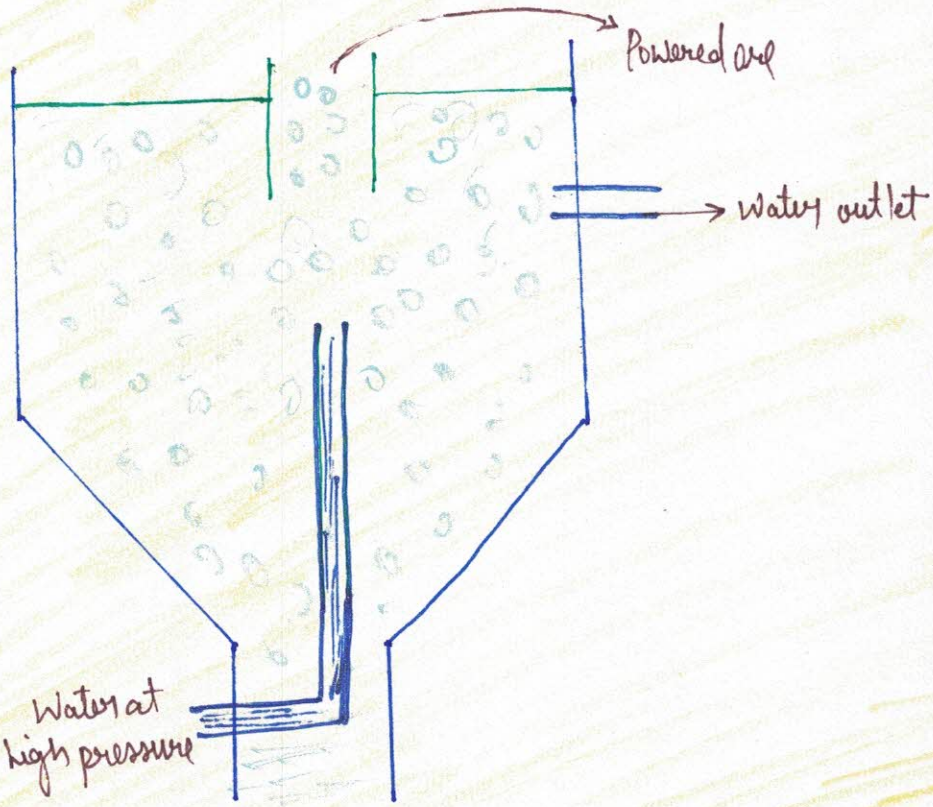
NOTE :- In this Chapter, Learn the concept behind using Hat concept process and for what kind of ore is the process being used.

Based on the type of impurity present with ore, following process are used -

1. **Hydraulic Washing (Lavigation)** - In this method, water soluble impurite present in powdred ore can be removed

This method is used for concentration of oxides and native ores.





Magnetic Separation

- Separation is based on difference in magnetic properties of ore and impurities.

Eg chromite ore (FeO, Cr_2O_3) containing silicious impurities (silica)

Non magnete ← magnetic → non-magnete

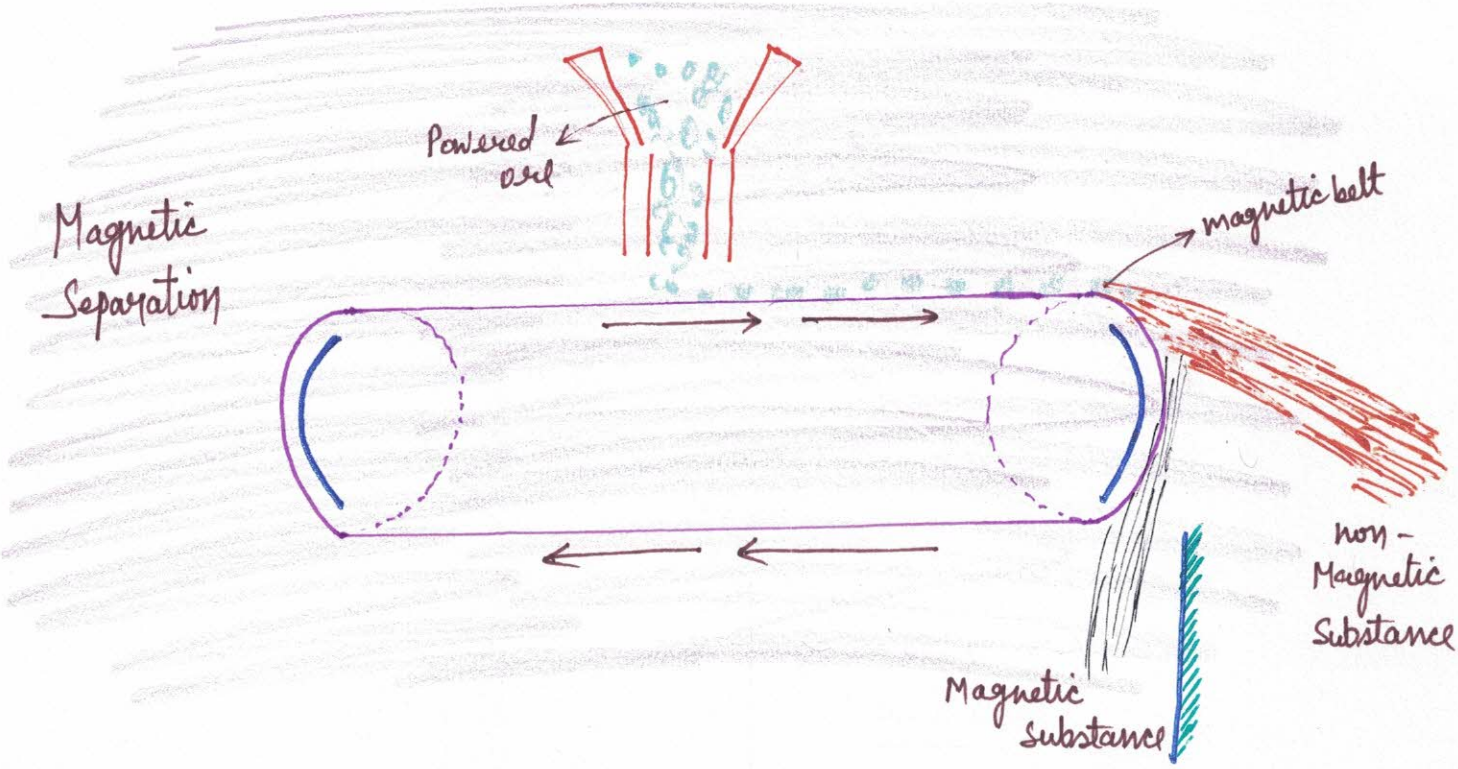
cassisterites ore (SHO_3) containing wolframite ($FeWO_4 + MnWO_4$).

→ Magnete

→ Rutile str.

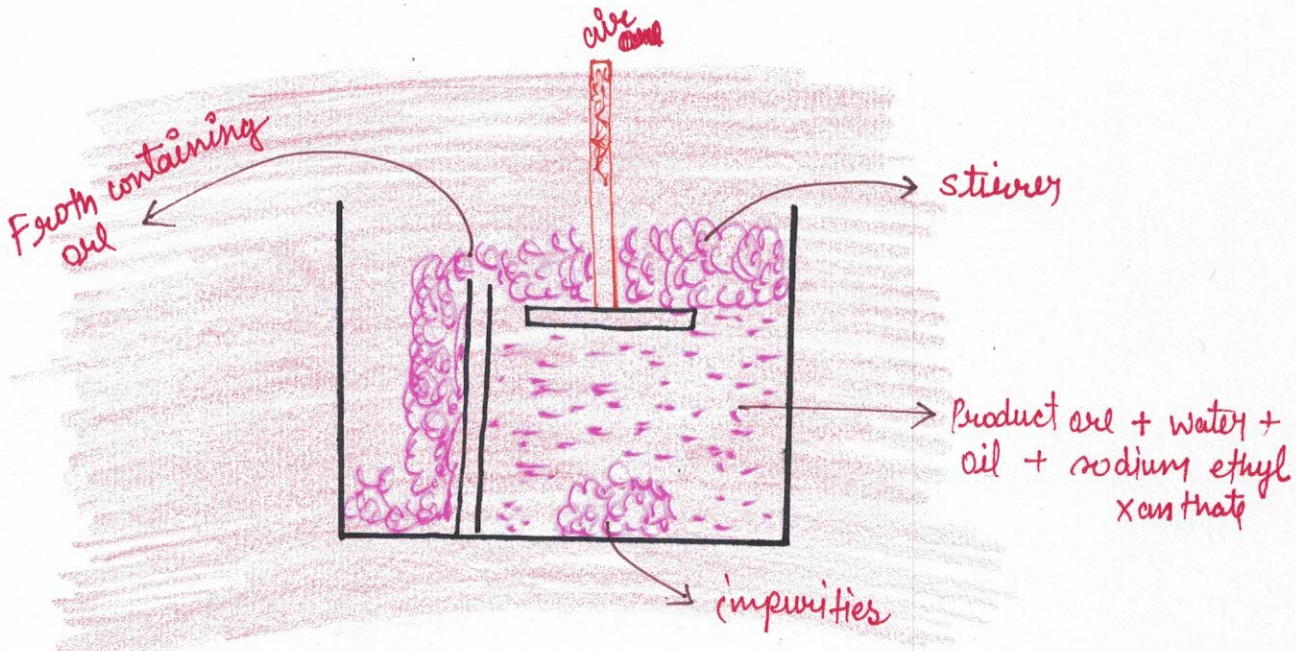
TiO_2 ore containing chloro apatite $3Ca_3(PO_4)_2 . CaCl_2$

↳ Magnetic ↳ Non-magnete



3. **Froth Floatation Process** - This method is generally used for concentration of low-grade sulphide ores (eg- PbS, ZnS, $CuFeS_2$ etc)

It is based on physical process known as adsorption.



FROATH FLOATATION PROCESS

Both floatation process can also be used for non sulphide ores by using suitable activated.

E.g. $CuCO_3 \cdot Cu(OH)_2 + Na_2S \longrightarrow Cu_2S$

Malachite Activator

Concentration is based on different wettability of ore and impurity. ore is wattable by oil and impurities ore wettable by water.

During froth flotation process, following substances are used -

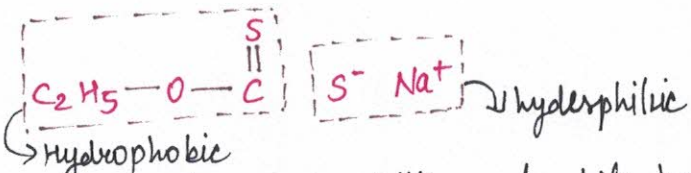
FROTHERS → camphor oil a pisse oil
(It reduces surface tension of water.) → some stabiligess like cresol and anilines are also used.

COLLECTORS → Sodium or potassium ethyl xanthates.

$\{R-O-\overset{\overset{S}{\|}}{C}-S^- \; Na^+/K^+\}$ $R = C_2H_5^-$

is used for collecting ore particles.

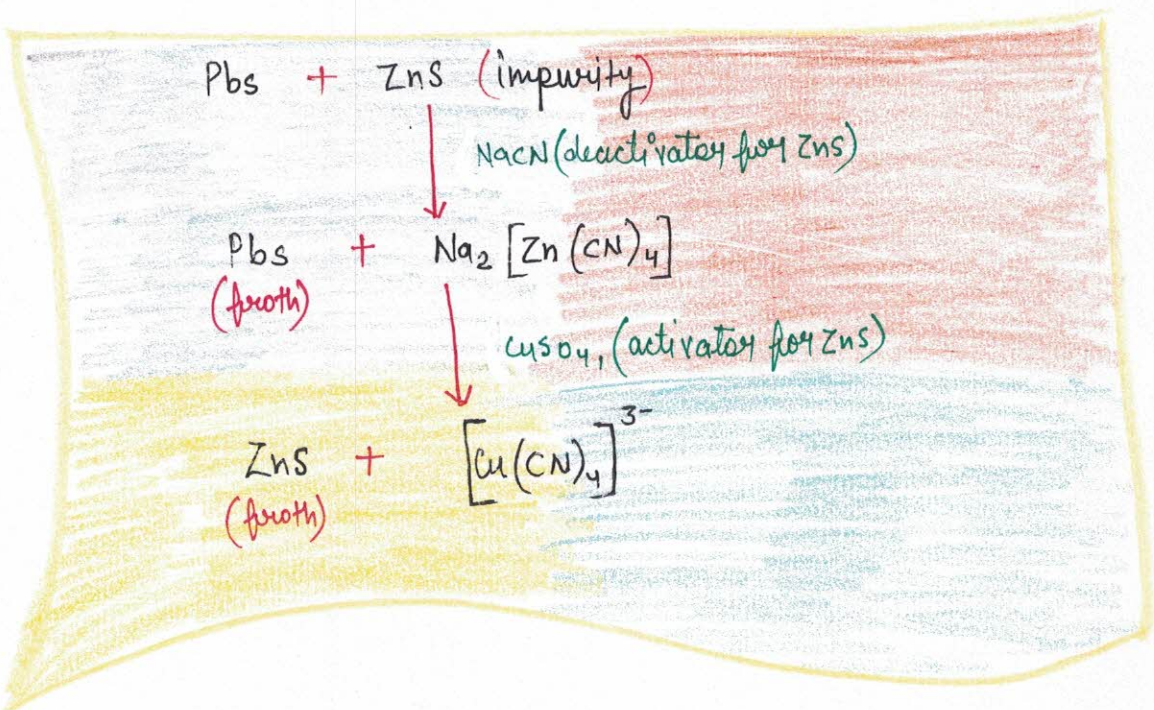
MECH



Sulphide ore is absorbed on hydrophillic end while hydrophobic end will act as water repellent which distinguish froth from water.

ACTIVATOR AND DEACTIVATOR

In Pbs ore, ZnS is present as impurity



4. LEACHING (HYDROMETALLURGY)

This process is used when the ore is soluble in a particular solvent but impurities are insoluble in it.

E.g. 1. **BAUXITE ORE** $\{Al_2O_3, 2H_2O\}$

impurities – Fe_2O_3, TiO_2, SiO_2

- Bauxite ore
  - RED Bauxite (Major impurity :- Fe_2O_3)
    - Bayer's process
    - Hall's process → Low grade ore
  - WHITE Bauxite (major impurity :- SiO_2) → Seepeck's process

Bayer's Process

Powered ore + NaOH (solvent) + Filter →
- $Fe_2O_3 + TiO_2$
- $Na[Al(OH)_4] + Na_2SiO_3$ → excess water + neutralize by CO_2 → $Al(OH)_3$ → ($1100^\circ C$, Δ) → Al_2O_3 (alumina)

Hall's Process

Powered ore + $Na_2CO_3 + ClO_3$ + Filter →
- insoluble → $Fe_2O_3 + TiO_2$
- $Na[Al(OH)_4] + Na_2SiO_3$ → excess water + neutralyte by CO_2 → $Al(OH)_3$ → ($1100^\circ C$, Δ) → Al_2O_3

SURPECK'S PROCESS

⊙ Powered ore $\xrightarrow[1800^\circ C]{Coke + N_2}$ $CO\uparrow + Si^\circ\uparrow$

$AlN + TiO_2 + Fe_2O_3$

↓ excess water + CO_2 neutralise

$Al(OH)_3 \xrightarrow[\Delta]{1100^\circ C} Al_2O_3$

⊙ $Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO\uparrow$

$SiO_2 + C \longrightarrow Si\uparrow + 2CO\uparrow$

$3AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

$\xrightarrow{\Delta} Al_2O_3$ (Pure aluminium)

2. Leaching of Au - Ag (Mac - Arthur Process)

Solvent used - NaCN

(Redox Reaction) $4Ag + 8\,NaCN + O + H_2O \longrightarrow 4Na[Ag(CN)_2] + 4\,NaOH$

Electropositive metal (like Zn) is used to remove Ag or Au from above complex (displacement reaction).

(Displacement Reac^n) $2\,Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$

Ag_2S is also concentrated by bearning with NaCN

$Ag_2S + NaCN \rightleftharpoons Na[Ag(CN)_2] + Na_2S$

$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$

3. Isolation Process

Isolation will occur in 2 steps

@ Oxide formation

- Calcination
- Roasting

(b) Reduction of oxide
- Smelting
- carbon or co-reduc
- Aluminium Thermite
- Reduction by AL.
- Self reduction
- Electrolytic reduction
- Reduction by magnesium and sodium

(a) OXIDE FORMATION

Calcination :- This method is used in the conversion of metal hydrate, metal hydroxide, metal carbonate into their respective oxides.

Heating of ore is done in absence of air or in limited amount of air before its melting point.

In this method volatile impurities, CO_2 or any volatile organic is also removed.

After calcination ores become porous and reduction of ore is kinetically favoured.

$$\underset{\text{Bauxite}}{Al_2O_3 \cdot 2H_2O} \xrightarrow{\Delta} Al_2O_3 + 2H_2O$$

$$\underset{\text{Limonite}}{Fe_2O_3 \cdot 3H_2O} \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$

$$\underset{\text{Dolomite}}{CaCO_3 \cdot MgCO_3} \xrightarrow{\Delta} CaO + MgO + 2CO_2\uparrow$$

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

Roasting :- It is used for sulphide ores to convert into respective oxides.

Heating of air is carried out in excess of air before melting point.

During roasting, volatile impurities of P, As, and S are removed in form of their respective oxides.

After roasting, ore becomes porous and lighter, which will support in kinetics & reduction.

E.g.

$$PbS + O_2 \longrightarrow PbO + SO_2$$
$$HgS + O_2 \longrightarrow HgO + SO_2$$
$$ZnS + O_2 \longrightarrow ZnO + SO_2$$

→ Can be used for H_2SO_4 formation

Roasting sometimes may not complete the combustion.

Roasting of $CuFeS_2$ (using SiO_2) fuse

$$CuFeS_2 + O_2 \longrightarrow CuFeS_2 + FeO + SO_2$$

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

Sometimes during roasting, if excess SO_2 is formed and temp. ($<750^\circ C$), sulphate can be formed which are thermally stable.

$$PbS + O_2 \longrightarrow PbO + SO_2$$

$$SO_2 + \tfrac{1}{2}O_2 + SO_3$$

$$PbO + SO_3 \longrightarrow PbSO_4 \text{ [Anglesite]}$$

(b) REDUCTION OF OXIDES

(i) Smelting

Separation based on melting through fusion.

(ii) Carbon/Co-Reduction

For carbon reduction, blast furnance is required.

In carbon and co, suitable reducing agent is selected by using ellingham diagram.

Ellingham Diagram is a diagram/curve b/w ΔG and T whose slope is ΔS

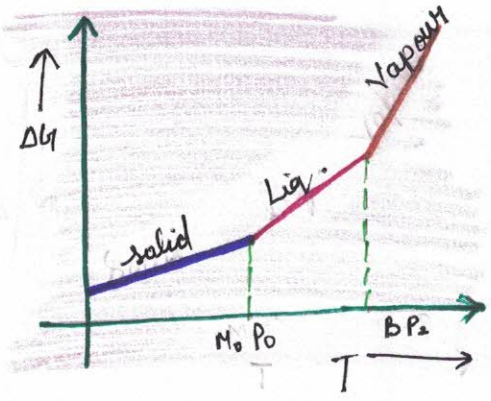
$$\{\underbrace{\Delta G}_{Y} = \underbrace{\Delta H}_{C} - \underbrace{T\Delta S}_{X\ M}\}$$

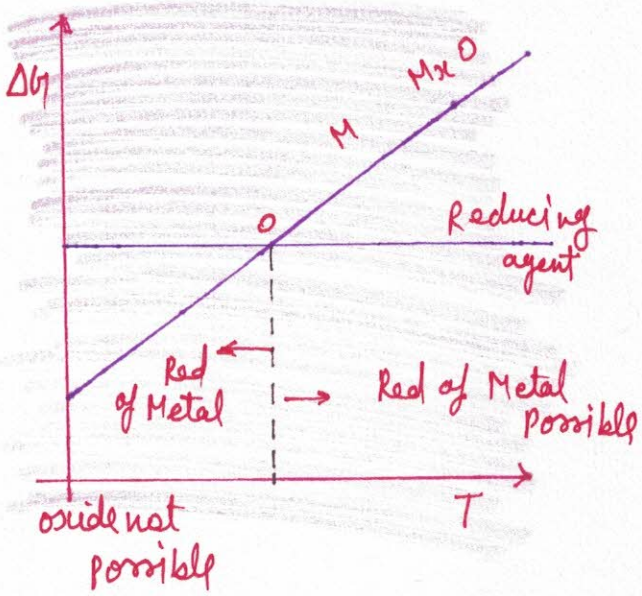
$$xM_{(s)} + \tfrac{1}{2}O_2(g) \longrightarrow M_xO_{(s)} \qquad \Delta S = -ve \quad T\uparrow \quad \Delta G\uparrow$$

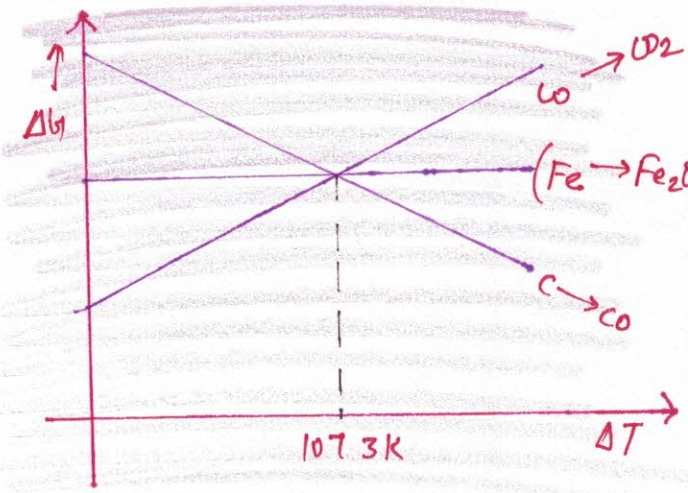
$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta S = +ve \quad T\uparrow \quad \Delta G\downarrow$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta S = 0 \quad T\uparrow \quad \Delta G = Const$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta S = +ve \quad T\uparrow \quad \Delta G\uparrow$$







For the reduction of Fe_2O_3, select type of Reducing agent.

for $T < 1073\,K$

$T > 1073\,K$

Solution:- $T < 1073\,K$

CO will act as reducing agent

$T > 1073\,K$

C will act as reducing agent

$Fe_2O_3 + C \longrightarrow Fe + CO$

C - Reduction method is used for:- (Zn, Pb, Sn, Fe) oxides

Carbon Reduction Method can't be used

(i) (S-block + Al) - metals have less B.P and M.P. due to which, these metals can evaporate as vapour in the blast furnance.

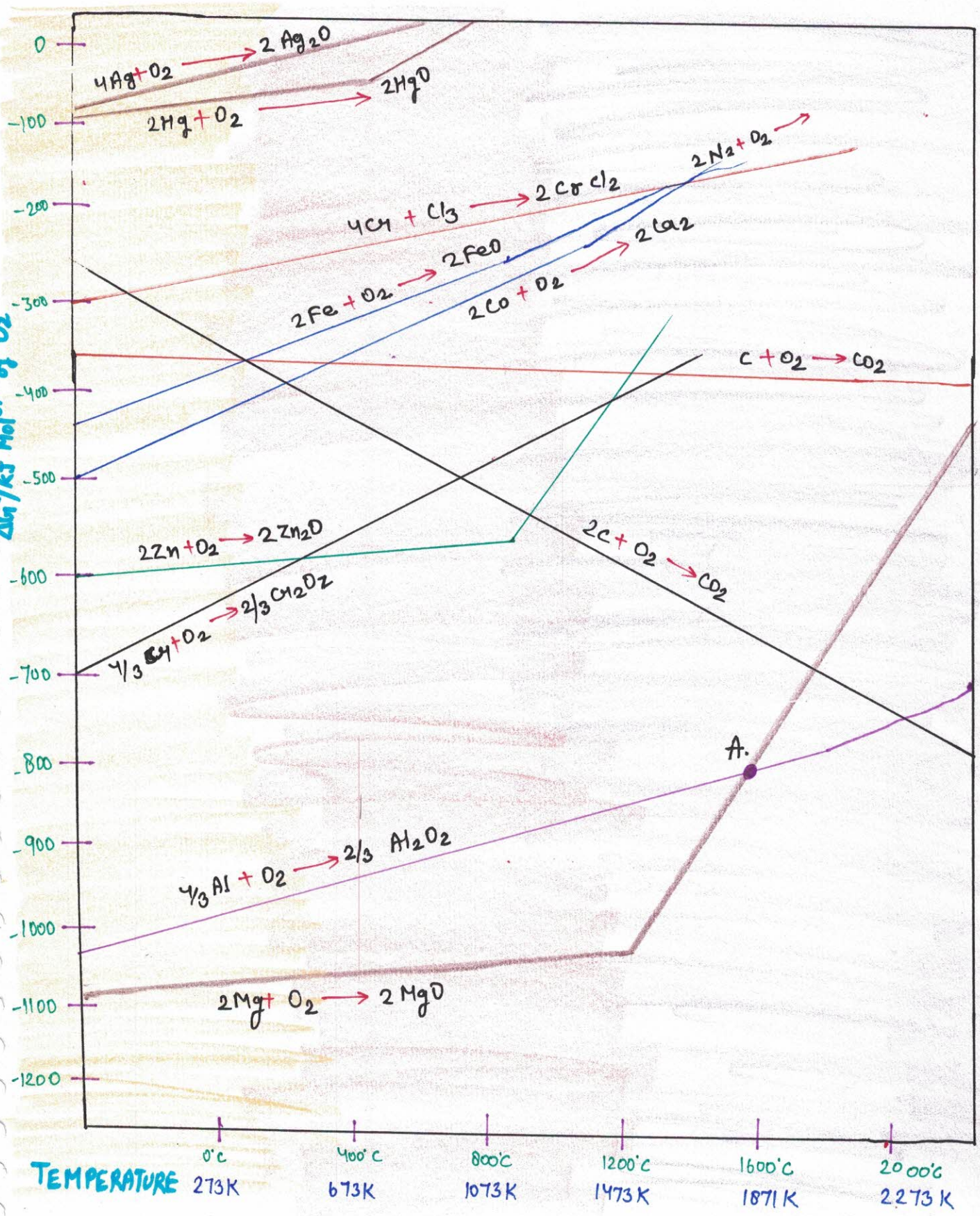
(ii) some metals oxides form respective carbides during reduction.

$CaO + C \longrightarrow CaC_2 + CO$

$MgO + C \longrightarrow Mg(v) + CO$

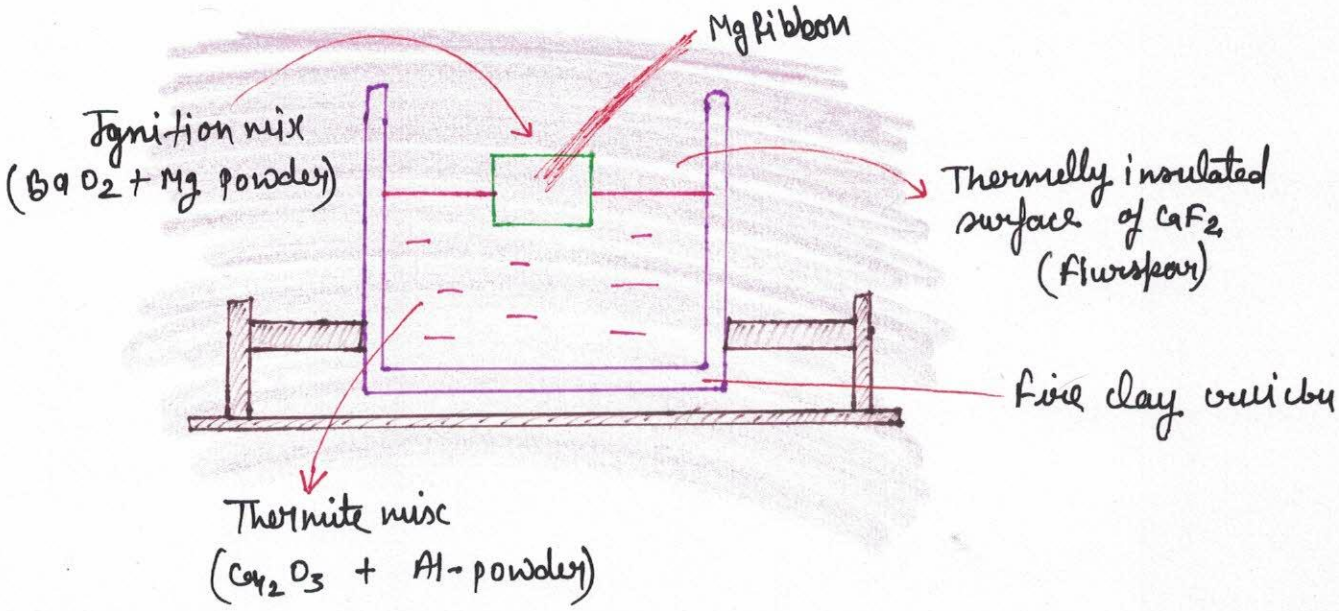
NOTE:- C act as reducing agent in high temp. Zone which CO act as reducing agent in Low temp. zone.

ELLINGHAM DIAGRAM OF OXIDES



(iii) Alumino Thermite Process

This method is used for the reduction of transitions metal oxides of high m.p. Reduction is carried out on the basis that Al has greater affinity for oxygen than transition metal and formation of Al_2O_3 is highly exothermic.



$$BaO_2 + Mg \longrightarrow BaO + MgO + \text{heat}$$

$$Cr_2O_3 + 2Al \longrightarrow 2Cr(l) + Al_2O_3 + \text{intense heat}$$

(reduction)

$$Mn_3O_4 + Al \longrightarrow Mn(l) + Al_2O_3$$

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

(3:1)

used in Thermite welding

(iv) Self Reduction Process

used for reduction of Pb, Hg, Cu, Ke sulphide

$$PbS + O_2 \longrightarrow PbO + SO_2 \quad \text{(Partial roasting)}$$

$$PbS + 2PbO \longrightarrow 3Pb + SO_2 \quad \text{(self reduction)}$$

$$HgS + O_2 \longrightarrow HgO + SO_2$$

$$2HgO + HgS \longrightarrow Hg + SO_2$$

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

$$Cu_2S + Cu_2O \longrightarrow Cu + SO_2$$

(iv) Reduction by Mg and Na

$TiCl_4 + 2Mg \longrightarrow Ti + 2MgCl$

$TiCl_4 + 4Na \longrightarrow Ti + 4NaCl$

IMI - Imperial Metal Industry

(vi) Electrolyte Reduction

used for reduction of high e^- metal oxides or metal of Low m.p & b.p

E.g Electrolytes Reduction of Aluminium (Al_2O_3)

(Hall - Haroult process)

Flux = CaF_2 + cryolite (Na_3AlF_6) ↑↑

decreases m.p & Al_2O_3

Cathod = steel, Anode - graphite / carbon

Cathod = $Al^{+3} + 3e^- \longrightarrow Al_{(s)}$ (reduction)

Anode = $C + O^{-2} \longrightarrow CO$ or $CO_2 + 2e^-$ (oxidation)

In this process carbon anode is replaced timely for containing the process.

(v) Purification or Refining

Physical Methods

- Liquation
- Zone Refining (fractional crystalliation)
- Distillation
- Parke Process
- Chromatography

Chemical Methods

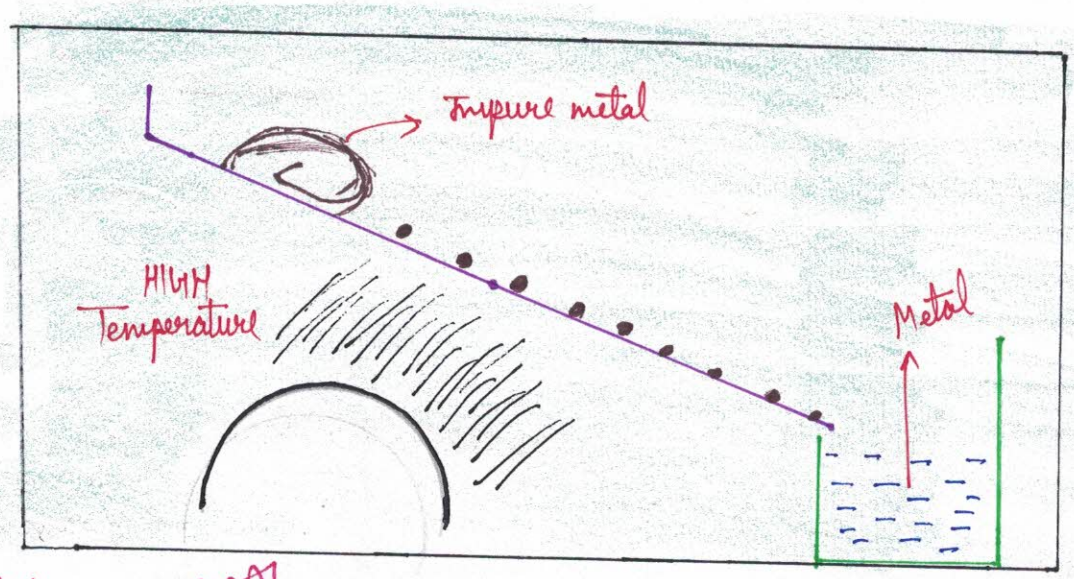
- Oxidation Refining
  - cupellation
  - Bessemerisation
  - Pudding Process
- Polling Process
- Electrolytic Refining
- Vapour-Phase Refining
  - Mond process
  - Van Arkel process

I. LIQUATION

This method is used where melting point of impurities is higher than metals.

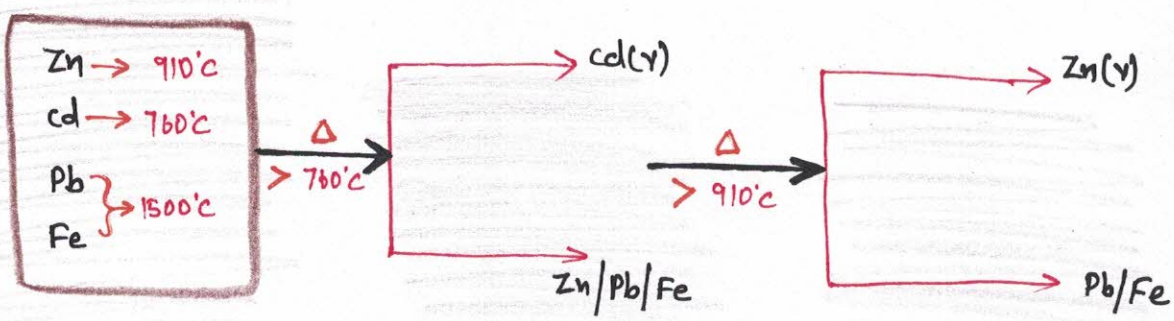
Sn, Pb, Bi, etc

↳ (C / Fe / W → high m.p. impurities)



II DISTILLATION

Refinning is based on difference in boiling point of metal and impurity (in which generally metal has less b.p. than impurity).



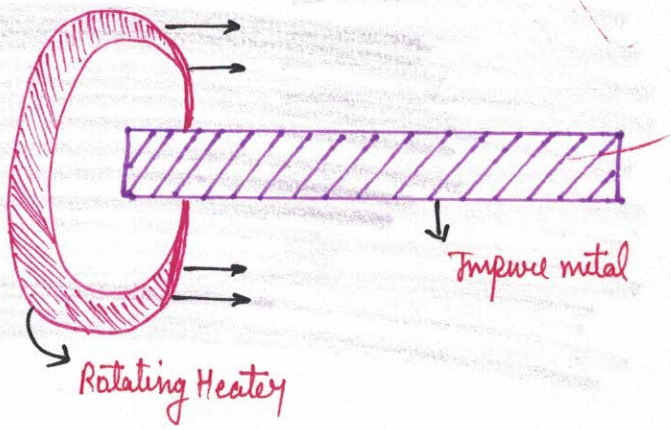
Spelter – impure Zn containing impurities of Cd, Hg, Fe.

III ZONE REFINING (FRACTIONAL DISTILLATION)

This method is based on the concept according to which impurities are more soluble in molten phase than in solid phase.

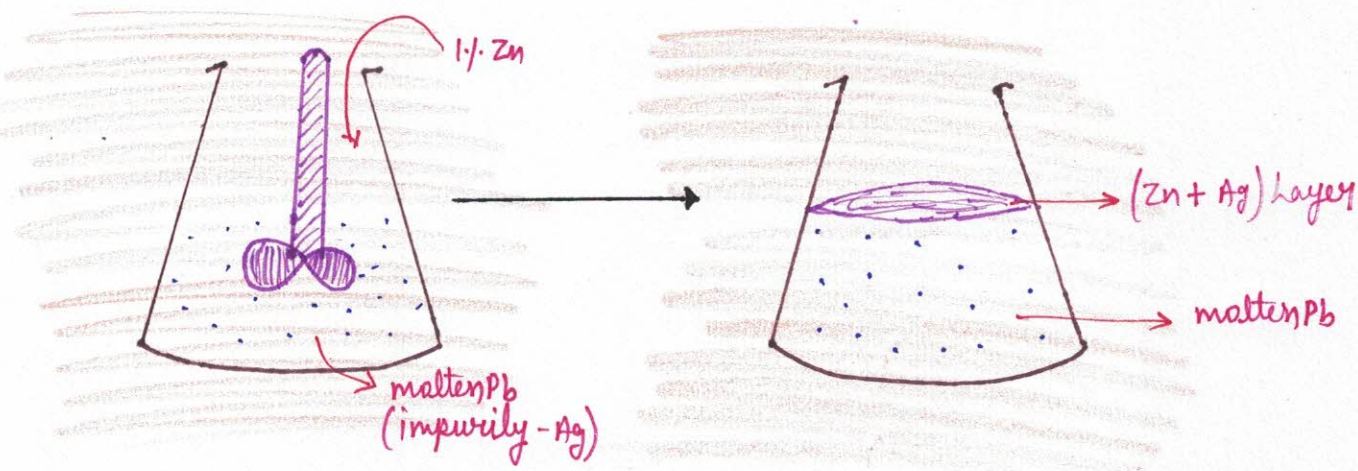
E.g. For ultrapurification of semiconductor material like Si, Ge, etc.

Ratio of impure : pure = (1:10)



IV PARK PROCESS

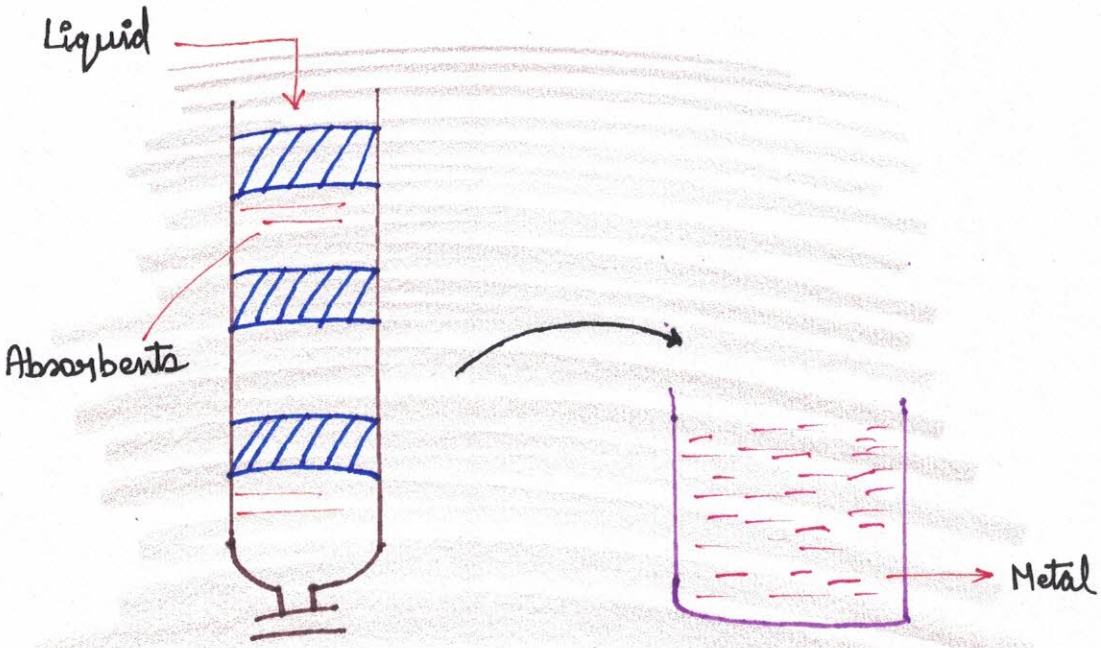
[Desilverisation of commercial Lead]



Zn is used bcz
- > Ag is 300 times more soluble in it than Pb.
- > It doesnot follow alloy with Pb.
- > It is lighter than Pb.

V CHROMATOGRAPHY

- Purification is based on physical process of adsorption
- Impure Metal has to be taken in gas or Liquid phase.
- The adsorbents in the bed adsorb the impurities of diff. kinds.



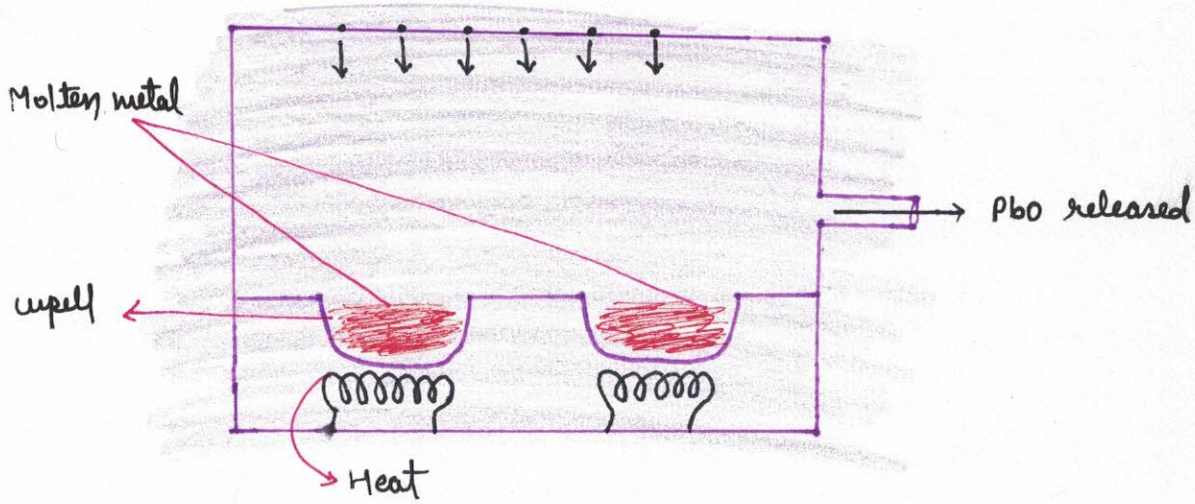
CHEMICAL PROCESS

@ OXIDATION REFINING

In this methode, impurity present has high affinity for oxygen and released in the form of vapour.

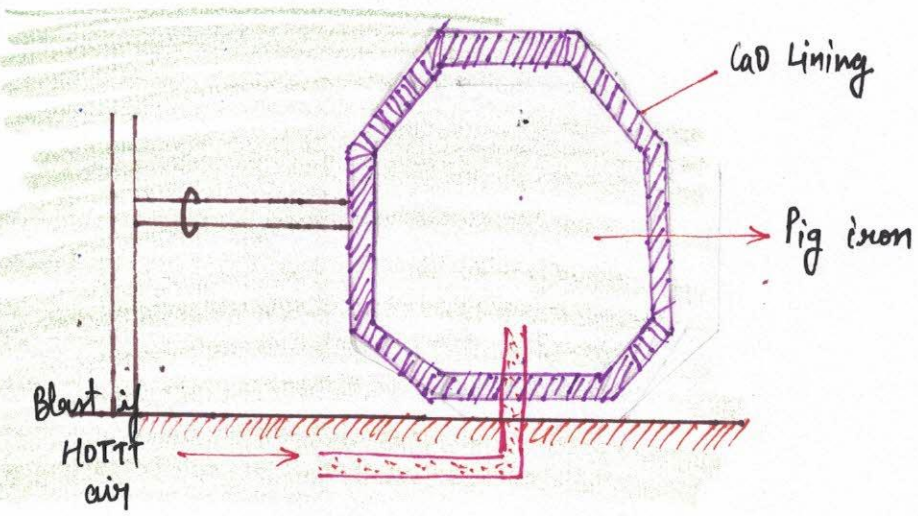
(ii) **Cupellation** - for purification of Ag/Au from Pb.

{ cupellation me Ag ki ore hote hai & Parke process me Pb ki ore hote hai }



[ii] BESSEMERISATION

For purification of pig iron into cast iron.



{ impurities (C/Mn/Si/P)

Bessemerisation = (CaO Lining) Pudding (Fe_2O_3 lining)

Reaction -

$C + O_2 \longrightarrow CO_2$

$Si + O_2 \longrightarrow SiO_2$

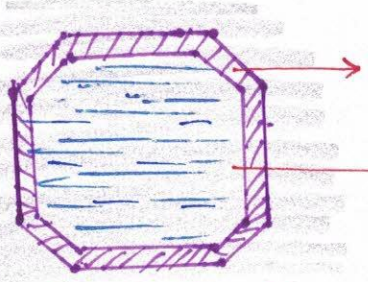
$Mn + O_2 \longrightarrow MnO_2$

$P + O_2 \longrightarrow P_4O_{10}$

$CaO + P_4O_{10} \longrightarrow Ca_3(PO_4)_2$

[iii] Puddling Process

For of cast into iron into wrought iron purest form of iron.



Reverberatory furnance

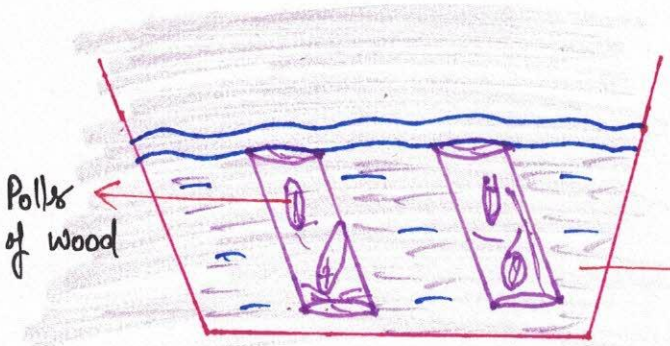
Reaxn :- $Fe_2O_3 + C \longrightarrow 2Fe + CO_2 \uparrow$

$Fe_2O_3 + Mn \longrightarrow 2Fe + MnO_2 \uparrow$

POLLING PROESS

- For purification of Cu_2O and SnO_2
- Impurities present with Cu → (S/As/Sb/Fe)
- Impurities present with Sn → (Fe/W)

Green wood —(coverbustion)→ CH_4



$Cu_2O + CH_4 \longrightarrow Cu + CO_2 + H_2O$

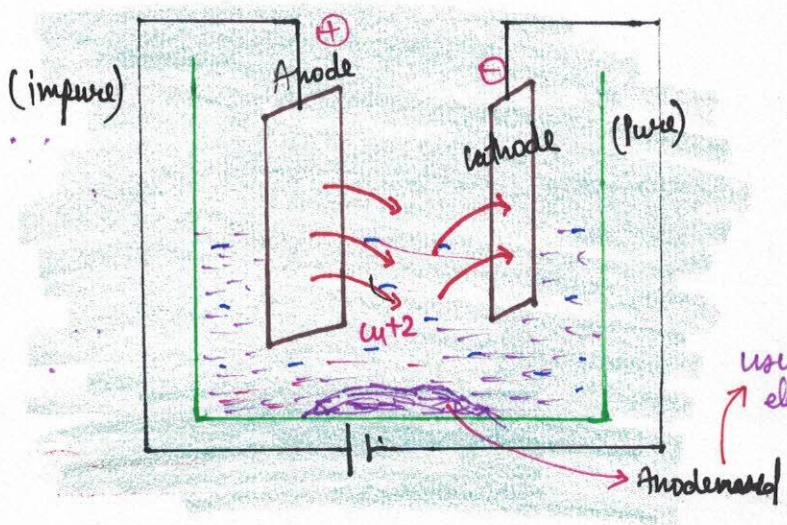
ELECTROLYTIC REFINING

used in refining of

C	H	A	A	P	A
copper	Hg	Al	Ag	Pt	Au

(For Al electrolytic Refining – Hooper process)

In Cu electrolysis – Anode – impure Cu
Cathode – pure Cu



usually use electropositive metals like Ag, Au, Pt.

Anode – $Cu(s) \longrightarrow Cu^{+2}_{(aq)} + 2e^-$

cathode – $Cu^{+2} + 2e^- \longrightarrow Cu(s)$ pure

EXTRA INFO.

Azenite → $2CuCO_3 . Cu(OH)_2$

Limonite → $Fe_2O_3 . 3H_2O$

Bett's electrolysis process for Pb.

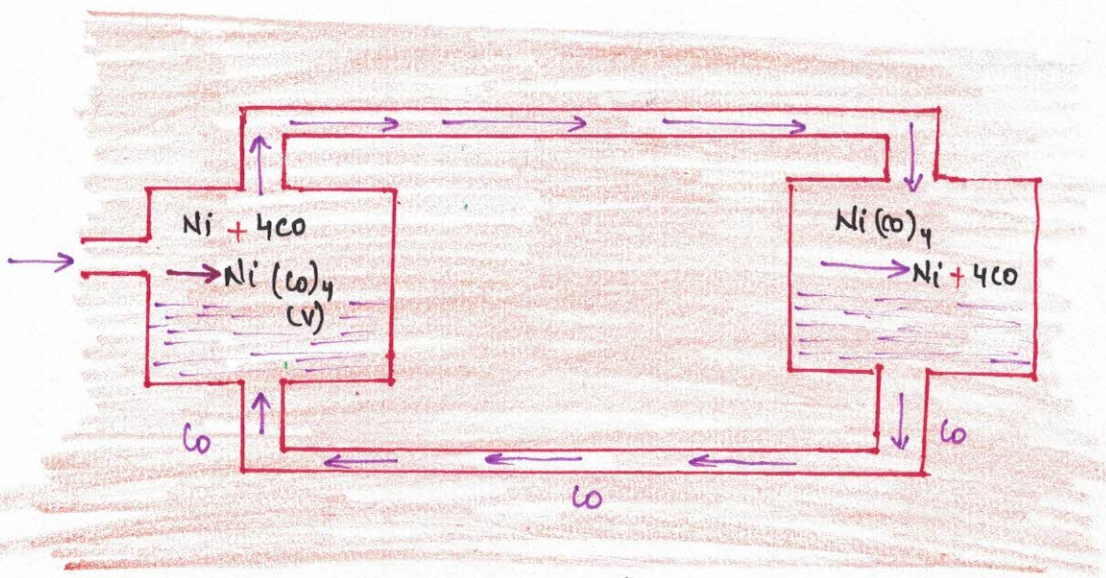
VAPOUR PHASE REFINING

[i] Mond Process

For purification of Ni

$$Ni + 4CO \xrightarrow{50^\circ C} Ni(CO)_4 \xrightarrow{200^\circ C} Ni + 4CO$$

(impure) — Vapour — (pure)



[ii] Van- Arkel Process

for Ti, Zr, Hg, B, Tn, etc

$$Ti + 2I_2 \xrightarrow{\sim 250^\circ C} TiI_4 \xrightarrow{1400^\circ C} Ti + 2I_2$$

(impure) — (pure)

PARTING PROCESS

To remove (Cu^+, Ag) from Au.

Parting can be done by -

- using H_2SO_4 or HNO_3 - ore should not have Au more than 30
- using Cl_2 - Ag will removes as AgCl

AMALGAMATION PROCESS

Impure metal + Hg → Metal amalgam $\xrightarrow{\Delta}$ Hg (vapour) + metal (pure)

E.g. - Au

Hg cannot form amalgam with Fe, Pt.

STEEL PRODUCTION

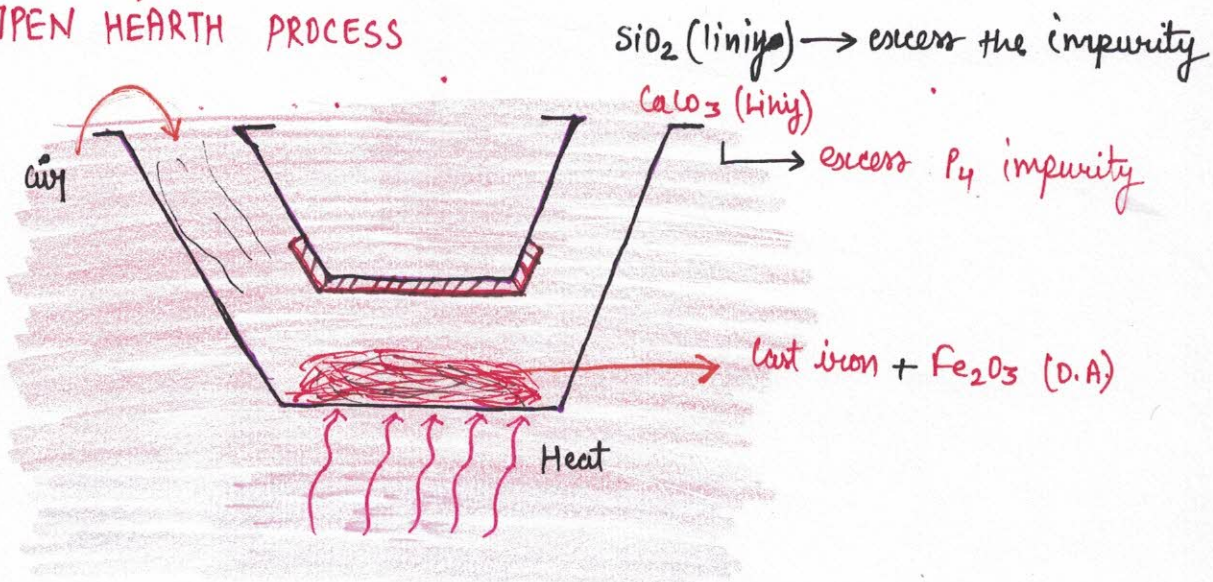
Process used -

Bessemerisation (Thomas process)

Open Hearth Process (Simon-Martin Process)

L.D. Process or BOP Process (Basic process or electric process)

OPEN HEARTH PROCESS

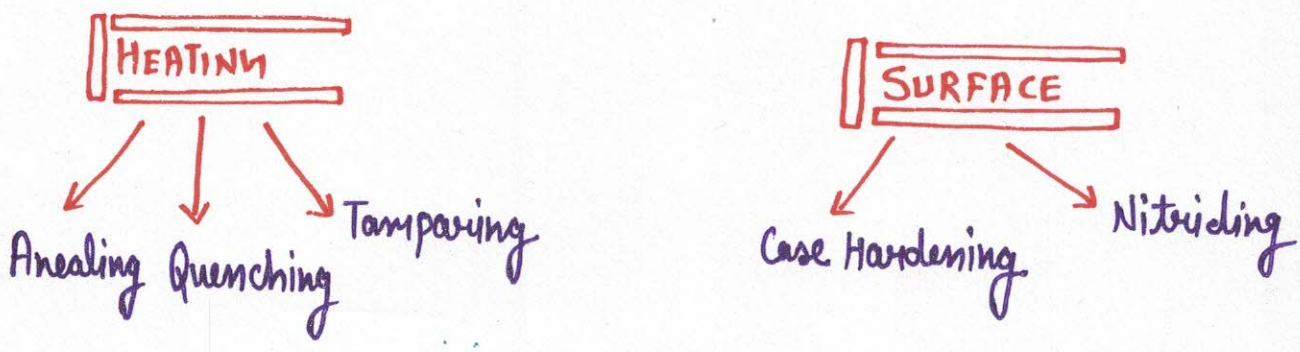


Some part of molten iron will be wasted in the form of iron nitride because of reaxn of Fe with air containing N_2.

L.D. PROCESS

This is the modern process for production of steel.
Reaction are same as of open hearth process.
At the place of air oxygen is used due to which loss of molten iron in the form of iron nitride will stop.
Heating effect is produced by electricity

STEEL OPERATION



- **Annealing** – Heating of steel upto Red Hot and cool it slowly.
  Steel become soft and elastic
- **Quenching** – Heating upto red Hot and suddenly cooling.
  Steel become hard. and ductile.
- **Tampering** – Slowly heating of quender steel and cooling it slowly.
  Steel remain hard but ductility removed.
- **Case Hardening** – Heating of steel under graphite which form Fe_3C layer on its surface.
- **Nitriding** – Heating of steel with N_2 form iron nitride layer on its surface

BEAST FURNANCE