1.7.19

Metallurgy

→ Extraction and purification of metals. is k/a metallurgy

* Ore → Mineral from which metal can be extracted profitably.

* ~~Ore~~ Minerals → Metal containing compound obtained by mining.

* ~~Ore~~

⇒ All ores are water insoluble.

* ~~Nitrates do not form water soluble, that is why they do not form ores.~~

* Generally nitrates do not form ores as they are water soluble.

* Gangue/Matrix – Impurities associated with ore particles.

* Flux – Chemical substance added to remove impurities.

(i) Acidic flux – Used for basic impurities.
→ E.g. SiO_2

(ii) Basic flux – Used for acidic impurities
→ E.g. CaO, FeO

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* Slag → Flux + impurities
Use :→ It prevents further oxidation of metals.
Property :→ Density ↓, M.P ↓ as compared to metals.

Types of Metallurgy

(i) Pyro Metallurgy
→ Heating effect is used

(ii) Hydro Metallurgy
Solvent is used

(iii) Electro metallurgy
Electrolysis is used.

*IMP
Some important ores

$* Cu

Cu_2O – Cuprite
Cu_2S – Copper glance
$CuFeS_2$ – Copper pyrites* (JEE-2019)
$CuCO_3.Cu(OH)_2$ – Malachite* (NEET-2019)

* Fe

Fe_2O_3 – Haemetite
Fe_3O_4 – Magnetite
$FeCO_3$ – Siderite
FeS_2 – Iron pyrite

* Al
  $Al_2O_3 \cdot xH_2O$ – Bauxite

* Zn
  ZnO – Zincite
  ZnS – Zinc blend / sphalarite
  $ZnCO_3$ – Calamine

* Pb
  PbS – Galena

* Sn
  SnO_2 – Tinstone / Casseterite

* Ag
  Ag_2S – Argentite

* Mn
  MnO_2 – pyrolusite

Crushed Ore —Concentration / Dressing→ Conc. Ore —(Calcination O_2 ✗ / Roasting O_2 ✓)→ Metal oxide —Reduction→ (impure) Metal —Refining→ Metal (pure)

Concentration / Dressing

- → Gravity separation
- → Magnetic separation
- → Froth Flotation (used for sulphide ores)
- → Leeching (chemical process) (used for native ores)
  - [Eg Al_2O_3 in presence of NaOH [Hall Herault process & Hoop's process]
  - 2. AgS in presence of Zn [Mc Arthur Forest cyanide process]

Reduction

- → Carbon Red^n: Fe, Sn, Pb, Zn
- → Alumino thermite Red^n: Cr, Mn, Fe
- → Thermal Red^n: Ag_2S, HgS
- → Self Red^n: Cu_2S, HgS, PbS
- → HMR (Hydro Metallurgical Red^n)
  - → Mc Arthur
  - → Low grade Cu
- → Electrolytic red^n
  - → All s-block & Al

Refining

- → Liquation: Sb, Sn, Pb, Bi
- → Distillation: Zn, Cd, Hg
- → Poling: Cu, Sn, Pb (impurities of their oxides)
- → Cupellation: Ag, Au
- → Zone refining (semi-conductors)
- → Vapour phase refining (All Back)
- → Electrolytic Refining: For all metals (Al, Fe, Zn, Sn, Pb, Ag, Au, Cu)

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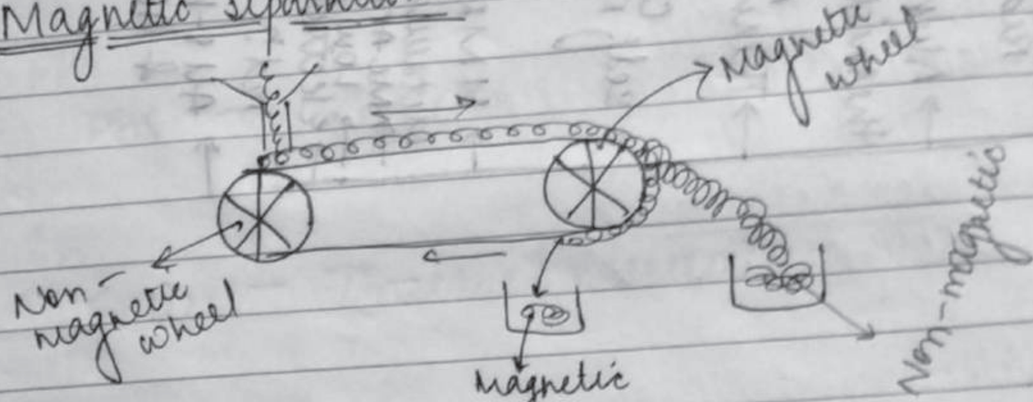
Step-I (A) Concentration / Dressing

(i) Gravity separation / Levigation / Hydrolic washing

→ It is based on difference in density of ore particles and impurities generally used for oxide ores.

(ii) Magnetic Separation



→ It is based on difference in magnetic properties of ore particle and impurities generally used for oxide ores.

E.g. SnO_2 + ($FeWO_4$ + $MnWO_4$)
Tinstone (Non-mag.) Wolframite (Magnetic impurities)

(2) $FeCr_2O_4$ + SiO_2
Chromite ore (Magnetic) Non-magnetic

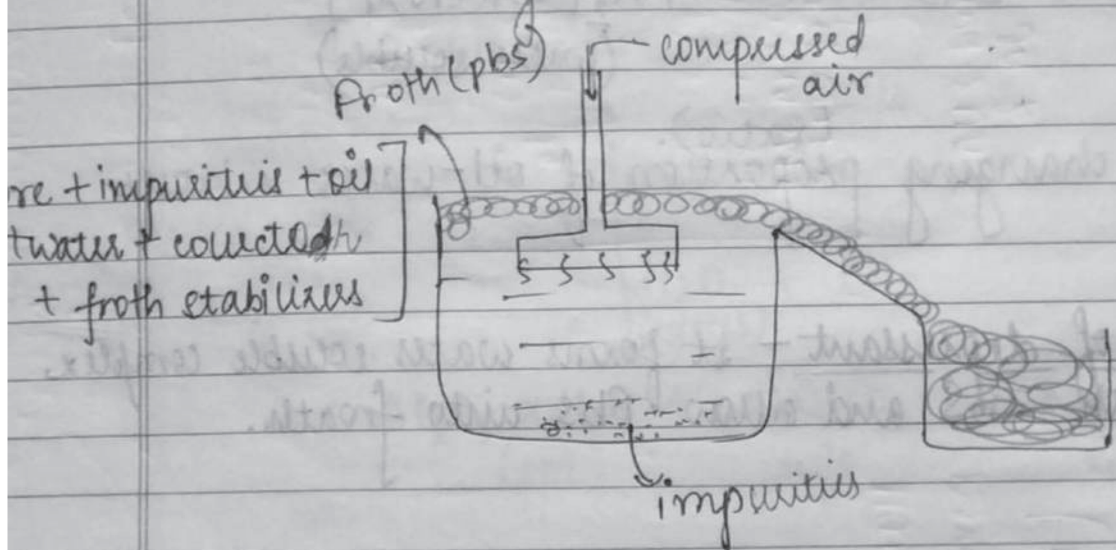
Imp
(iii) ★ **Froth Flotation**

→ Generally, used for sulphide ores.

→ It is based on different ~~absorption~~ adsorption pptys of sulphide ores and gangue.

sulphide ores ↓ wetted/absorbed by oil.

gangue ↓ wetted by water.



→ (oil, Collector) — Frothing agent

oil ⟶ Pine oil

Collector ⟶ Sodium ethyl Xanthate

$$C_2H_5-O-C(=S)-S^- \quad Na^+$$

C_2H_5 — hydrophobic end.

$-C(=S)S^-$ — hydrophillic end

Use of collector — It enhance non-wettability of ore particles with water.

Froth stabilizers — Aniline, cresol.

* When Fe_2O_3 (Red) is major → Bauxite c/a red Bauxite.
* When SiO_2 is major → White Bauxite

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Separation of two different Sulphide ores

(i) By using Depressant
↓
($NaCN$ | KCN)

$$PbS + ZnS \xrightarrow{NaCN} Na_2[Zn(CN)_4]$$
(water soluble)

(ii) By changing proportion (ratio) of oil-water mixture

* Use of depressant - It forms water soluble complex with ZnS and allow PbS into froath.

(iv) Leaching

→ When ore particle is soluble in solvent

X (ore) w/i + Y impurities w/i

↓ Z (solvent)

XZ w/s

(A) Conc^n of Bauxite ore

~~Al_2O_3~~

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$Al_2O_3 . xH_2O$ + Fe_2O_3 + SiO_2
(Ampho.) ~~(Acidic~~ (Basic) (Acidic)

↓ NaOH (Fe_2O_3 ↓)

$Na[Al(OH)_4]$ + Na_2SiO_3
Sod. Aluminate
w/s w/s

↓ Acidification

Seeded with freshly prepared Al_2O_3 → H_2O + CO_2 (excess)

↓

$Al_2O_3 . xH_2O$ + $NaHCO_3$ + Na_2SiO_3
(ppt) w/s w/s

⇒ $Al_2O_3 . xH_2O$

↓ Calcination (1200°C)

Al_2O_3

↓ Hall Herault process | Electrolytic red^n

Al (imp)

↓ Hoop's Process | Electrolytic Refining

Al (pure)

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(B) Extraction of Ag from Ag_2S

$$\overset{+1}{Ag_2}S + NaCN + H_2O + O_2 \text{ (O.A)}$$

$$\downarrow$$

$$Na[Ag(CN)_2] \text{ (w/s)} + Na_2\overset{-2}{S} \text{ (w/s)}$$

($Na_2\overset{-2}{S}$ + O_2 → $Na_2\overset{+6}{S}O_4$)

$$Na[Ag(CN)_2] \xrightarrow{Zn \text{ (R.A)}} Na_2[Zn(CN)_4] \text{ (w/s)} + \overset{0}{Ag}\downarrow \text{ (ppt.)}$$

(Ag ↓ → ~~hydrometallurgy~~ HMR)

→ This is k/a Mc. Arthur Forest cyanide process.

→ It is a hydro-metallurgical redⁿ in which less reactive metal is reduced & replaced by more reactive metal.

→ O_2 is used as oxidising agent which convert $Na_2\overset{-2}{S}$ to $Na_2\overset{+6}{S}O_4$ and prevent reaction from backward direction.

→ This process can also be used for <u>native ores</u>.

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$M = Ag / Au / Pt$ → Native ores

$$M^{0} + CN^{-} + H_2O + O_2 \text{ (O.A)}$$
+ impurities

↓

$$[\overset{+1}{M}(CN)_2]^{-1}$$
w/s

↓ Zn (R.A)

$$[Zn(CN)_4]^{-2} + M^{0}\downarrow$$
w/s ppt.

Step-II (B) Formation of Metal Oxides

(i) Calcination

→ * Heating ore in absence of O_2. (below melting point of metal). (bcoz melted metal becomes more reactive)

→ * Generally used for oxygenated ores
(O_2 prsnt in any form)

→ Carried out in Reverberatory Furnace.

→ Organic & volatile impurities are removed.

→ Impurities of P, S, and Arsenic are removed in elemental state. (melting point low [illegible])

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→ *After calcination, metal oxide become porous ↓ surface area ↑ → Reduction easy.

→ Hydrated ores becomes anhydrous.

$PbCO_3 \xrightarrow{\Delta} PbO + CO_2 \uparrow$

$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2 \uparrow$

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

$Al_2O_3 . xH_2O \xrightarrow{\Delta} Al_2O_3 + xH_2O \uparrow$

(ii) Roasting

→ Heating of ore in the presence of O_2 (below the melting point of metals).

→ Generally used for sulphide ores.

→ Carried out in Reverberatory furnace.

→ Organic & volatile impurities are removed.

→ Impurities of P, S, and As are removed in their oxide forms.

→ After roasting, metal oxide become porous ↓ surface area ↑ → Reduct^n easy.

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$$MS + O_2 \xrightarrow{\Delta} MO + SO_2$$

$$ZnS + O_2 \xrightarrow{\Delta} ZnO + SO_2\uparrow$$
$$FeS_2 + O_2 \xrightarrow{\Delta} FeO + SO_2\uparrow$$

(SO_2) used in contact process. (Formatⁿ of H_2SO_4)

* Partial Roasting (Cu_2S, HgS, PbS)
~~Ro Reductⁿ~~
~~Red~~ Reductⁿ in the absence of solvent is self Redⁿ.

(1) $$Cu_2S + O_2 \xrightarrow{\Delta} Cu_2O + SO_2\uparrow$$
excess limited (Partial Roasting)

$$\overset{+1}{Cu_2}S + Cu_2O \xrightarrow[\text{No air}]{\Delta} \overset{0}{Cu} + SO_2\uparrow$$
(self Reductⁿ)

Cu: 98% pure Blistered copper.

(2) $$Pb_2S + O_2 \xrightarrow{\Delta} Pb_2O + SO_2\uparrow \text{ (P.R)}$$
(limited)

$$Pb_2S + Pb_2O \xrightarrow[\text{No air}]{\Delta} \overset{0}{Pb} + SO_2\uparrow \text{ (S.R)}$$

Step-II Reduction

(i) Carbon Reduction

R.A ⇒ C / CO → good R.A at low temp

$$MO \xrightarrow{(s)C\,/\,CO(g)} M + \underset{(g)}{CO_2}\uparrow$$

C → good R.A at high temp.

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Metals which can be reduced,

Car se Fe Sn Pb Zn
Fisley Sant Prabhu Jan.

(ii) Self Reduction (cinnabar)
Cu_2S, HgS, PbS

(iii) Thermal Reduction
Ag_2S, HgS

$$Ag_2S \xrightarrow{\Delta} \overset{+1}{Ag_2O} \xrightarrow{\Delta} \overset{0}{Ag} + \frac{1}{2}O_2$$

(iv) Alumino Thermite Reduction
→ Gold smith Alumino Thermite Reduction.
→ R.A = Al.
→ Used for : (24) Cr, (25) Mn, ~~Fe~~ (26) Fe

* Ignitor = BaO_2 → used to initiate the rxn.

$$Cr_2O_3 + Al \xrightarrow{\Delta} Cr + Al_2O_3 + Heat$$

*(Highly exothermic)

$$Fe_2O_3 + Al \xrightarrow{\Delta} Fe + Al_2O_3 + Heat$$

* used in welding of railway tracks.

★ M.P of Al_2O_3 = 2200°C (approx.)

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(v) HMR – Hydrometallurgical Reduction.
E.g. (1) Mc. Arthur Forest.

(2)

Low grade Cu ore —Acid / Bacterial Leeching→ Cu^{+2} —Zn→ Rxn ✓ (Unprofitable) as Zn is more expensive as compared to Cu

Bacterial Leeching ↓ organic impurities removed

Cu^{+2} —H_2 or Fe scrape→ Rxn ✓ (Profitable)

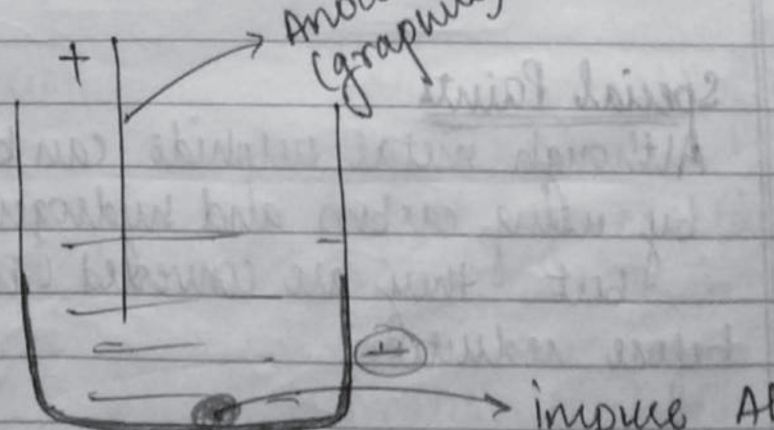
(vi) ~~E~~ Electrolytic Reduction

→ Used for highly reactive metals like s-block and Al.

→ Electrolytic reduction for Al. (Hall Herault process)

→ Molten salt electrolysis (~~aqueous medium~~)

→



Al_2O_3 + Na_3AlF_6 (→ Cryolite) + CaF_2 (→ Fluorspar)

Reduce M.P of Al_2O_3 so that Rxn takes at low temp.

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★ Cryolite } → use:-
Fluorspar } → * M.P of Al_2O_3 ↓
* conductance ↑se

⟹ At Cathode (Reduction)

$$Al^{+3} + e^- \longrightarrow Al$$

⟹ At anode (Oxidation)

$$O^{-2} + C \longrightarrow CO / CO_2 \uparrow$$

(graphite)

→ Anode gets ~~decade~~ decayed due to formation of CO & CO_2, so, it should be changed after regular intervals.

⟹ Tatal Reaction

$$Al_2O_3 + C \longrightarrow Al + CO / CO_2$$

C → graphite
↓
(R.A) ✗✗
(Anode) ✓

Special Paints

→ Although metal sulphide can be reduced directly by using carbon and hydrogen as reducing agent but they are converted into oxide (roasting) before reduction.