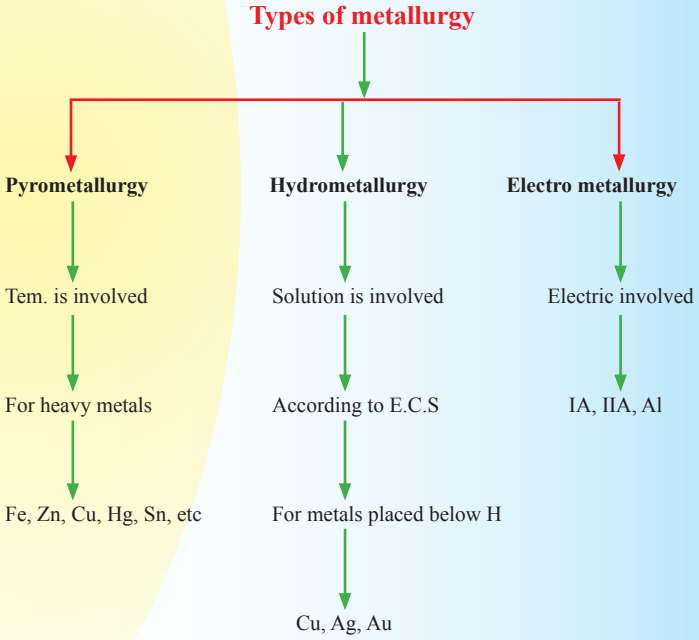
CHAPTER 31

Metallurgy

Bunch of Process to Extract Metal from their Respective Ore

Ore : Minerals from which metal can be extracted economically :



Metallurgical process :

1. **Mining :** Ore obtain in big lumps (less reactive)
2. **Crushing/grinding/pulverization :** big lumps convert into powder (more reactive)
3. **Concentration :** To remove matrix/gangue from ore
   To increase the concentration of ore particle in ore sample.

Concentration

- **(I) Physical process**
  - (a) Gravity separation/Hydrolic washing/Levigation
    - Based on diff. in sp. gravity
      - for oxides/ carbonates ore
  - (b) Magnetic separation
    - Based on diff. in mag. properties
      - Used to separate s & p block compound from transitional elements compounds
  - (c) Froath floatation
    - Based on diff. in wetting properties
      - Sulphide ores
        - Frother - Pine oil Collector - Sodium ethyl xanthate depressant - NaCN
        - Stablizer : Cresol or Aniline Derivative
- **(II) Chemical/leaching**
  - for Al Ag, Cu
    - Dissolve insuitable solvent in white metallic ore is soluble & impurity Insolution

Ag, Au, are concentrated by cyanide process.

Calcination & Roasting

- **(I) Calcination**
  - In absence of air
    - for Oxide / Oxysalt ore
      - CO_2 & H_2O are to be removed
        - $MCO_3 \rightarrow MO + CO_2\uparrow$
        - $M(OH)_2 \rightarrow MO + H_2O\uparrow$
- **(II) Roasting**
  - In presence of air
    - for sulphide ore
      - Impurity of S, P, As, is removed in the form of volatile oxide
      - Impurity of S, P, As, is removed in the form of volatile oxide
        - $MS + O_2 \rightarrow MO + SO_2\uparrow$

Reduction : To obtains metal (95 to 98%) from metal oxide.

Self reduction

- Sulphide ore itself act as reducing agent.

  eg. $PbS + 2PbO \xrightarrow{\Delta} 2Pb + SO_2$
- Thermal decomposition

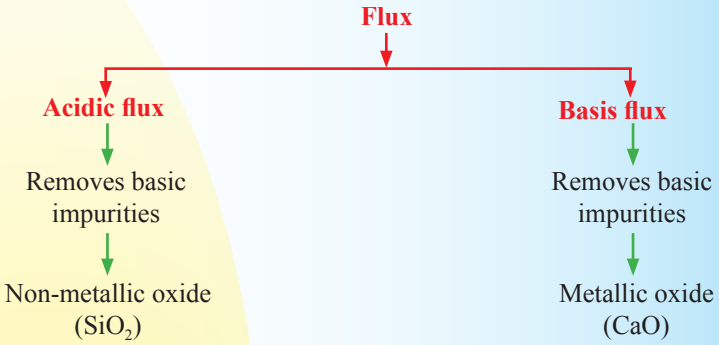
  eg. $HgO \xrightarrow{\Delta} Hg + \frac{1}{2}O_2$

Carbon reduction (Smelting) : Reducing agent C/CO

- eg. $Fe_2O_3 + 3CO \xrightarrow{250^\circ - 700^\circ C} 2Fe + 3CO_2$

$ZnO + C \xrightarrow{\approx 1200^\circ C} Zn + CO$

Flux - substance to convert non-fusible impurities to fusible one.



Imp. point – Above 710° C is reducing agent.
– Below 710°C CO is better reducing agent.

Aluminum reduction method : (Thermite process)

- Al act as reducing agent

eg. $Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr$

Thermite mixture mass ratio : $Cr_2O_3 : Al = 3 : 1$

METAL DISPLACEMENT REDUCTION

- Metal placed below H. in E.C.S.
- Ag, Au, Cu

Example of extraction of

(i) Cynidation (Leaching Process)

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

$Au + 2KCN + H_2O \longrightarrow K[Au(CN)_2]$

(ii) Recovery of Ag/Au (Metal displacement Reactions)

$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN_4)] + 2Ag \downarrow$

$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN_4)] + 2Au \downarrow$

ELECTROLYTIC REDUCTION

- For IA, IIA, Al
- Electolysis of molten solution

Example :-

(i) Extraction of Al(Hall-Herault)

– Al can be extracted from Al_2O_3

– To decrease fusion temp. of Al_2O_3, Na_3AlF_6 & CaF_2 is to added as auxilary electrolytes.

–Na_3AlF_6 & CaF_2 increase the conductivity & reduce the fusion temp.

(ii) At cathode impure Al is collected and at anode O_2, CO, CO_2 is released.

(iii) Extraction of Na (Down cell process)

– Na can be extracted from NaCl

– Down Process Neutral flux ($CaCl_2$) to be added to decrease the fusion temp. of NaCl

– Neutral flux - substance used to increase the conductivity of NaCl

Auxilary Electrolyte – decrease the fusion temp. of ionic compounds of (IA, IIA, Al) which is more than the melting point of metal.

To obtain metal (99.98%)

Refining / Physical Process

- (a) Liquation (Sn, Pb, Bi, Sb) → Low M.P. metal
- (b) Distillation (Zn, Cd, Hg) → Low M.P. metal → Volatile metal
- (c) Zone refining/Fractional crystallization (Ge, Ga, Si, Tl, B) → Ultrapure metal → Volatile metal

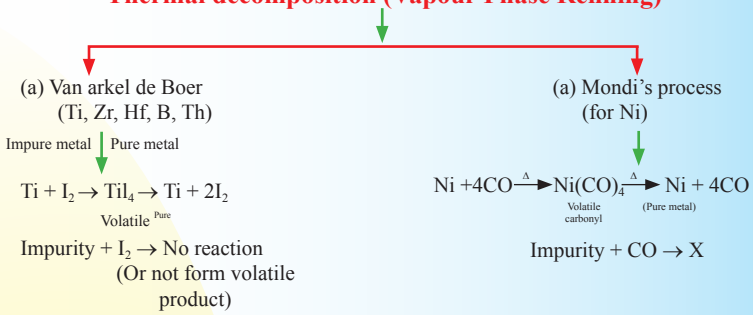
Chemical Process

- (a) Cupellation → For Ag or Au having the impurity of Pb → Δ → $Ag + PbO\uparrow$
- (b) Polling → CuSn, Pb having the impurity of their own oxide → Scum is form at the surface
- (c) Bessemerization → * For Cu

* In Cu metallurgy it is not purification method.

* It is used to manufacture steel from cast iron.

Thermal decomposition (Vapour Phase Refining)



(I) Electrolytic refining

Anode–made up of impure metal

Cathode–pure metal

impurity deposited below anode as anode mud or goes to electrolytic solution pure metal deposited at cathod.

THERMODYNAMICS PRINCIPLE OF METALLURGY

- The graphical representation of Gibbs energy was first used by H.I.T. Ellingham. This provide a sound basis for considering the choice of reducing agent in the reduction of oxides. this is known as Ellingham diagram such diagram help us in predicting the feasibility of thermal reduction of an ore.
- The Criteria of feasibility is that at a given temperatue. Gibbs energy of reaction must be negative.
- At high temperature 'C' is the best reducing agent.
- At low temperature 'CO' is the best redusing agent.
- In blast fornace reduction takes plae at low temperature i.e. why CO is the reducing agent (For Fe).

A summary of the occurence and Extraction of some Metals is presented in the following table:

Metal	Occurrence	Common method of extraction	Reffining	Remarks
Aluminium $E^o = -1.66$	1. Bauxite, $Al_2O_3.xH_2O$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten $Na_3AlF_6 + CaF_2$	Electrolytic refining by Hoop's cell	For the extraction, a good source of electricity is required

Metal	Occurrence	Common method of extraction	Reffining	Remarks
Iron $E^o = -0.44$	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4 3. Limonite, $Fe_2O_3.3H_2O$ 4. Siderite, $FeCO_3$	Reduction of the oxide with CO and coke in Blast furnace	Bessemerization (impurites has more affinity for O_2 as compare to Fe)	Temperature approaching 2170K is required
Copper $E^o = -0.34$	1. Copper pyrites, $CuFeS_2$ 2. Copper glance, Cu_2S 3. Malachite, $CuCO_3.Cu(OH)_2$ 4. Cuprite, Cu_2O 5. Azurite, $2CuCO_3.Cu(OH)_2$	Roasting of sulphide partially and reduction	(i) Polling (ii) Electrolytic method	It is self reduction in a specially designed converted. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc $E^o = -0.76$	1. Zinc blende or Sphalerite, ZnS 2. Calamine, $ZnCO_3$ 3. Zincite, ZnO	Roasting of sulphide ore or calcination of $ZnCO_3$ followed by reduction with coke	The metal may be purifed by fractional distillation	For ZnO, carbon is better reducing agent then CO and Zn is obtain is vapours form $ZnO + C \xrightarrow{1673K} Zn + CO$
Mg $E^o = -2.36$	1. Carnallite, $KCl.MgCl_2.6H_2O$ 2. Magnesite, $MgCO_3$	Electrolysis of fused $MgCl_2$ with KCl		$MgCl_2.6H_2O$ is heated in the excess current of dry HCl gas to produce anhydrous $MgCl_2$
Sn $E^o = -0.14$	1. Cassiterite, SnO_2 (Tin stone)	Reduction of the SnO_2 with carbon. $SnO_2 + 2C \rightarrow Sn + 2CO$	Polling and Liquidation	Ore contain impurity of wolframite, $FeWO_4 + MnWO_4$ (magnetic sepration)

Metal	Occurrence	Common method of extraction	Reffining	Remarks
Pb $E^o = -0.13$	1. Galena, Pbs	Roasting, then self reduction or Reduction of PbO (Roasted ore) with carbon $PbS+2PbO \rightarrow 3Pb+SO_2$ $PbO+C \rightarrow Pb+CO$	Liquadation & electrolytic method.	
Ag $E^o = 0.80$	1. Argentite- Ag_2S, native Silver	Hydro metallurgy $Ag_2S + 4NaCN$ $2NaAg(CN)_2 + N_2S$ $2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$	Cupelation & electrolytic method	In hydro mettallurgy Ag obtain in the form of dark amorphous ppt.
Au $E^o = 1.40$	Native ore	1. Amalgamation. 2. Cynide process	Cupelation & electrolysis method.	In hydro mettallurgy Au obtain in the form of dark amorphous ppt.