GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

INTRODUCTION OF METALLURGY

❖ **METALLURGY**

INTRODUCTION

◆ **Metallurgy**

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

◆ **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 of compounds having fixed chemical composition.

◆ **Ore**

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

◆ **Gangue or Matrix**

The undesirable impurities present in an ore are called gangue.

◆ **Mining Process**

Process of taking out ore from earth crust is called mining.

TYPES OF METALLURGY

(a) Pyro Metallurgy: Extraction of metal from ore by using heat energy.

Steps involved are: Calcination, roasting, reduction etc.

Ex. Less reactive metals: Cu, Fe, CO, Ni, Zn, Sn, Pb etc.

(b) Hydro Metallurgy: (Ag, Au, Cu) – This is wet metallurgy process.

$$Cu \longrightarrow Pyro + Hydro$$

$$Ag \text{ and } Au \longrightarrow \text{By cynide process.}$$

Steps are:

(i) Complex formation

(ii) Metal displacement

(i) $AgCl \text{ or } AuCl \xrightarrow{Na\ CN} Na[Ag(CN)_2]$

(Sodium argento cynide)

(ii) $2Na\,[Ag(CN)_2] \xrightarrow{Zn} Ag\downarrow + Na_2\,[Zn(CN)_4]$

(Impure)

(c) **Electrical Metallurgy:** This process used for highly electro positive metal (s-block and Aℓ) metal obtained by electrolysis of fused salt/anhydrous medium.

(d) **Ion Exchange Metallurgy:** Trans-Uranic (elements after Uranium in periodic table) elements are obtained by this method.

❖ **STEPS INVOLVED IN THE EXTRACTION OF METALS**

The extraction of a metal from its ore is completed in the following four steps.

(a) Crushing and grinding (b) Pulverization

(c) Concentration of the ore (d) Reduction to the metal

(e) Refining of the metal.

CONCENTRATION OF THE ORE

The removal of impurities from the ore is called its concentration. It is carried out in one or more of the following steps. These undesired impurities are gangue or matrix.

BY PHYSICALS SEPARATION

(a) Gravity Separation (Lavigation)

This method of concentration of the ore is based on the difference in the specific lavigation 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 Ores.

(b) 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.

(i) Frothers

They generate a stable froth which rises to the top of the tank. Example of frothier is pine oil, Eucalyptus oil, etc.

(ii) Collectors or Floating Agents

These attach themselves by polar group to the grains of the ores which then become water repellant and pass on into the froth. Example: sodium ethyl /ethyl xanthate.

(iii) Activators or Depressants

These reagents activate or depress the flotation properly and help in the separation of different sulphide ores present in a mixture.

An example of depressant is NaCN. An activator is $CuSO_4$.

(c) Magnetic Separation

If the ore and not the gangue or the gangue and not the ore is attracted by a magnet, the two can be separated by this method.

Magnetite (Fe_3O_4) is concentrated by this method,($FeWO_4$) wolframite removed from SnO_2, FeO removed from chromite ($FeCr_2O_4 \Rightarrow Cr_2O_3 \cdot FeO$).

❖ **BY CHEMICAL SEPARATION**

Some of the ores are concentrated by means of chemical treatment.

◆ **Leaching:** It involves the treatment of the ore with a suitable reagent. as to make it soluble while impurity remain insoluble. The ore is recovered from the solution by suitable chemical method.

(i) Bayer's Process

Ex. Bauxite ore contain impurity Fe_2O_3, TiO_2, SiO_2 when it dissolves in aq. NaOH/pressure + 150°C T bauxite is dissolved but other are not dissolve.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

$$\downarrow \Delta$$

$$Al_2O_3 + 3H_2O$$

(ii) Cyanide Process : Their process used for Au, Ag by

(Mac-Arthur forrest cyanide process).

◆ **CALCINATION**

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

For Example

(i) $Al_2O_3.2H_2O \longrightarrow Al_2O_3 + 2H_2O,\ 2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

(ii) $2Fe_2O_3.3H_2O \longrightarrow 2Fe_2O_3 + 3H_2O$

(iii) $CaCO_3 \longrightarrow CaO + CO_2$

(iv) $CaCO_3.MgCO_3 \longrightarrow CaO + MgO + 2CO_2\uparrow$

(v) $MgCO_3 \longrightarrow MgO + CO_2\uparrow$

(vi) $ZnCO_3 \longrightarrow ZnO + CO_2\uparrow$

(vii) $FeCO_3 \longrightarrow FeO + CO_2\uparrow$

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 metal become porous and easily workable

◆ ROASTING

$$(\text{Metal sulphides} \longrightarrow \text{Metal oxide} + SO_2)$$

The removal of the excess sulphur contained in sulphide ores by heating in an excess of air is called roasting.

The concentrated sulphide ore is heated in reverberatory furnace, below its melting point or fusion temperature in the presence of an excess of air with or without the addition of an external substance.

In roasting definite chemical like oxidation, chlorination etc. take place but in calcination does not occur any major chemical changes.

(i) $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

(ii) $ZnS + 2O_2 \longrightarrow ZnSO_4$

(iii) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + SO_2\uparrow$

(iv) $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

(v) $HgS + O_2 \longrightarrow HgO + SO_2$

(vi) $2As_2S_3 + 9O_2 \longrightarrow 2As_2O_3 + 6SO_2$

Advantages of Roasting

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

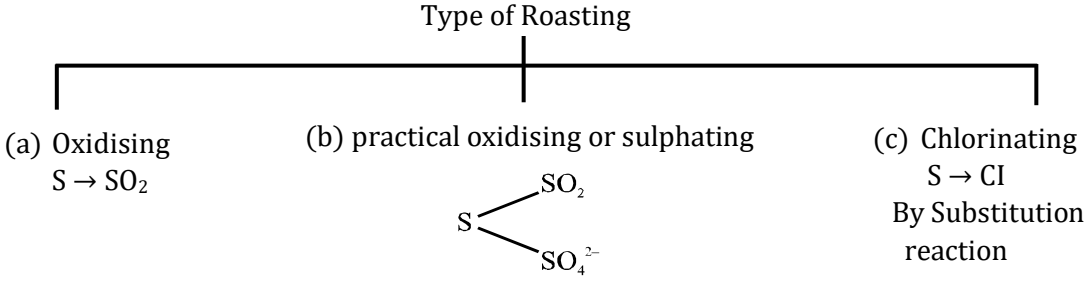
$$S + O_2 \rightarrow SO_2\uparrow$$

(air)

(ii) The metal sulphide is converted into metal oxide.

(iii) Impurities of arsenic and antimony are removed as their volatile oxides.

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



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

In practical roasting process: In PbS or ZnS

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$PbS + 2O_2 \longrightarrow PbSO_4$$

Reduction of Ore to the Metal

The calcined or roasted ore is then reduced to the metallic state in either of the following ways.

(a) **Reduction by Carbon (Smelting):** (This is common method of reduction)

"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 by strongly heating them with coal or coke, in the blast furnace.

Slag: Fusible metarial during reduction process.

Slag: Gangue + substance (for remove gangue)

Fluxes: Substance used for removing gangue

Fluxes acidic: Borax, SiO_2 (remove basic impurity)

Fluxes basic: MgO, $MgCO_3$, $CaCO_3$ (remove acidic impurity)

Smelting

- Concentrate ore(ore +gangue)+ RA (carbon) + Flux(RA $\Rightarrow$ Reducing agent)

$$\downarrow$$

Metal + Slag + gases

Cr_2O_3, Mn_3O_4, MnO_2 $\longrightarrow$ Carbon is not used for reduction

- Coke is not used for reduction of s-block oxide Al_2O_3 (due to formation of metal carbides)

$$CaO + 2C \longrightarrow CaC_2 + CO$$

Some reactions

(i) $CuO + CO \longrightarrow CO_2 + Cu$

$PbO + C \longrightarrow Pb + CO$

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

$ZnO + C \longrightarrow Zn + CO$

$ZnO + CO \longrightarrow Zn + CO_2$

(ii) (gangue) acidic impurity (flux) (slag)

$SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2 \uparrow$

$P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2$

(iii) Basic impurity + Flux $\longrightarrow$ slag

$MgCO_3 + SiO_2 \longrightarrow MgSiO_3 + CO_2 \uparrow$

$FeO + SiO_2 \longrightarrow FeSiO_3$

Note: – Blue flame is obtained by burning of CO in smelting process.

(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.

Self-Reduction for Pb

(i) $2PbS + 3O_2 \xrightarrow{\text{ROASTING}} 2PbO + 2SO_2 \uparrow$

(Galena) (air)

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

(unroasted ore) (roasted ore) (Self reduction)

(ii) $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6\,Cu + SO_2$

(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.

(i) Ziervogel process for silver.

$$Ag_2S + 2O_2 \xrightarrow{85^\circ C} Ag_2SO_4$$

Argentite

$$Ag_2SO_4\,(aq) + Cu \rightarrow CuSO_4\,(aq) + 2Ag\,(S)$$

(Scrap Copper)

(ii) Separation Ag by Complex formation (Cyanide process)

Silver and gold are extracted by a method involving complex formation.

$$Ag_2S + 4NaCN \xrightarrow{air} 2Na\,[Ag(CN)_2] + Na_2SO_4$$

(Powdered argentite)

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

Black ppt.

(d) Electrolytic Reduction

This process is mainly used for the extraction of highly electropositive metals. 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 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 electrolyzed between graphite anode and iron cathode. The various reactions that take place are

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

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

(Metallic sodium)

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

(e) Reduction by Al

This process is employed in the case of those metals which have very high melting points and are to be extracted from their oxides

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

$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$$