B. INORGANIC CHEMISTRY

Chapter-7 Metallurgy

⇒ **Mineral**: The natural material in which the metal or their compounds occur in the earth's crust is known as mineral.
Example: Bauxite ($Al_2O_3 \cdot 2H_2O$) and Kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) are the minerals of Aluminium.

⇒ **Ores**: Ores are the minerals from which the concerned metals can be extracted conveniently and profitably.
Example: Both Bauxite and Kaolin are the minerals of "Al". However, "Al" can be extracted easily and profitably from Bauxite. Thus, Bauxite is an ore of "Al". On the other hand, it is difficult and non-profitable to extract "Al" from Kaolin, thus Kaolin is only a mineral of "Al".
N.B: All Ores are minerals, but all minerals are not ores.

⇒ **Difference between Minerals and Ores:**

Minerals	Ores
1. The combined state occurrences of metals are called Minerals and extraction of metals from minerals is difficult and non-profitable.	These are the minerals from which the concerned metals can be extracted easily and economically.
2. Minerals contain low percentage of metals and high percentage of impurities.	Ores contain high percentage of metals but low percentage of impurities.
3. All minerals are not ores.	All ores are minerals.
Example: Kaolin and Bauxite are the minerals of Aluminium.	Example: Only Bauxite is the ore of Aluminium between them.

⇒ **Gangue**:- The ores and even the native metals usually contain worthless material (clay, sand, limestone etc.) called Matrix or Gangue.
It is therefore, very essential to eliminate the gangue before the actual process for the extraction of a metal is taken. These processes are known as Mineral beneficiation.

* **Flux**: The substance which combines with gangue to form light and easily fusible material is called Flux.

* **Slag**: The easily fusible material which is not soluble in the molten metal is called slag. Being lighter, the slag can be easily removed from the surface of the fused metal. The type of flux to be used depends upon the nature of the impurities present in the ore. That means, when the impurities are acidic, basic flux are used and vice-versa.

⇒ **Metallurgy** :- The art of extraction of metals from ores conveniently and economically is called metallurgy or metallurgical operation.

The following steps are followed during the process of metallurgical operation;
1. Crushing and Grinding
2. Concentration or Ore dressing
3. Oxidation.
4. Reduction
5. Refining

1. Crushing and Grinding :-

Most of the ores obtained from mines are in the form of huge lumps or solid rocks. It is difficult to treat the ores in this form. Therefore, these are first crushed into small pieces with the help of jaw crusher and grinded into their powder form with the help of stamp mill or ball mill. The powdered form of ore is called pulverized ore.

2. Concentration or Ore dressing :-

The process of removal of maximum impurities (gangue or matrix) from the powdered ore is called concentration of ore. The method of concentration to be followed depends upon the nature of the impurities present. Following are the different methods of concentration:

(i) Gravity separation Method :-

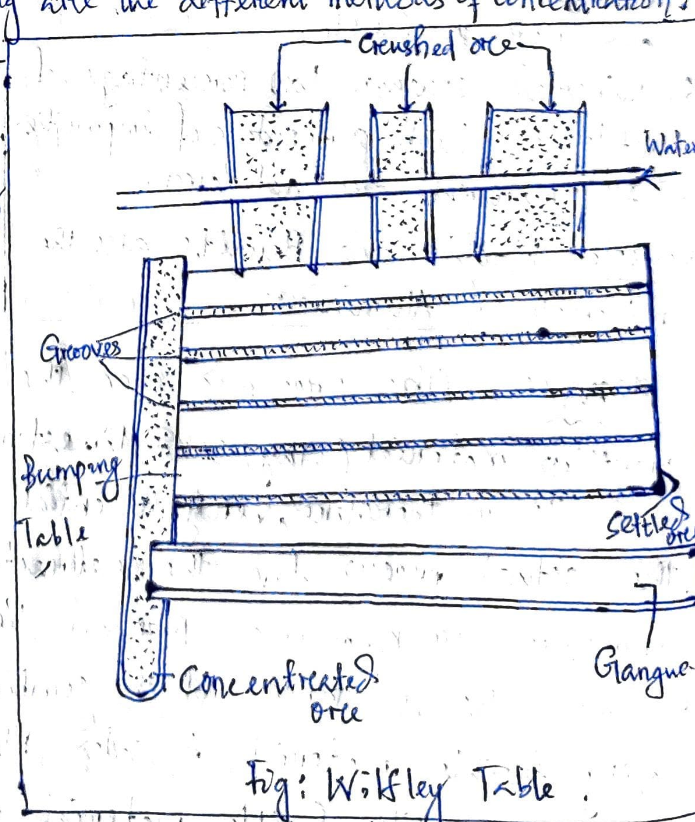

Fig: Wilfley Table.

This method of concentration is adopted only when there is a gravity difference between the ore and impurities. Normally, Carbonate and oxide ores are heavier than the impurities associated with them and hence they are concentrated by this method. In this method, the powdered ores are kept in some containers over a specially designed table called Wilfley Table (fig).

The table contains a no. of horizontal grooves. The table is kept slightly inclined in position and is provided with a rocking motion. When water is spread over the ore, lighter impurities are washed away while heavier ore particles get deposited in the grooves, which are finally carried out into the main canal.

(ii) Froth Flotation Method

This method is suitable for the concentration of Sulphide Ores only. In this method, two interconnected tanks are used. In one of the tanks, a mixture of ore, oil (Pine oil), water and a little quantity of mineral acid is agitated strongly by blowing air through it. Due to the preferential wetting of the sulphide ores by oil than by water, a layer of oil gets covered over the surface of sulphide ores. These sulphide ores become lighter and float over the surface of the mixture, which are carried out into the second container along with the foam formed due to agitation.

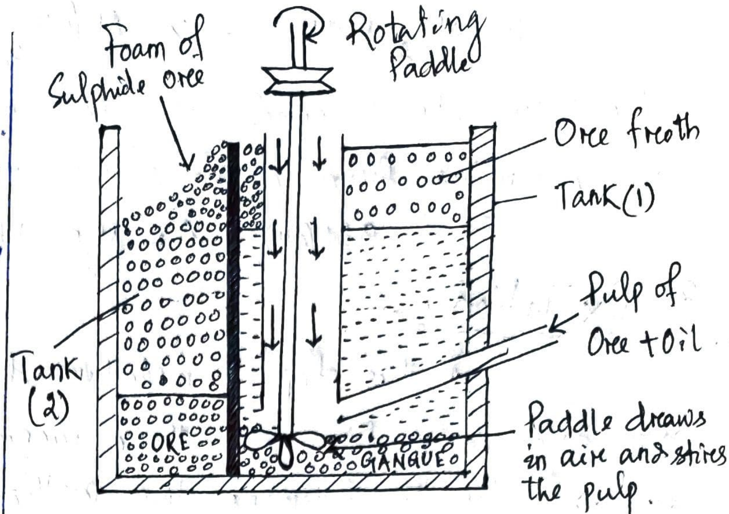

Fig: Froth floation Process.

(iii) Magnetic Separation Method :-

This method of concentration is suitable when there is a difference in the magnetic behaviour between the ores and the impurities. Normally, the magnetic ores containing non-magnetic impurities are concentrated by this method. In this method, a belt is tied over two rollers of which one is made of a magnet. Powdered ore is added over the belt through a hopper. The magnetic part of the ore is attracted by the magnetic roller and forms a heap near it. whereas the nonmagnetic part of the ore forms a separate heap a little away from the magnetic part.

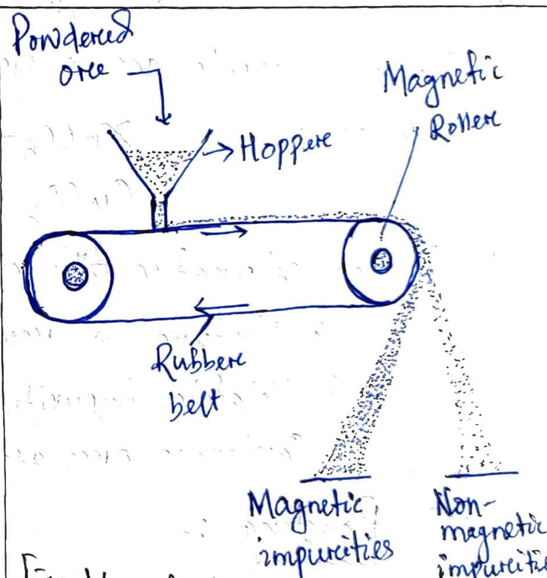

Fig: Magnetic separation Process.

(iv) Leaching :-

This is a chemical method in which the impure ore is treated with a suitable solvent which dissolves the ore leaving behind the impurities. The solution is filtered, impurities are removed, and the mother liquor is treated with another suitable chemical reagent to get the pure ore.

For example: Impure bauxite ore is treated with dil. NaOH solution which dissolves Bauxite to form soluble sodium meta-aluminate.

$$Al_2O_3 \cdot 2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$$

The solution is filtered to remove the impurities. The solution obtained is diluted with plenty of distilled water when a precipitate of $Al(OH)_3$ is formed

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

The precipitate obtained is dried and heated strongly to get pure alumina from which aluminium is extracted.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

3. **Oxidation :-**

In this step of metallurgical operation, the concentrated ores are converted into their respective metal oxides. This is achieved by the following two methods :

(i) **Calcination :-**

* The process of heating an ore strongly below its melting point in the absence of air or, in the limited supply of air is called Calcination.
* This method is employed for carbonate ores and hydrated ores.
* Carbon dioxide gas is produced along with metal oxides.

Examples :

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
$$CuCO_3 \longrightarrow CuO + CO_2$$

* During calcination following changes take place :
  - (a) Moisture is removed : $Fe_2O_3 \cdot 2H_2O \xrightarrow{\Delta} Fe_2O_3 + 2H_2O$
  - (b) Volatile impurities are removed : S, P etc. are removed as vapours.
  - (c) Carbonate ores get converted into oxides : $FeCO_3 \longrightarrow FeO + CO_2 \uparrow$

(ii) **Roasting :-**

* The process of heating an ore strongly below its melting point in a free but controlled supply of air is called Roasting.
* This method is employed for sulphide ores.
* Sulphur dioxide gas is produced along with metal oxides.

Examples :

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

* The changes takes place during roasting are :
  - (a) Moisture is removed.
  - (b) Volatile impurities are removed.
  - (c) Impurities like Sulphur, Arsenic, Phosphorous etc. are removed in the form of their gaseous oxides :

$$S + O_2 \rightarrow SO_2$$

$$P_4 + 5O_2 \rightarrow 2P_2O_5$$

$$4As + 3O_2 \rightarrow 2As_2O_3$$

(d) It makes the ore porous.

(e) The process of roasting is carried out in a reverberatory furnace.

4. Reduction :-

In this step of metallurgical operation, the roasted ores are reduced to convert the metal oxides into the respective metals. The various methods of reduction are :

(i) Smelting :-

The process of heating a roasted ore strongly above its melting point with a suitable quantity of coke or charcoal is called smelting. During the process of smelting, metal oxides are reduced into their respective metals. For the reduction of the oxides of less electropositive metals such as Zn, Fe, Cu, Cr etc., the reducing agents like CO, Na, K, H_2O etc. are used.

Examples : $PbO + C \rightarrow Pb + CO$

$CuO + CO \rightarrow Cu + CO_2$

During the process of smelting, an additional chemical substances called "flux" is added which combines with the solid impurities to form "fusible slag".

Impurity + Flux → Slag.

Flux: A substance added during the process of smelting to convert the solid gangue into fusible mass (slag) is called flux.

The nature of the flux to be added depends upon the nature of the impurity present. For acidic impurities basic flux are used and for basic impurities acidic flux are used.

⇒ **Acidic flux:** It is used to remove basic impurities such as metallic oxides. Example : $FeO + SiO_2 \rightarrow FeSiO_3$

Impurity (Basic) flux (Acidic) (Slag)

⇒ **Basic flux:** It is used to remove acidic impurity such as sand.

$$\underset{\text{Impurity (Acidic)}}{SiO_2} + \underset{\text{flux (Basic)}}{CaO} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

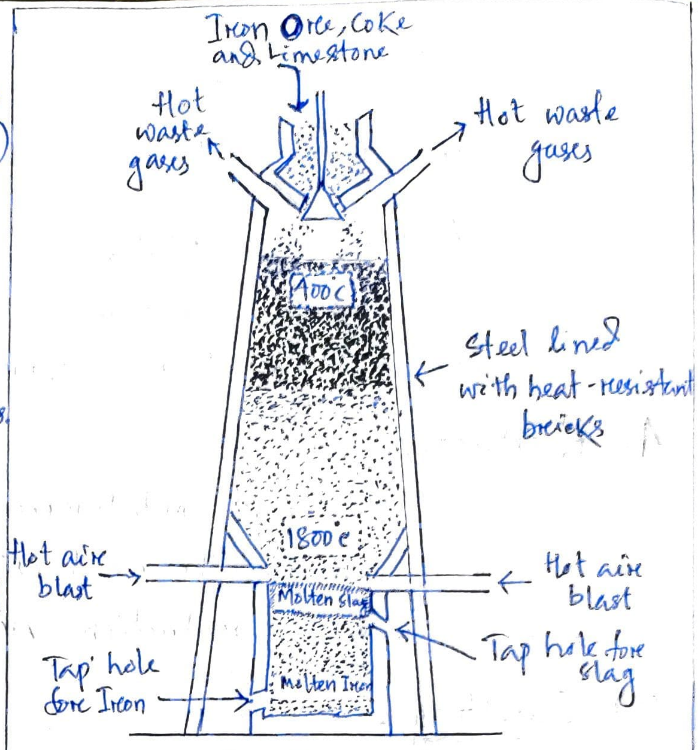

Fig: Blast Furnace

Slag: It is the fusible mass obtained during the process of smelting when flux combines with the solid impurities.

Example: $SiO_2 + CaO \rightarrow CaSiO_3$.

Smelting is carried out in a blast furnace (fig) which is a tall cylindrical furnace made of steel plates lined inside with fire bricks. Since the density of slag is lower, it floats over the molten metal. The molten metal is tapped out at the bottom of the furnace.

5. Refining :-

The metals obtained after reduction still contain some impurities. The process of removal of impurities from crude metal is called refining. The method of refining to be followed depends upon the nature of the metal and the impurity contaminated with it. The following are the methods of refining.

(i) **Distillation Method** :- This method of refining is suitable for volatile metals like Hg, Zn, Pb contaminated with non-volatile impurities. The impure metal is heated in a distillation flask attached with a water condenser. During heating the volatile metal gets evaporated and condensed which is collected in a separate container while the non-volatile impurities are left at the bottom of the distillation flask.

(ii) **Electro refining** :-

This method is employed to refine the less electropositive metals such as Zn, Pb, Cu, Al. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode (Fig). Both the electrodes are dipped in a suitable aqueous salt solution of the concerned metal. During the process of electrolysis the impure metal dissolves in its aqueous salt solution providing metal ions which get discharged and deposited at the cathode.

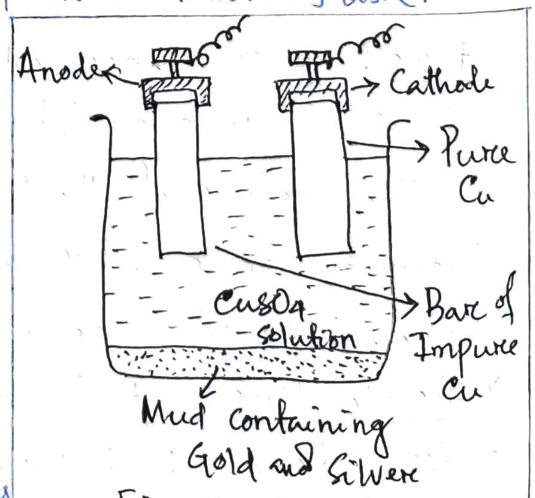

Fig: Electrorefining