METALLURGY

Metals are present in nature as
1. Native 2. Combined state

1. **Native** :- A few metals which are found in nature in the free or elemental condition are called Native. Ex: Ag, Au, Pt etc.

2. **Combined state** :-

(i) As oxides. Cu, Zn, Al, Sn, Fe and Mn
(ii) As sulphides. Cu, Zn, Ag, Pb, Fe, Hg, As, Sb and Cd
(iii) As Carbonates. Cu, Zn, Pb, Fe, Ca, Ba, Sr, Na, Mg
(iv) As halides.
  (a) As Chlorides : Ag, Na, K, Mg
  (b) As Fluorides : Al, Na, Ca
(v) As Sulphates. Ba, Sr, Ca, and Pb
(vi) As Nitrates. Na and K
(vii) As Phosphates. Ca
(viii) As Silicates. Al, Mg, Ca, Na, K

→ The combined state of metals are found as minerals and ores.

Minerals: The natural materials in which the metals or their compounds are found in the earth's crust are called minerals. They also contain impurities like sand. Ex: Cu_2S, Cu_2O and $CuFeS_2$ are minerals of copper.

Some minerals contain large percentage of the metal while others contain only a small percentage of metal.

Thus all the minerals can not be used for the extraction of metals.

Ores:- The minerals from which the metal can be extracted economically, conveniently and profitably are called ores.

An ore contains high percentage of metal and is free from objectionable impurities.

All the ores are minerals but all the minerals are not ores.

Ex:- Hematite (Fe_2O_3) and Iron pyrites (FeS_2) are minerals of iron. Hematite contains higher percentage of iron, whereas Iron pyrite contains lower percentage of iron and is associated with objectionable impurities like Sulphur, Phosphorus. Hence, Iron pyrite is not used for the extraction of iron. Thus, Iron pyrite is not an ore of iron.

Chief ore of some metals are given in the table.

Metals	Chief Ores
Iron (Fe)	Hematite (Fe_2O_3), Magnetite (Fe_3O_4)
Aluminium (Al)	Bauxite ($Al_2O_3 \cdot 2H_2O$) Corundum (Al_2O_3)
Copper (Cu)	Cuprite (Cu_2O), Copper Pyrite ($CuFeS_2$)
Manganese (Mn)	Pyrolusite (MnO_2)
Calcium (Ca)	Calcite ($CaCO_3$), Limestone, ($CaCO_3$), Gypsum ($CaSO_4 \cdot 2H_2O$)

Metals	Chief Ores
Magnesium (Mg)	Magnesite ($MgCO_3$), Dolomite ($CaCO_3 \cdot MgCO_3$)
	Carnalite ($KCl \cdot MgCl_2 \cdot 6H_2O$)
Zinc (Zn)	Zinc Blende (ZnS), Zincite (ZnO)
Lead (Pb)	Galena (PbS), Cerrusite ($PbCO_3$)
Mercury (Hg)	Cinnabar (HgS)
Tin (Sn)	Tin stone (SnO_2)
Chromium (Cr)	Chromite ($FeCr_2O_4$ or $FeO \cdot Cr_2O_3$)

Extraction of Metals or Metallurgy

→ The art of extracting of metal from its ores is called Metallurgy.

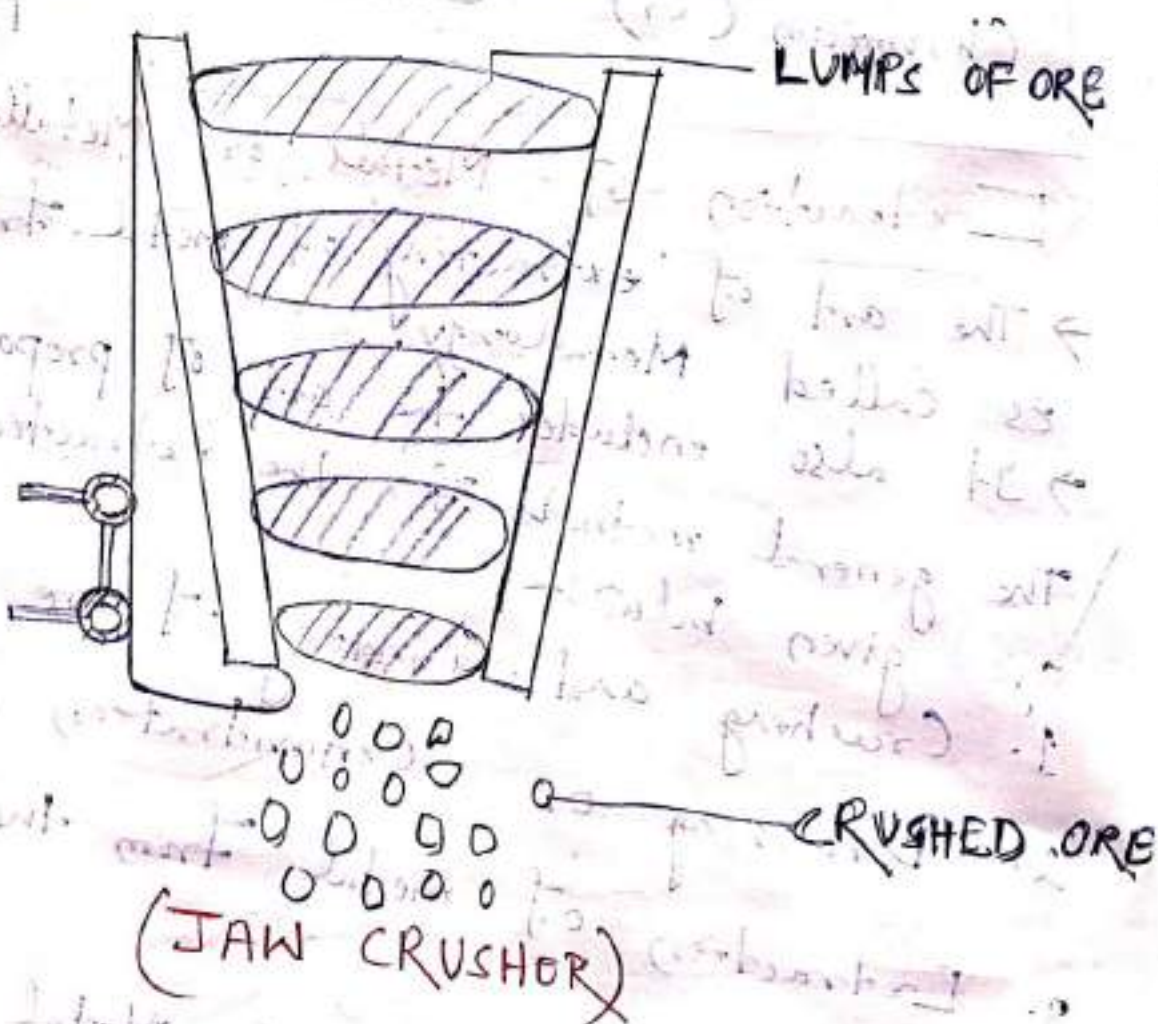
→ It also includes the art of preparing alloys.

The general methods for the extraction of metal are given below:-

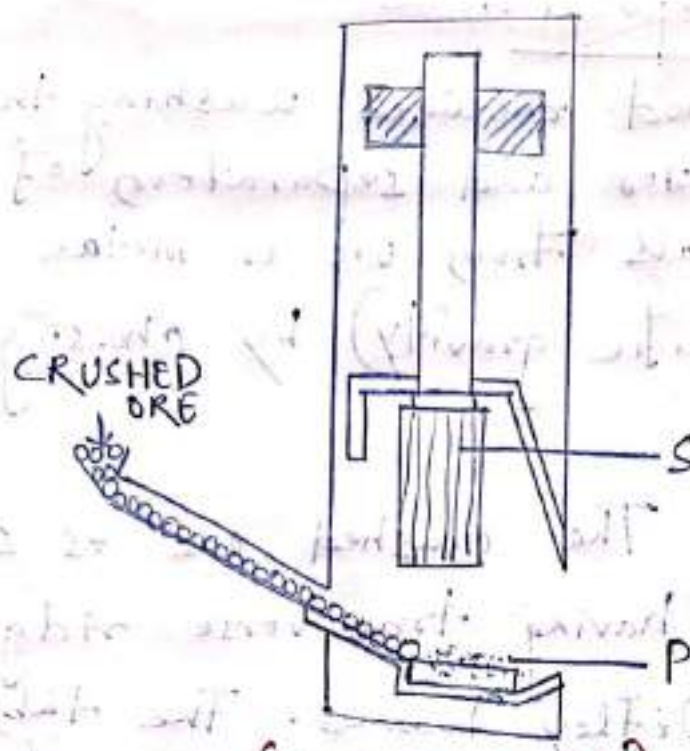
1. Crushing and Grinding of Ore
2. Dressing or Concentration of the ore
3. Extraction of metal from the concentrated Ore
4. Refining of the Crude Metal

1. Crushing and Grinding of Ore :-

Most of the ores are found in the form of huge lumps and it is difficult to treat the ores in this form. Therefore, it is converted into powder form to make the extraction process convenient. The huge lumps of ores are broken into smaller pieces with the help of jaw crushers. Then the small pieces of ores are converted into a fine powder with the help of stamp mill or ball mill. This process is called Pulverisation of the Ore.



(JAW CRUSHER)



(STAMP MILL)

2. Dressing or Concentration of the Ore:—

→ Concentration is the process of removing maximum gangue from the ore.

(The impurity present in the ore is called gangue.)

The following methods are used for the concentration of the ore.

(a) Gravity Separation

(b) Froth Floatation

(c) Magnetic Separation

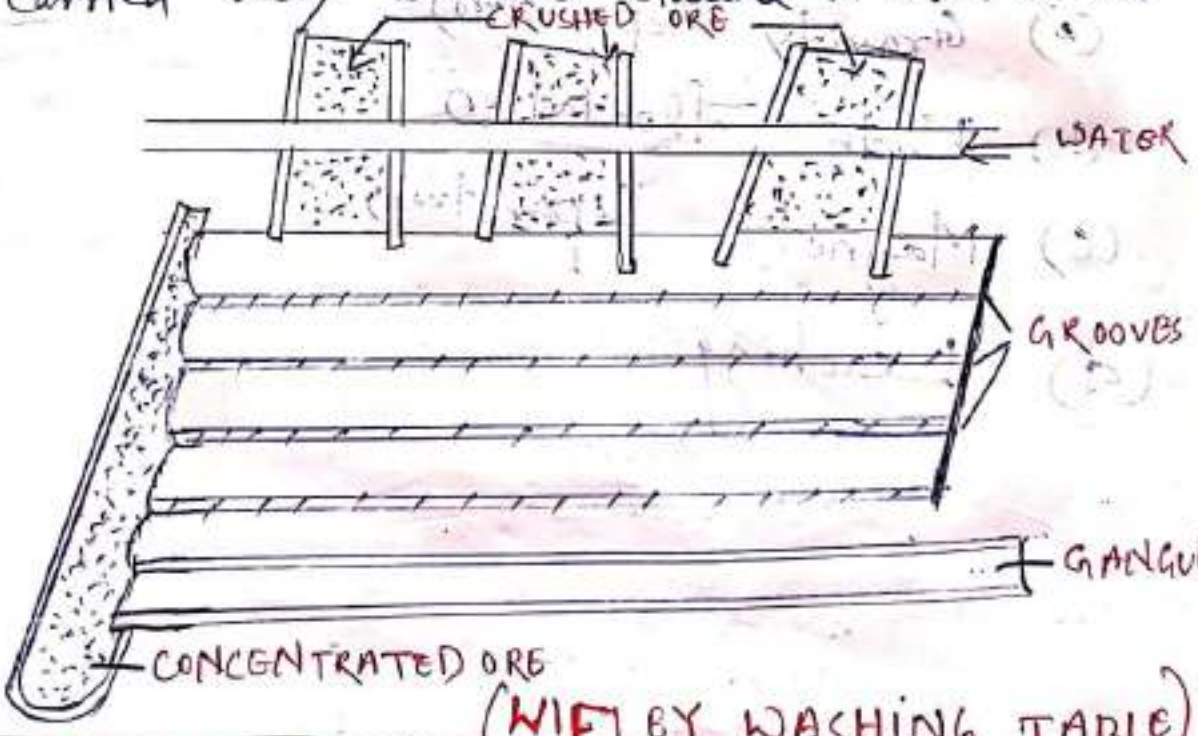
(d) Leaching

(a) Gravity Separation:—

This method includes washing the crushed ore with water and separation of less dense gangue materials from ore or metal with high density (specific gravity) by choosing a suitable medium.

Procedure:— The crushed ore is spread on long tables having transverse ridges, which is called Wifley Tables. The tables are given rocking motion and stream of water is flown over the crushed ore. The gangue material being lighter is carried away with with water whereas the ore is detained by the ridges.

Ex:- Galena (PbS) is concentrated by this process which contains Lime stone as the impurity. When a stream of water is flown over the crushed ore, the less dense Limestone is carried away whereas Galena is left behind.



(WIFLEY WASHING TABLE)

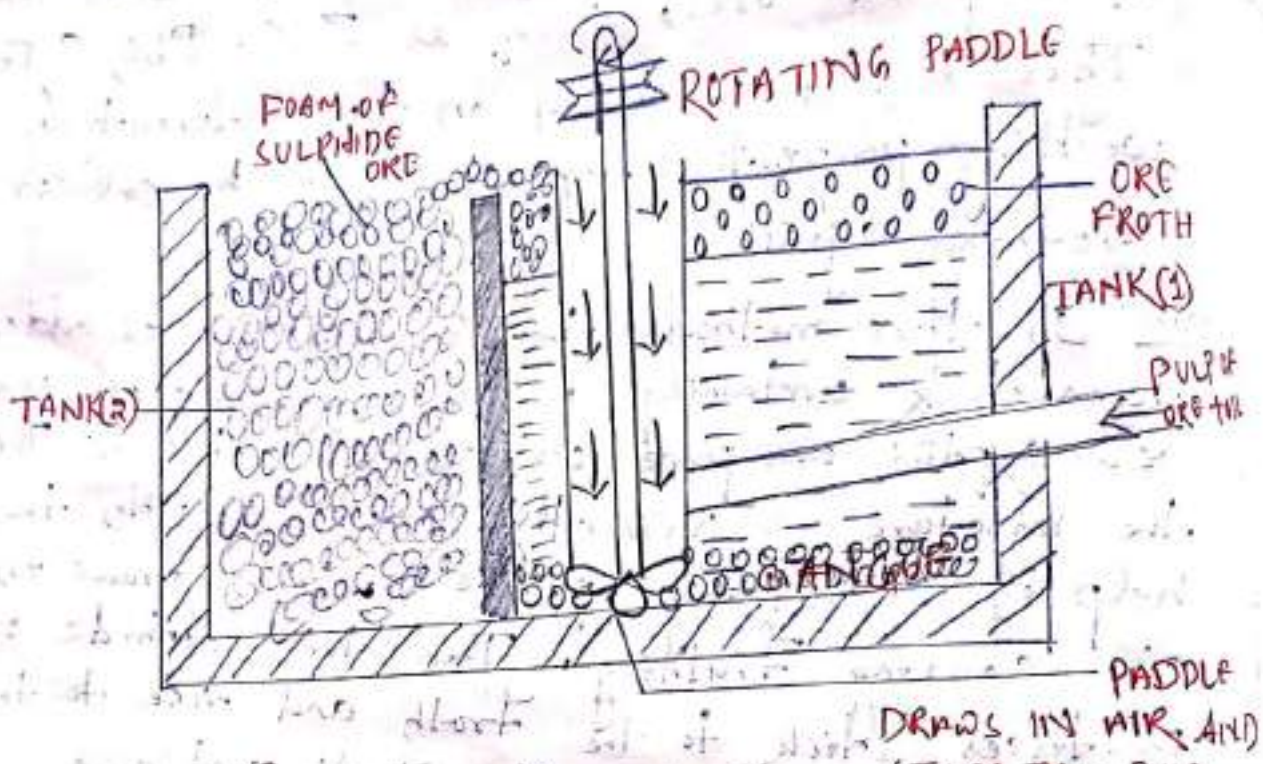
Froth Floatation Process :—

This method is employed for the concentration of sulphide ores, such as ZnS, PbS, $CuFeS_2$. This method is based on the preferential wetting properties of the ore by oil or frothing agent.

Procedure:- In this method, the crushed ore is added to a tank containing water. A cheap oil like eucalyptus or pine oil is added to it. Then the mixture is violently agitated with the help of a rotating paddle which draws in air causing frothing. Then the sulphide ore particles stick to the froth and rise to the surface with froth. The froth containing sulphide particles is kept in tank 2. After sometimes the froth settles down and the concentrated sulphide ore is obtained. Whereas the gangue particles are left behind in tank 1.

In the actual process, small quantities of other reagents, called Collectors (Xanthates and fatty acids) which enhance the binding force between the foam and the ore particles and froth stabilisers (Cresols and Aniline) are added which stabilise the ore. The ore particles which are preferentially wetted by oil become lighter and then rise to the surface along with the froth. On the otherhand, the gangue particles which are preferentially wetted by water become heavier and settles down at the bottom. Thus

froth is skimmed off, allowed to collapse and finally dried to get the concentrated ore



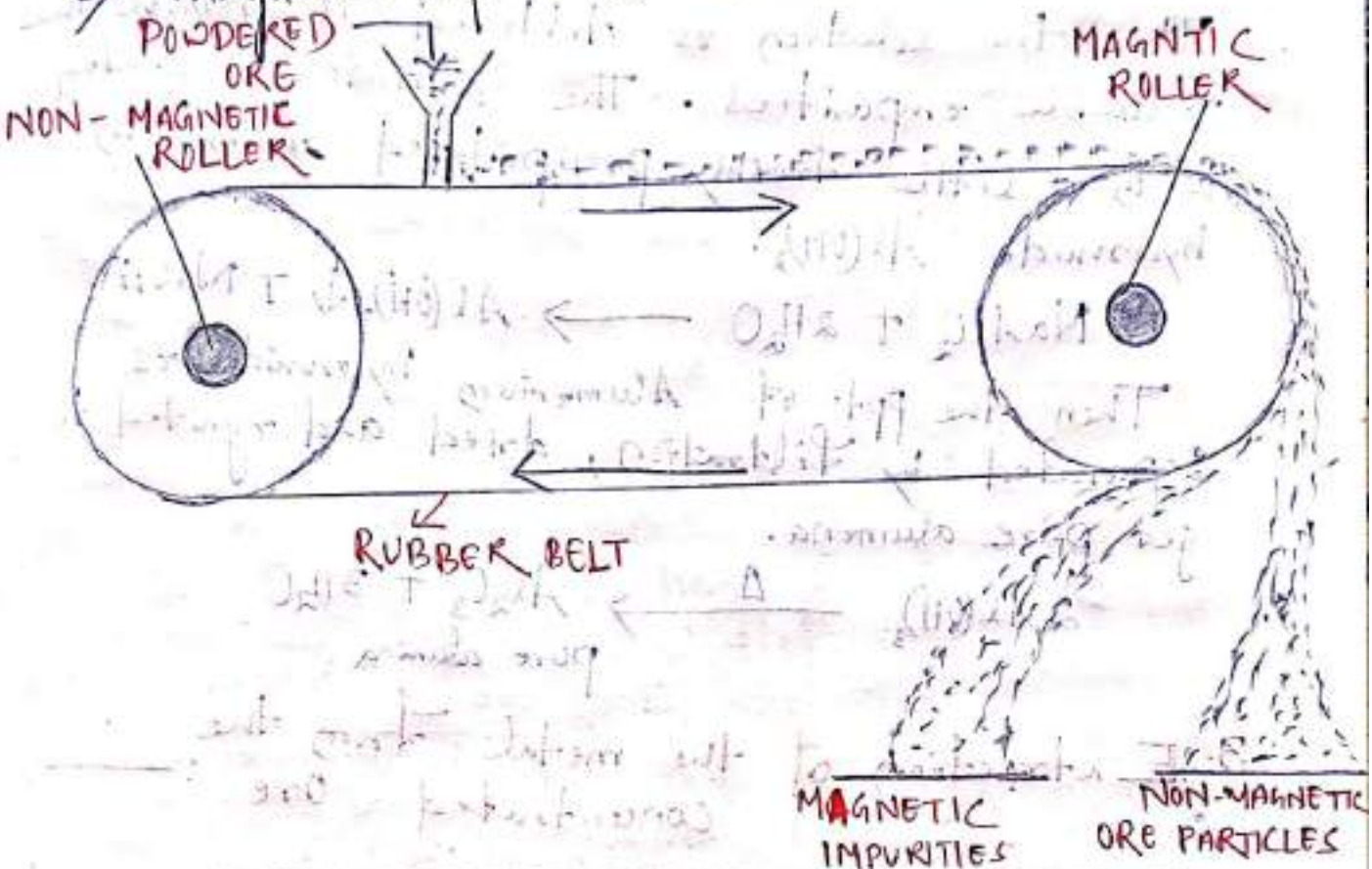
(FROTH FLOATATION PROCESS)

(c) Magnetic Separation :—

This method is applicable for the concentration such ores which differ from their impurities in magnetic character.

Procedure :— In this method the powdered ore is dropped over a belt revolving around the two rollers. Out of the two rollers, one is magnetic and another is non-magnetic roller. The magnetic part of the ore is attracted by the magnetic roller and forms a heap near it whereas the non-magnetic part of the ore repelled by the magnetic roller and forms a separate heap little away from it.

Ex:- The main impurity present in Tin stone (SnO_2) is ferrous tungstate ($FeWO_4$), called Wolfram. Here Tin stone is diamagnetic (repelled by the magnet) where as $FeWO_4$ is ferromagnetic (attracted by the magnet). They are separated by magnetic separation method.



(MAGNETIC SEPARATION METHOD)

(d) Leaching:- It is a chemical method for the concentration of the ore. In this method the powdered ore is treated with a suitable reagent which dissolves the ore but not the impurities. Then the ore is recovered from the solution by a suitable chemical means.

Ex:- Bauxite is leached with an ore of Aluminium. It is concentrated by leaching process.

Bauxite is leached with 45% solution of NaOH, when Al_2O_3 goes into solution forming soluble sodium meta-aluminate (NaAlO$_2$)

$$Al_2O_3 + 2NaOH \longrightarrow \underset{\text{Sod. Metaaluminate}}{2NaAlO_2} + H_2O$$

Impure Alumina

Then the solution is filtered to remove the insoluble impurities. The filtrate is seeded with a little freshly precipitated Aluminium hydroxide $Al(OH)_3$.

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

Then the ppt. of Aluminium hydroxide is separated by filtration, dried and ignited to get pure alumina.

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

3. Extraction of the metal from the concentrated Ore

The extraction of the metal from the concentrated ore involves the following steps :—

(a) Conversion of the concentrated ore into metal oxide

(b) Conversion of metal oxide into metal by reduction process

(a) Conversion of the concentrated ore into metal oxide :—

It is usually two process. i.e.

(i) Calcination & (ii) Roasting

(i) Calcination :—

It is a process of heating the concentrated ore in absence of air or in the limited supply of air at a temperature just below its melting point.

This process helps to remove moisture, volatile impurities like As, Sb etc. Usually Carbonates ores are decomposed to form oxides.

Ex:- $Fe_2O_3 \cdot 3H_2O \longrightarrow Fe_2O_3 + 3H_2O\uparrow$

$CaCO_3 \longrightarrow CaO + CO_2\uparrow$

$CaCO_3 MgCO_3 \longrightarrow CaO + MgO + 2CO_2\uparrow$

(ii) Roasting :—

It is a process of heating the concentrated ore strongly in a controlled supply of oxygen in a reverberatory furnace to get metal oxides. This process generally used to convert sulphide ores into metal oxides.

The main functions of roasting are :—

(i) It removes moisture in the form of steam.

(ii) It removes volatile impurities like As, Sb etc.

(iii) It oxidises substances which can be easily oxidised:

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

$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$

$2Cu_2S + 2O_2 \longrightarrow 2Cu_2O + 2SO_2$

$2FeS + 2O_2 \longrightarrow 2FeO + 2SO_2$

$4As + 3O_2 \longrightarrow 2As_2O_3\uparrow$

$P_4 + 5O_2 \longrightarrow 2P_2O_5\uparrow$ (volatile impurities)

(b) Conversion of Metal Oxide onto metal by reduction:—

The metal oxide formed in the process of calcination or roasting is reduced to the metal by the following method.

Smelting:—

In this method, the roasted ore is mixed with the suitable quantity of coke or charcoal which acts as a reducing agent. The mixture is heated to a high temperature above its melting point.

$$M_xO_y + yC \longrightarrow xM + yCO$$

For the extraction of less electropositive metals such as Pb, Zn, Fe etc. powerful reducing agents such as C, H_2, CO, water gas, Na, K, Mg, Al may be used.

$$PbO + C \longrightarrow Pb + CO$$

$$PbO + CO \longrightarrow Pb + CO_2\uparrow$$

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$

(Tungsten)

$$CuO + CO \longrightarrow Cu + CO_2\uparrow$$

$$BeCl_2 + 2Na \longrightarrow Be + 2NaCl$$

$$CaI_2 + 2K \longrightarrow Ca + 2KI$$

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

During the smelting process an additional substance is added into the ore which reacts with the impurities still present

to the ore to form a fusible product. The additional substance added to the ore is called Flux and the fusible product formed is called Slag.

Flux + Impurities (Gangue) → Slag

Flux :- It is of 2 types.
(a) Acidic flux & (b) Basic flux

(a) Acidic flux :-

If the impurities present in the ore are basic, then acidic flux are used.

Ex :- SiO_2 + CaO → $CaSiO_3$
(Acidic flux) (Basic Impurity) Slag

(b) Basic flux :-

If the impurities present in the ore are acidic, then basic flux are used.

CaO + P_2O_5 → $Ca_3(PO_4)_2$
(Basic flux) (Acidic impurity) Slag

Slag is usually lighter and it floats on the surface of the molten metal which can be easily removed.

4. Refining of the Crude Metal :—

→ The metals obtained contain the following type of impurities :-

(a) Metals other than the metal under extraction
(b) Oxide left unreduced
(c) Oxidisable impurities like As, P, Si, C etc
(d) Residual slag or flux

The process of the removal of these impurities from a crude metal is called Refining.

The following methods are generally employed for the refining of metals.

(a) Distillation :—

Some volatile metals like Mercury (Hg), Zn, Pb etc contain non-volatile impurities. For the purification of such types of metals distillation is done. During the distillation process, the pure metal volatilise whereas the impurities are left behind.

(b) Electro-refining :—

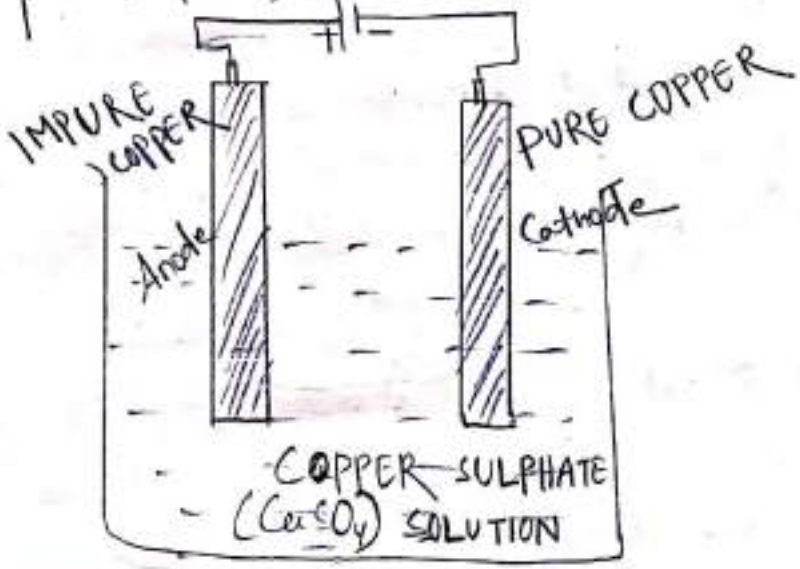
Refining of crude metal by the process of electrolysis is called Electro-refining. In this method, a suitable electrolyte is chosen and put into an electrolytic cell. Pure metal plate is dipped into the electrolyte and taken as Cathode. The impure metal is taken as Anode.

Then a suitable e.m.f is applied to the electrolytic cell. The pure metal from the electrolyte get deposited on the cathode and equivalent quantity of metal from the anode goes into solution.

Metals like Cu, Al, Zn, Pb, Sn are purified by this method.

Electro-refining of Copper :—

In the electro-refining of copper, pure Cu metal is taken as cathode and impure Cu metal is taken as Anode. Any soluble salt of Cu is taken as electrolytic solution. During the electrolysis process, pure metal from the Anode goes into solution and get deposited on the cathode.



$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

At Cathode :- $Cu^{2+} + 2e^- \longrightarrow Cu$

At Anode :- $Cu \longrightarrow Cu^{2+} + 2e^-$