LECTURE NOTE-(INORGANIC CHEMISTRY)

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Chapter: 7 –Metallurgy

Minerals: Compounds which contain metals in combined state and are found under the earth's crust. They contain impurities.

Ex: Minerals of Na: NaCl, $NaNO_3$, Na_2SO_4

Al: $Al_2O_3.2H_2O$(Bauxite), Al_2O_3,$2SiO_2.2H_2O$(Kaolin)

Cu: Cu_2S(Copper glance), Cu_2O(Cuprite), $CuFeS_2$(Copper pyrite)

All minerals can't be used for extraction of metals.

Ore: An ore is a mineral from which the metal can be extracted conveniently, economically and profitably.

Ex: For Al: Bauxite, for Cu: Copper pyrite

Ores contain high % of metal and less % of objectionable impurities.

*All ores are minerals but all minerals can't be ores

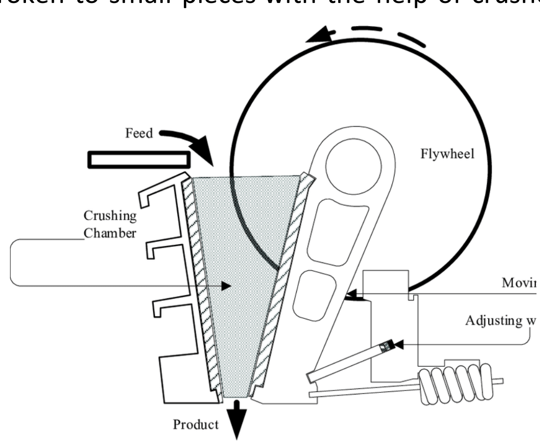
GANGUE: The earthy impurities such as sand, clay, rocks etc. associated with ore are collectively known as gangue or matrix.

GENERAL METHODS FOR EXTRACTION OF METALS:

1. Grinding/Crushing of ore
2. Pulverising the ore
3. Concentration/Ore Dressing
    a. Gravity Separation
    b. Froth floatation
    c. Magnetic separation
    d. Leaching
4. Oxidation(Conversion of concentrated ore into metallic oxides)
    a. Calcination
    b. Roasting
5. Reduction(Extraction of metal from calcinated or roasted ore)-Smelting
6. Purification(Refining of metal)
    a. Electrorefining
    b. Distillation

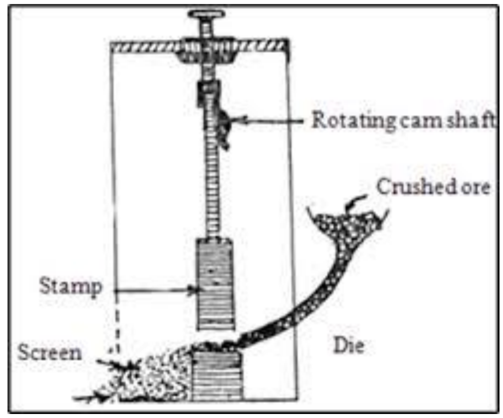
1. Grinding/Crushing of ore

The ores occur in nature as huge lumps. They are broken to small pieces with the help of crushers or grinders.



2. **Pulverising the ore**

These pieces are then reduced to fine powder with the help of a ball mill or stamp mill. This process is called **pulverisation.**



3. **Concentration/Ore Dressing**

The ores are usually found mixed up with large amounts of non-metallic impurities such as, sand, mica, limestone, felspar, earthy and rocky impurities. These unwanted impurities are called gangue or matrix and have to be removed before extracting the metals. The process of removal of unwanted impurities (gangue) from the ore is called ore concentration or ore dressing or ore benefaction. The powdered ore is concentrated by one of the following methods depending upon the differences in physical properties of the compound of the metal present and the impurities/gangue) present in the ore.

a. Gravity Separation
b. Froth floatation
c. Magnetic separation
d. Leaching

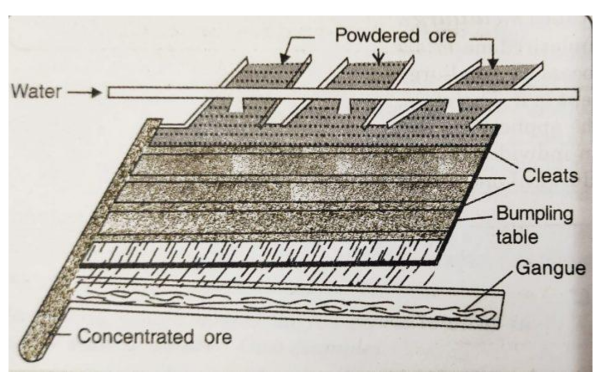
a. Gravity Separation:

This method is based on the differences in the specific gravities/densities of metallic ores and the gangue particles. Therefore, this method is known as gravity separation. This method is frequently used when the ore particles are heavier than the earthy or rocky gangue particles.
For example: this method is used for oxide ores such as hematite, tin stone, galena and native ore of Au, Ag, etc. The powdered ore is fed into a stream of running water when the impurities are washed away and the heavier ore particles are left-behind.
In order to concentrate the ores in bulk, two commonly used methods of gravity separation are:

i. Wilfley washing Table
ii. Hydraulic classifier

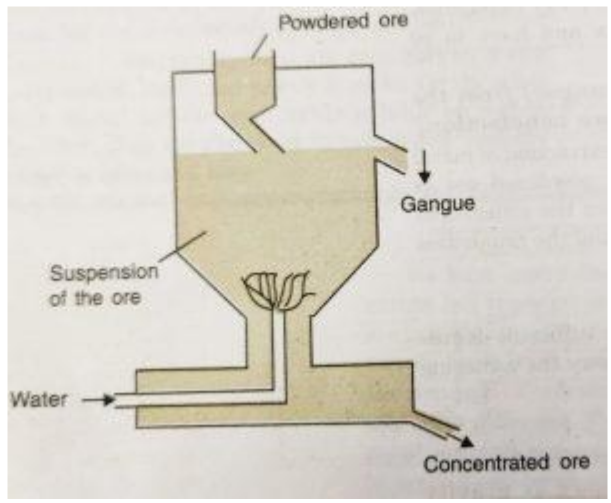
(i) Wilfley's Washing Table

(a) A Wilfley table is a sloping wooden table having slanting floor on which long wooden strips called riffles or cleats are fixed.
(b) The powdered ore is mixed with water and introduced at one end of the table.
(c) The table is given regular rocky motion.



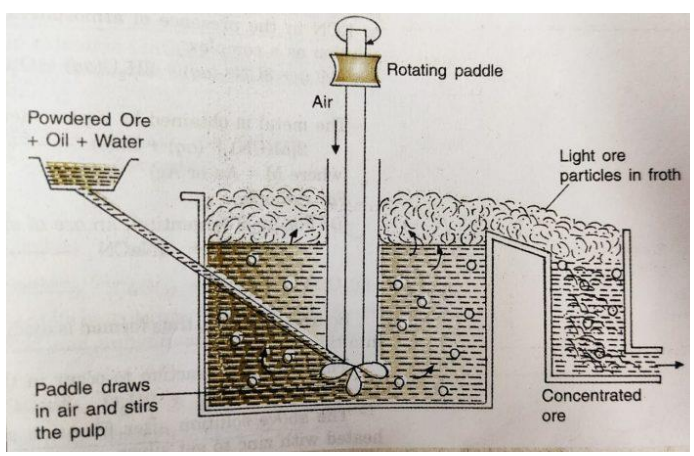
(d) The heavier ore particles are obstructed by the riffles while the lighter impurities are carried away by the stream of water.
(e) The heavier ore particles which get collected behind the riffles move to one side as a result of motion of the table and are collected.
(f) This method is particularly useful for the concentration of native gold ore or cassiterite (SnO.). Also to separate galena(PbS) from lime(CaO)

(ii) **Hydraulic Classifier:**



a) The hydraulic classifier consists of a large conical reservoir fitted with an ore inlet at the top and water inlet at the bottom.
b) There is a provision to remove light gangue particles from the side near the top and concentrated ore from the bottom.
c) In this method, the powdered ore is dropped through a hopper into the hydraulic classifier from the top.
d) A powerful stream of water is forced into it through the pipe at the bottom of the reservoir.
e) The lighter particles of the gangue are carried up by the current of water and pass out along with water flowing out from the outlet near the top.
f) The heavier particles of the ore get collected at the base of the cone.
g) The conical shape of the reservoir helps in reducing the velocity of water and this prevents the ore particles from being carried away along with the stream of water.
h) This method is also called levigation and is used for iron, gold, chromium, etc.

b. Froth Floatation:

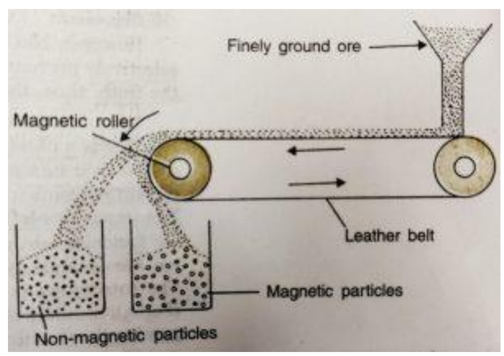


This method is based on the **principle** of difference in the wetting properties of the ore and gangue particles with water and oil. It is used for the extraction of those metals in which the ore particles are preferentially wetted by oil and gangue by water.
This method has been used for the concentration of sulphide ores, such as galena (PbS), zinc blende (ZnS), copper pyrites ($CuFeS_2$), etc. The sulphide ore particles are preferentially wetted by oil and gangue particles by water.
a) In this method, the powdered ore is mixed with water to form a suspension in a tank.
b) To this suspension small quantities of collectors and froth stabilisers are added.

c) Collectors (e.g., pine oil, eucalyptus oil, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilizers (e.g., aeresols, aniline) help in stabilization of the froth.
d) The mineral ore particles become wet by oil while the gangue(impurities) particles by water.
e) A current of compressed air is circulated into the tank or the water is agitated by a rotating paddle or by blowing air violently, when froth (or foam) is formed.
f) During the process, the ore particles which are preferentially wetted by the oil become lighter. The froth carries the lighter ore particles along with it to the surface.
g) The heavier impurities are left behind in water and these sink to the bottom. Since the ore particles float with the froth at the surface, this process is called froth floatation process.
h) The froth is either skimmed off from the surface or transferred into another tank. The froth is broken by adding some acid and ore particles are separated by filtration and dried.
i) Depressants are used to prevent certain types of particles from forming the froth with air bubbles.
For example: sodium cyanide can be used as a depressant in the separation of zinc sulphide ore (ZnS) and lead sulphide ore (PbS). Sodium cyanide forms a layer of zinc complex, $Na_2[Zn(CN)_4]$ on the surface of ZnS and therefore prevents it from forming the froth.Therefore, it acts as a depressant.
$4\ NaCN + ZnS \longrightarrow Na_2[Zn(CN)_4] + Na_2S$
However, NaCN does not prevent PbS from forming the froth. Thus it selectively prevents ZnS from coming to the froth but allows PbS to come with the froth. Thus, the two ores can be separated by the use of a depressant

c. Magnetic separation:

This is based on the differences in magnetic properties of the ore components. If either ore or the gangue (one of these two) is attracted by a magnet then ore can be separated from the impurities with the help of magnetic separation method.



For example:

- The magnetic impurities such as iron and manganese tungstates ($FeWO_4$,$MnWO_4$)-(Wulframite ores) present in tin stone (SnO_2, non-magnetic) are separated by this method.
- Chromite ($FeO.Cr_2O_3$) is magnetic and it can be separated from non-magnetic silicious gangue by this method. This method is also used for the concentration of haematite (Fe_2O_3) or magnetite (Fe_3O_4), pyrolusite (MnO_2), ilmenite (ore of titanium), etc.

a) It consists of a brass or leather belt moving over two rollers, one of which is magnetic in nature and the other is non magnetic.
b) Powdered ore is dropped over the moving belt at one end.
c) At the other end, the magnetic portion of the ore is attracted by the magnetic roller and falls nearer to the roller forming a heap while the non-magnetic impurities fall farther apart.

d. Leaching:

This is a chemical method of concentration and is useful in case the ore is soluble in a suitable solvent. In this method, the powdered ore is treated certain reagents in which the ore is soluble but the impurities are not soluble.The impurities left undissolved are removed by filtration. Leaching method is used for concentrating ores of aluminium, silver, gold etc.

For example:

a) The ore of aluminium, bauxite, is concentrated by this method. The bauxite ore is contaminated with impurities of silica (SiO_2), iron oxides (Fe_2O_3), titanium oxide (TiO_2), etc.

b) Concentration is carried out by digesting powdered ore with a 45% solution of sodium hydroxide.

c) In this process Al_2O_3 dissolves in alkali to form soluble sodium aluminate and silica (SiO_2) dissolves as sodium silicate, leaving behind the impurities(TiO_2 , SiO_2).

$Al_2O_3.H_2O$ (s) + 2 NaOH (aq)——> 2 $NaAlO_2$ + 3 H_2O (l)

d) The solution of sodium aluminate is filtered, cooled and treated with H_2O when $Al(OH)_3$ is precipitated.

$NaAlO_2$ (S)+ H_2O(aq) ———> $Al(OH)_3$ (s) + $3H_2O$(l)

f) The sodium precipitate is then separated by filtration , dried and ignited to get pure alumina.

$Al(OH)_3$ (s) ———> Al_2O_3 + $3H_2O$

This process is known as **Baeyer's process.**

- It is also employed in concentrating Ag & Au ores.

For example

(1) For Ag_2S (argentite), an ore of silver the reactions are :

Ag_2S + 4NaCN ——> 2Na[$Ag(CN)_2$] + Na_2S

Sodium dicyanoargentate(I)

Sodium sulphide, thus formed is oxidised to sodium sulphate by blowing air into the solution. This helps the reaction to occur in the forward direction.

$4Na_2S$ + $5O_2$+ $2H_2O$ ——> $2Na_2SO_4$ + 4NaOH + 2S

The above solution after filtration and removing insoluble impurities heated with zinc to get silver.

2Na [$Ag(CN)_2$] + Zn ———> Na_2[$Zn(CN)_4$] + 2Ag

4. Oxidation(Conversion of concentrated ore into metallic oxides):

a) Calcination

b) Roasting

a) Calcination:

Calcination can be defined as the process of converting ore into an oxide by heating it strongly. The ore is heated below the melting point either in limited supply or absence of air. This method is used for converting hydroxides and carbonates to their respective oxides.

As a result of calcination,

- The moisture impurities are removed.
- Gases are expelled
- Volatile impurities like S, Sb,As etc get escape out

- The mass becomes porous
- Thermal decomposition of the ore takes place

Ex:

$CaCO_3$ ———> $CaO + CO_2$
(Calcite)
$MgCO_3$ ———> $MgO + CO_2$
(Magnesite)
$MgCO_3.\ CaCO_3$ ———> $MgO + CaO + CO_2$
$CuCO_3.Cu(OH)_2$ ———> $2CuO + H_2O + CO_2$
(Malachite)
$ZnCO_3$ ———> $MgO + CO_2$
(Calamite)
$2Fe_2O_3.3H_2O$ ———> $2Fe_2O_3 + 3H_2O$
(Limonite)
$2Al(OH)_3$ ———> $Al_2O_3 + 3H_2O$

b) <u>Roasting:</u>

It is a process in which the concentrated ore is strongly heated in excess of air at a temp. below its melting point. It is carried out in reverberatory furnace/blast furnace. This process is generally used to convert sulphide ores into metallic oxide.

During Roasting:

- Moisture is removed
- Volatile impurities like S, Sb,As etc get oxidized and escape out as volatile gases SO_2, Sb_2O_3, As_2O_3 etc
- Sulphide ores decompose to their oxides evolving SO_2
- Ferrous compounds are oxidized to ferric compounds

<u>Ex:</u>

$2ZnS + 3O_2$ ———> $2ZnO + 2SO_2$
(Zinc blend)
$2PbS + 3O_2$ ———> $2PbO + 2SO_2$
(Galena)
$2CuFeS_2 + O_2$ ———> $Cu_2O + 2FeS + 2SO_2$
(Copper pyrite) (decomposed)
$2Cu_2S + 3O_2$ ———> $2CuO + 2SO_2$
$2FeS + 3O_2$ ———> $2FeO + 2SO_2$
$4FeCO_3 + O_2$ ———> $2Fe_2O_3 + 4CO_2$

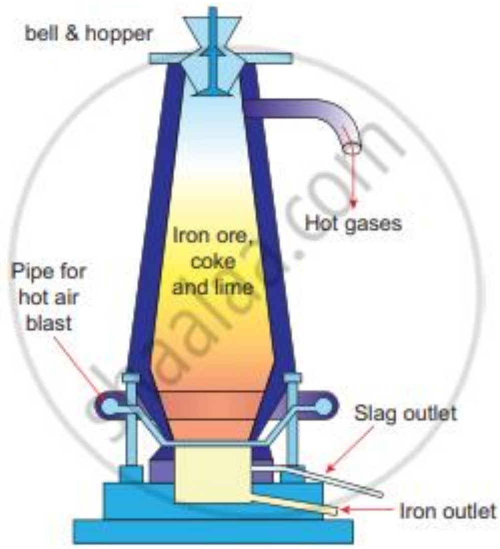
$S + O_2$ ———> SO_2
$4As + 3O_2$ ———> $2As_2O_3$
$P_4 + 5O_2$ ———> $2As_2O_3$

5. Reduction(Smelting):

In this process the calcinated or roasted ore is mixed with a suitable reducing agent & the mixture is heated to a very high temperature above its melting point. It is generally carried out in a blast furnace and high temperature is produced by burning coal or by using electric energy.

In smelting, the roasted/calcinated ore is mixed with coke/charcoal & then heated in a furnace. The coke/charcoal acts as reducing agent which reduce the oxides into metals by incomplete combustion of C.

During smelting an additional compound is added to the ore which reacts with the impurities (gangue/matrix) to form a fusible mass. The additional substance is called flux and the fusible product is called slag.



Flux and Slag:

Flux: It is defined as a substance which combines with gangue to form light and easily fusible material.

Slag: The easily fusible material which is not soluble in molten metal is called slag. Being lighter it can be easily removed from the surface of the metal. The slag is removed & used in road making or manufacture of cement/fertilizer.

(i) Acidic Flux:

When the ore is associated with basic impurities like CaO, FeO etc, the flux used is some acidic substance such as silica, borax.

$CaO + SiO_2 \rightarrow CaSiO_3$

Gangue (basic) Flux (acidic) Slag

$FeO + SiO_2 \rightarrow FeSiO_3$

Gangue (basic) Flux (acidic) Slag

$MnO + SiO_2 \rightarrow MnSiO_3$

Gangue (basic) Flux (acidic) Slag

(ii) Basic Flux:

When the ore is associated with acidic impurities like SiO_2, the flux used is some basic substance $CaCO_3$, $MgCO_3$ etc.

$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2$

Gangue (acidic) | Flux (basic) | Slag

$P_2O_5 + 2CaO \rightarrow Ca_3(PO_4)_2$

Gangue (acidic) | Flux (basic) | Slag

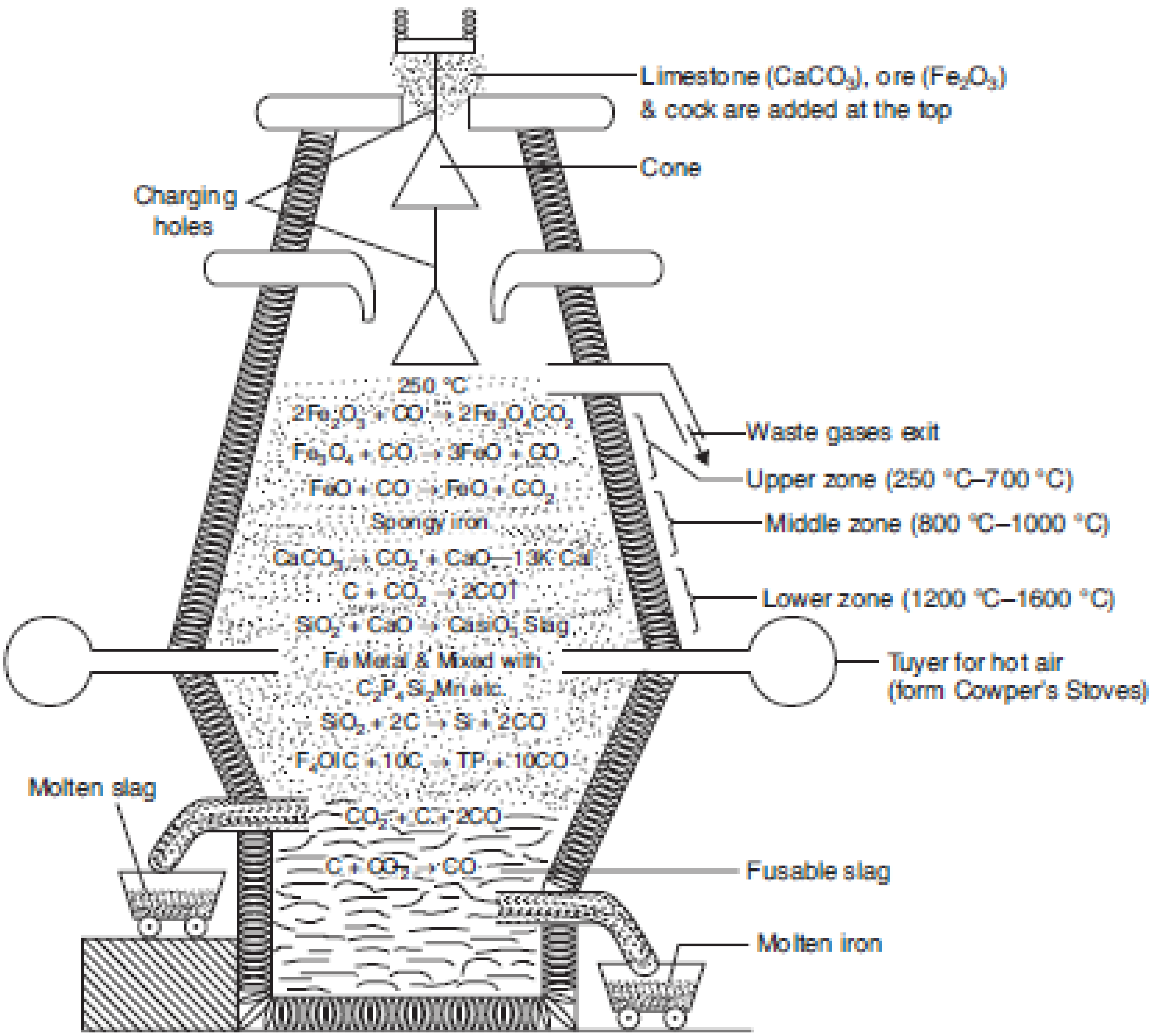


Fig. 14.8 Blast furnace (displaying reactions of iron extraction in various zones of the furnace).

Smelting/Reduction can be carried out by following methods:

1. Reduction By Coke/Charcoal- Carbon Reduction Process
2. Reduction by H/Water gas
3. Reduction by Al- Aluminothermy
4. Self Reduction
5. Reduction by Na/K
6. Electrolytic reduction

1. <u>Reduction By Coke/Charcoal- Carbon Reduction Process</u>

In this process oxides of less electropositive metals(Fe, Pb, Zn, Mn, Sn) are reduced by strongly heating with Coke/charcoal

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

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

$$ZnO + C \longrightarrow Zn + CO$$
$$MnO_2 + 2C \longrightarrow Mn + CO$$
$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

2. <u>Reduction By H/Water Gas-(W,In,Ca,Ni)</u>

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$
$$NiO + 2H \longrightarrow Ni + H_2O$$
$$In_2O_3 + 3H_2 \longrightarrow 2In + 3H_2O$$
$$Co_2O_3 + 6H \longrightarrow 2Co + 3H_2O$$

3. <u>Reduction By Al-Aluminothermy-(Mn,Cr,Fe)</u>

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + \triangle$$
$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3 + \triangle$$
$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3 + \triangle$$

4. <u>Self Reduction-(Pb,Hg,Cu)</u>

This method does not involve any additional reducing agent & is similar to reduction by heating in air. In this method sulphide ore is heated in air until a part of it is converted into oxide. On further heating in air, the unchanged sulphide reduces the oxide to metal.

For ex:

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$2PbO + PbS \longrightarrow 3Pb + SO_2$$
$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$
$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$$
$$HgS + 2HgO \longrightarrow 3Hg + SO_2$$

5. Reduction by Na/K---(Ti, Be, Ca)-

$$TiCl_4 + 4Na \longrightarrow Ti + 4NaCl$$
$$BeCl_2 + 2Na \longrightarrow Be + 2NaCl$$
$$CaI_2 + 2K \longrightarrow Ca + 2KI$$

6. Electrolytic Reduction ---(Na,Mg,Ca)

Chemically active and high electropositive metals such as alkali metals & alkaline earth metals & metals with high positive oxidation potential can be reduced by this method.

Ex: NaCl, $MgCl_2$, $KCl.MgCl_2.6H_2O$(Carnalite), Ca, Ba and Sr Ores as carbonates, which can be easily converted to their halides

$NaCl \longrightarrow Na^+ + Cl^-$

At Cathode: $Na^+ + e^- \longrightarrow Na$

At anone: $2Cl^- \longrightarrow Cl + e^-$

6. Purification/Refining of Ore:

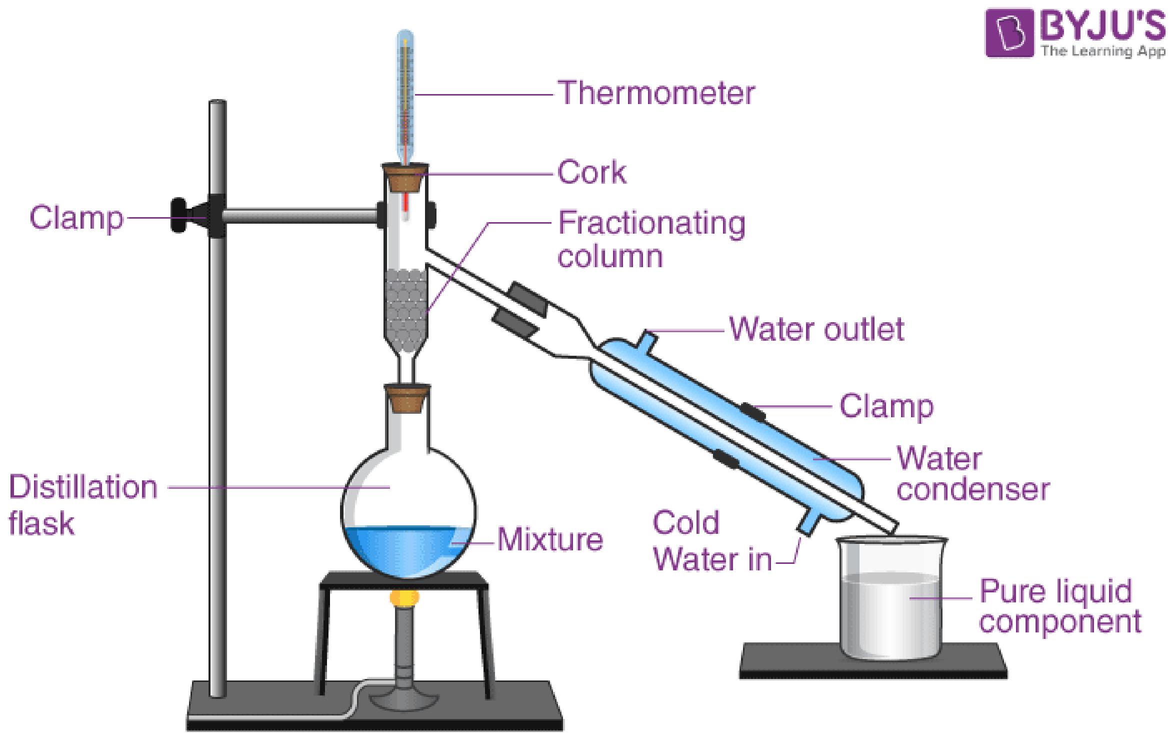
The metals obtained by the above methods is not pure. It still contain the following impurities:

1. Metals other than metal under extraction
2. Oxides left unreduced
3. Oxidisable impurities like P,Si, C etc
4. Residual Slag /Flux

Hence, metals obtained by other methods require adequate refining , which can be accomplished by a large no. of methods.

(i) Distillation: (Zn,Cd,Hg, Bi,etc)

Easily volatile/Low boiling point metals are refined by distillation method. The process consist of heating the impure metal in a retort; as a result of which pure metal distils over & collects in a receiver which the non-volatile impurities are left behind.



(i) Electrorefining: (Cu,Ag, Pb,Au,Ni,Sn,Zn etc)

This is one of the most convenient and important method of refining and gives metal of high purity.

The blocks of impure metal slab forms the anode and a thin sheet of pure metal forms the cathode. A salt solution of the metal is taken as the electrolyte. On passing electric current through the solution, pure metal dissolves from the anode and deposits on the cathode.

At the same time, more ions of metal enters the electrolyte by oxidation of anode. The insoluble impurities either dissolve in the electrolyte or fall at the bottom & collected as anode mud.