- The compound of a metal found in nature is called a mineral. A mineral may be a single compound or a complex mixture. Those minerals from which metal can be economically extracted are called ores. Thus all ores are minerals but all minerals are not ores. Ores may be divided into four groups

i) Native Ores: These ores contain the metal in free state eg. Silver gold etc. These are usually formed in the company of rock or alluvial impurities like clay, sand etc.

ii) Oxidised Ores: These ores consist of oxides or oxysalts (eg. carbonates, phosphate) and silicate of metal. Important oxide ore includes, Fe_2O_3, $Al_2O_3.2H_2O$ etc. and important cabonate ores are limestone ($CaCO_3$), Calamine ($ZnCO_3$) etc.

iii) Sulphurised Ores: These ores consist of sulfides of metals like iron, lead, mercury etc. Examples are iron pyrites (FeS_2). galena (PbS), Cinnabar (HgS)

iv) Halide ores: Metallic halides are very few in nature. Chlorides are most common examples include horn silver (AgCl) carnallite KCl. $MgCl_2.6H_2O$ and fluorspar (CaF_2) etc.

Major ores of our interest are:

ORES

1. Iron

i) Haematite Fe_2O_3
ii) Magnetite Fe_3O_4
iii) Limonite or hydrated ferric oxide $Fe_2O_3.\ 3H_2O$
iv) Siderite $FeCO_3$
v) Iron pyrites FeS_2

2. Copper

i) Copper pyrites or chalcopyrites $CuFeS_2$ or $Cu_2S.\ Fe_2S_3$
ii) Copper glance or Chalcocite Cu_2S
iii) Basic copper carbonate or malachite $CuCO_3.\ Cu(OH)_2$
iv) Cuprite Cu_2O
v) Bornite or peacock ore* Cu_5FeS_4
vi) Azurite $2\ CuCO_3.\ Cu(OH)_2$

(* The name peacock ore is given because it has a mixture of irridescent colours like peacock's feather.)

3. Lead

i) Galena PbS
ii) Cerussite $PbCO_3$
iii) Anglesite $PbSO_4$

4. Magnesium

i) Magnesite $MgCO_3$

ii) Dolomite $MgCO_3.CaCO_3$
iii) Epsomite or Epsom salt $MgSO_4.7H_2O$
iv) Caranallite $MgCl_2.KCl.6H_2O$
v) Kieserite $MgSO_4.H_2O$
vi) Kainite $K_2SO_4.MgSO_4.MgCl_2.6H_2O$

5. Aluminium

i) Bauxite $Al_2O_3.2H_2O$
ii) Kaolin $Al_2O_3.2SiO_2.2H_2O$
iii) Cryolite Na_3AlF_6
iv) Felspar $K_2O. Al_2O_3. 6SiO_2$

6. Silver

i) Argentite or Silver glance Ag_2S
ii) Horn silver or Chlorargyrite AgCl
iii) Ruby silver (pyrargyrite) Ag_3SbS_3

EXTRACTIVE METALLURGY

It is the process of extracting a metal from its ores. The following operations are carried out for obtaining the metal in the pure form.

i) Crushing of the ore
ii) Dressing or concentration of the ore.
iii) Reduction of metal.
iv) Purification or refining of the metal

- Ores usually contain soil, sand, stones and other useless silicates. These undesired impurities present in ores are called Gangue or Matrix. The removal of these impurities from the ores is known as concentration. The concentration process involve physical as well as chemical method.

Physical Method

a) **Gravity separation**: The separation is based on the difference in the specific gravities of the gangue particles and ore particles.

b) **Froth Floatation Process:** The method is based upon preferential wetting of surfaces by liquids.

c) **Electro Magnetic Separator:** When one component either ore or the impurity is magnetic in nature this method can be used for separation.

Chemical Methods

a) **Calcination**: Calcination is a process in which the ore are usually carbonate or hydrated oxide is subjected to the action of heat in order of expel water from hydrated oxide and carbon dioxide from a carbonate. Calcination is generally done in a reverberatory furnace.

b) **Roasting:** Roasting is a process in which ores (usually sulphide ores) either alone or along with some other materials are subjected to the action of heat and air at temperatures below their melting points in order to bring about chemical changes in them. Calcination is also roasting but in this case we are concerned mainly with the changes due to the expulsion of some ingredients such as water, carbon dioxide and no other chemical change occurs. But during roasting chemical changes like oxidation, chlorination etc. takes places. Roasting is generally carried out in a reverberatory furnace or in a blast furnace.

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

Reduction of Free Metal

a) **Smelting:** The reduction of a metal from its ore by a process involving melting is known as smelting. It is generally done in a reverberatory furnace or a blast furnace in a controlled supply of air. Several reducing agents such as sodium, magnesium and aluminium are used for reduction.

b) **Flux:** The ores even after concentration contain some earthy matter called gangue which is heated combine with this earthy matter to form an easily fusible material. Such a substance is known as flux and the fusible material formed during reduction process is called slag. Slag is usually lighter and floats on the surface of the molten metal.

$$\text{Concentrated ore + gangue + reduction agent + flux} \xrightarrow{\text{heated}} \text{Metal + slag + gases}$$

Fluxes are of the following two types:

i) Acidic fluxes like silica, borax etc.

ii) Basic fluxes like CaO, lime stone ($CaCO_3$), magnesite ($MgCO_3$), haematite (Fe_2O_3) etc.

The other methods used for the reduction of metals are electrolytic reduction, hydro metallurgy and amalgamation method.

Refining or purification

The metals obtained by the application of above reduction methods from the concentration ores are usually impure. The impure metal is thus subjected to some purifying process known as refining in order to remove undesired impurities. Various process for this are

a) Liquation process
b) Distillation process
c) Cupellation
d) Poling
e) Elecrolytic refining
f) Bessemerisation

1. **Iron**

Extraction of iron from its ores involves two processes.

i) Smelting to obtain the curde metal.
ii) Refining of the crude metal

The iron so obtained by reduction method contains carbon and other impurities and it is known as *pig iron* or *cast iron*. The pig iron is then converted to *wrought iron* or *steel* according to the requirement.

Smelting is carried out in a furnace, it is almost *cylindrical furnace*, lined with fire bricks. Iron ore (haematite - Fe_2O_3) is calcined to remove volatile impurities like sulphur and arsenic. The calcined ore (8 parts) along with limestone (1 part) and coke (4 parts) are lifted to the top of the furnace and released when needed. Preheated air at a temperature of about 873 K is passed into the furnace through a number of nozzles. Near the bottom, preheated air comes in contact with the falling coke and combustion of coke take place and region is known as *combustion zone*

$$C + O_2 \rightarrow CO_2$$

i) CO_2 so produced goes upwards and comes into contact with layers of coke and gets reduced to CO.

ii) CO acts as a reducing agent and reduces iron oxide to iron.

$$FeO_3 + 3CO \rightarrow 2Fe + 3CO_2$$
$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
$$FeO + C \rightarrow Fe + CO.$$

Molten iron thus formed is collected at the bottom from where it is tapped off.

Limestone which acts as a flux decomposes at about 1073 K. The quicklime reacts with sandy impurities (SiO_2) to form a slag of calcium silicate.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3\text{(slag)}$$

The molten slag is less dense than iron and floats on the top. When both molten iron and slag are drawn off, coke and limestone are added. The gases leaving the furnace contain CO and are used to heat the incoming air - blast. The whole blast furnace process is continuous.

The molten iron tapped off from the furnace is solidified into blocks known as 'pigs'. This form of iron is called *'pig iron'* or *cast iron*. It contains about 3-5% carbon and varying amounts of Mn, Si, S and P.

2. **Tin**

The chief ore of tin is *cassiterite* or *tin stone*, SnO_2. It contains about 10% of tin. The crushed ore is washed with water to remove lighter impurities. The ore is then roasted to remove arsenic and sulphur as volatile oxides. Tin is obtained by reducing SnO_2 with carbon at 1200- 1300^{0}C in an electric furnace.

$$SnO_2 + 2\,C \xrightarrow{1200-} Sn + 2\,CO$$

The product often contains traces of Fe, which make the metal hard. Fe is removed by blowing air through the molten mixture to oxidise the iron to FeO, which then floats to the surface.

3. Copper

The ore is crushed and concentrated by *froth floatation process,* this is then roasted in a limited supply of air in a *reverberatory furnace* to convert iron into iron(II) oxide. Arsenic and antimony present as impurites are removed as volatile oxides.

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

Sand is added to remove the iron as iron silicate slag $FeSiO_3$ which floats on the surface. Air is blown through the liquid matte of Cu_2S with wazzu some FeS and silica, causing partial oxidation.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3 \text{ (slag)}$$

Iron (II) silicate

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

After some time the air is turned off and *self reduction* of the oxide and sulphide occurs, giving impure *blister copper* which is 98% - 99% pure.

$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

Impure copper is further refined electrolytically to obtain 99.95 - 99.99% pure copper by using a solution of Cu (II) sulphate as an electrolyte.

4. Lead

The principal ore of lead is *Galena,* PbS. The ore is first concentrated by *froth floatation process*. The concentrated ore is roasted in air to convert it into lead oxide PbO and lead sulphate. Some galena is also left unchanged. If the air supply is now reduced, the unreacted PbS reacts with PbO and $PbSO_4$ to produce metal

$$3PbS + 5O_2 \longrightarrow 2PbO + PbSO_4 + SO_2$$

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

$$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$$

5. Magnesium

Magnesium from sea-water is obtained by the *Dow's process.* It consists of electrolysis of molten magnesium chloride using an iron cathode and a graphite anode. Following are the steps that involved during the process.

1. Mg^{+2} is precipitated as magnesium hydroxide by the addition of slaked lime, $Ca(OH)_2$ to the sea water.

$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+}$

2. Magnesium hydroxide on treatment with hydrochloric acid is converted to chloride which is crystallised as $MgCl_2.6H_2O$

   $Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$

3. Now for electrolysis, magnesium chloride is fused as follows:

   On passing a current of dry HCl gas it get partially dehydrated and the chloride thus obtained is added to a molten mix. of sodium chloride and calcium chloride (temp. range 973 - 1023 K).Under this condition $MgCl_2$ melt with the loss of water.

   If magnesium chloride hydrate is heated strongly, it hydrolyses to yield magnesia (magnesium oxide) which is a refractory.

   $$MgCl_2.6\,H_2O \longrightarrow MgO + 2HCl + 5H_2O$$

4. Molten mixture of $MgCl_2$, NaCl and $CaCl_2$ is electrolysed. Magnesium is formed at the cathode and chlorine is evolved at the anode. The chlorine is used to make HCl acid which in turn is required for making magnesium chloride.

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

   Anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

6. Aluminium

Aluminium is extracted from *Bauxite* and it involves two steps:

i) Purification of bauxite (ii) Electrolysis of pure alumina

i) Purification of bauxite: Bauxite is treated with a hot conc. solution (45%) of sodium hydroxide. Aluminium dissolves to form sodium aluminate $NaAlO_2$, leaving behind iron oxide which is present as impurity.

Actually the chemistry of aluminates is complex. Aluminium hydroxide which is formed redissolves in excess of sodium hydroxide to form sodium aluminate, $NaAl(OH)_4$ which is not stable and on heating gets converted to $NaAlO_2$ which is called sodium meta-aluminate. Silica SiO_2 also dissolves in sodium hydroxide to form soluble sodium silicate, Na_2SiO_3

$Al_2O_3.2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2O$

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

The impurities are filtered out and the solution containing sodium meta- aluminate and sodium silicate is seeded with freshly precipitated aluminium hydroxide. Aluminium hydroxide precipitates leaving behind sodium silicate in solution. This is filtered and heated at 1473 K to yield pure alumina.

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

$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$

ii) **Electrolysis of pure alumina** : Alumina is dissolved in a fused mixture of cryolite

(Na_3AlF_6) with a little fluorspar (CaF_2), which lowers the temp. of the melt and electrolysed at about 1173 K. The oxygen evolved at the anode burns the carbon anode producing carbon dioxide and carbon monoxide, due to this anodes should be replaced periodically.

Cathode: $Al^{3+} + 3e^- \longrightarrow Al$

Anode : $C + O^{2-} \longrightarrow CO + 2e^-$

$C + 2O^{2-} \longrightarrow CO_2 + 4e^-$

7. Silver

The powdered ore is treated with a dilute solution of sodium cyanide (0.5%) for several hours and the mixture is continously agitated by a current of air. Silver from the ore goes to the solution in the form of complex ion, $[Ag(CN)_2]^-$.

$2Ag_2S + 8CN^- + O_2 + 2H_2O \longrightarrow 4[Ag(CN)_2]^- + 4OH^- + 2S$.

The soluble silver complex is removed and treated with zinc dust silver precipitates out.

$2[Ag(CN)_2]^- + Zn \longrightarrow 2Ag\downarrow + [Zn(CN)_2]^{2-}$

Further silver is purified by electrolysis of a solution of silver nitrate and nitric acid having impure silver as anode and pure strip of silver as cathode. On passing electric current pure silver gets deposited at cathode whereas impurities fall down below anode as *anode mud*

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

At anode : $Ag \longrightarrow Ag^+ + e^-$.