General Principles & Processes of Isolation of Metals

Types of Ores:

Ores may be divided into four groups

- **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.
- **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.
- **Sulphurised Ores**: These ores consist of sulfides of metals like iron, lead, mercury etc. Examples are iron pyrites (FeS2). galena (PbS), Cinnabar (HgS)
- **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.

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.

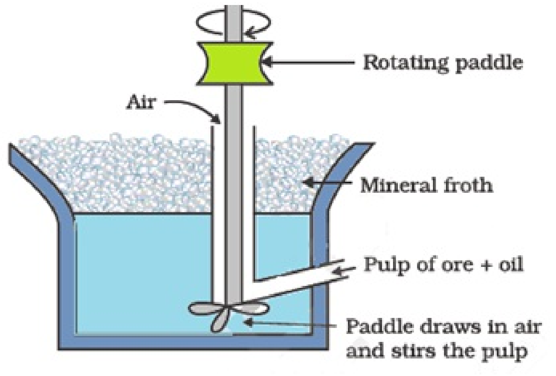
- Crushing of the ore
- Dressing or concentration of the ore.
- Reduction of metal.
- Purification or refining of the metal

Concentration

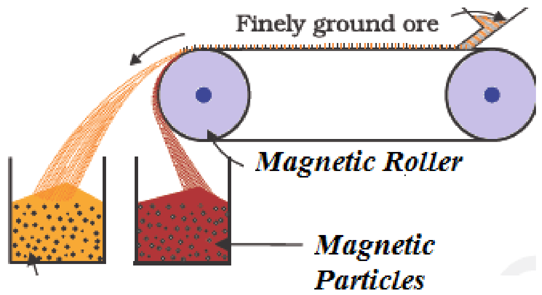
Physical Method

Gravity separation: The powdered ores is agitated with water or washed with a running stream of water. The heavy ore particles of sand, clay etc. are washed away.

Froth Floatation Process*:* The finely divided ore is introduced into water containing small quantity of oil (e.g. Pine Oil). The mixture is agitated violently with air a froth is formed which carries away along with it the metallic particles on account of the surface tension forces. The froth is transferred to another bath where gangue-free ore settles down**.**



Electro Magnetic Separator:. A magnetic separator consists of a belt moving over two rollers, one of which is magnetic. The powdered ore is dropped on the belt at the other end. Magnetic portion of the ore is attracted by the magnetic roller and falls near to the roller while the non-magnetic impurity falls farther off



Chemical Methods

Calcination: Carbonate or hydrated oxide ores are subjected to the action of heat in order of expel water from hydrated oxide and carbon dioxide from a carbonate.

Examples:

$ZnCO_3$ --> $ZnO + CO_2$

$CaCO_3$ --> $CaO + CO_2$

$Al_2O_3 \times 2H_2O$ --> $Al_2O_3 + 2H_2O$

$2Fe_2O_3 \times 3H_2O$ --> $2Fe_2O_3 + 3H_2O$

Roasting: Sulphide ores either are subjected to the action of heat and air at temperatures below their melting points in order to bring about chemical changes in them.

Examples:

$2PbS + 3O_2$ --> $2PbO + 2SO_2$

$PbS + 2O_2$ --> $PbSO_4$

$2ZnS + 3O_2$ --> $2ZnO + 2SO_2$

$ZnS + 2O_2$ --> $ZnSO_4$

$CuS + 2O_2 \rightarrow CuSO_4$

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

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.

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

Reduction of Free Metal:

Smelting:

Reduction of a metal from its ore by a process involving melting

Several reducing agents such as sodium, magnesium and aluminium are used for reduction.

The calcinated or roasted ore is mixed with carbon (coal or coke) and heated in a reverberatory or a blast furnace.

Carbon and carbon monoxide produced by incomplete combustion of carbon reduce the oxide to the metal.

$$\left.\begin{array}{l} PbO + C \rightarrow Pb + CO \\ PbO + CO \rightarrow Pb + CO_2 \\ SnO_2 + 2C \rightarrow Sn + 2CO \end{array}\right\} \text{Carbon reduction process}$$

$$\left.\begin{array}{l} Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 \\ 3Mn_3O_4 + 8Al \rightarrow 9Mn + 4Al_2O_3 \end{array}\right\} \text{Aluminium reduction process (Gold - Schimidt alumino thermic process)}$$

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.

- **Acidic fluxes** like silica, borax etc are used when the gangue is basic such as lime or other metallic oxides like MnO, FeO, etc
- **Basic fluxes** like CaO, lime stone ($CaCO_3$), magnesite ($MgCO_3$), haematite (Fe_2O_3) etc are used when the gangue is acidic like silica, P_4O_{10} etc.

Refining

> 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

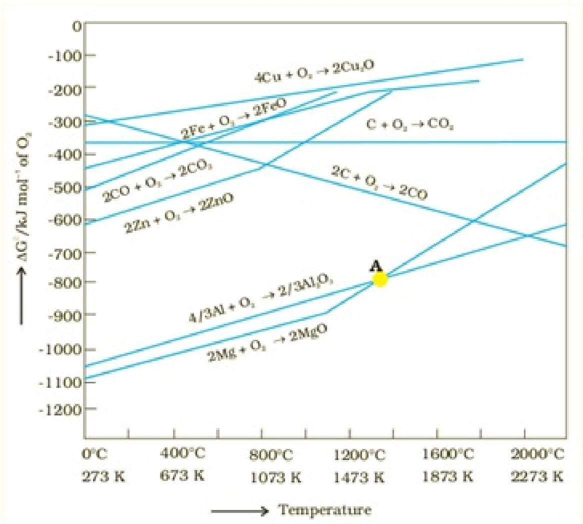
> c) Cupellation d) Poling

e) Elecrolytic refining f) Bessemerisation

Thermodynamic Principles of Metallurgy:

$\Delta G = \Delta H - TS$

or $\Delta G^0 = -RT \ln K$



An element A can reduce element B if ΔG value for oxidation of A to AO is lower than the ΔG value for oxidation of B to BO.

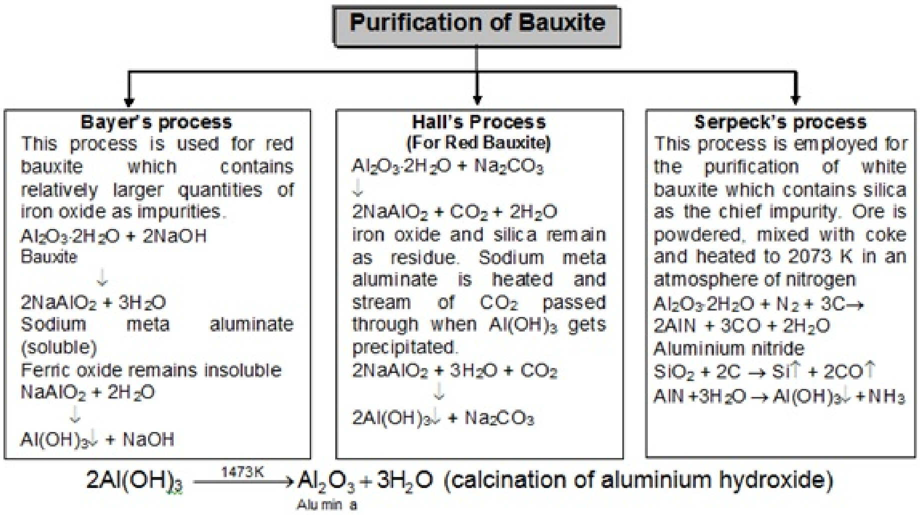
i.e. $\Delta G_{(A \rightarrow AO)} < \Delta G_{(B \rightarrow BO)}$

Extraction of Aluminium:

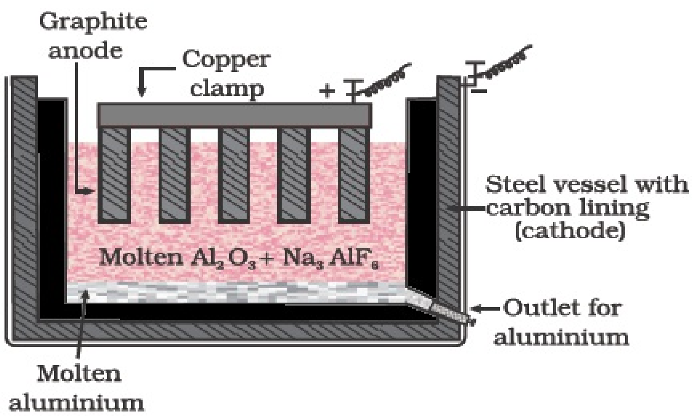
Important Ores of Aluminium:

- Bauxite : $Al_2O_3 \times 2H_2O$Cryolite: Na_3AlF_6
- Feldspar: $K_2OAl_2O_3 \times 6SiO_2$ or $KAlSi_3O8$
- Mica: $K2O \times 3Al_2O_3 \times 6SiO_2 \times 2H_2O$
- Corundum: Al_2O_3
- Alumstone or Alunite: $K_2SO_4 \times Al_2(SO_4)_3 \times 4Al(OH)_3$

Purification of Bauxite



Electrolysis of fused pure alumina (Hall & Herwlt Method)



The addition of cryolite (Na_3AlF_6) and fluorspar (CaF_2) makes alumina a good conductor of electricity and lowers its Fusion temperature from 2323 to 1140 K. the reaction taking place during electrolysis.

$Na_3AlF_6 \rightleftharpoons 3NaF + AlF_3$

$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$

At cathode

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

At anode

$F^- \longrightarrow F + e^-$

$2Al_2O_3 + 12\ F \longrightarrow 4AlF_3 + 3O_2$

$2C + O_2 \longrightarrow 2CO$

$2CO + O_2 \longrightarrow 2CO_2$

Refining of Aluminium:

The graphite rods dipped in pure aluminium and Cu–Al alloy rod at the bottom in the impure aluminium work as conductors. On electrolysis, aluminium is deposited at cathode from the middle layer and equivalent amount of aluminium is taken up by the middle layer from the bottom layer (impure aluminium). Therefore, aluminium is transferred from bottom to the top layer through middle layer while the impurities are left behind. Aluminium thus obtained is 99.98% pure.

Hyrdrometallurgy (solvent extraction)

Solvent extraction is the latest separation technique and has become popular because of its elegance, simplicity and speed. The method is based on preferential solubility principles.

Solvent or liquid-liquid extraction is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents, one of which is usually water and the other an organic solvent such as benzene, carbon tetrachloride or chloroform. In certain cases, the solute can be more or less completely transferred into the organic phase.

Extraction of Iron:

a) Important Ores of Iron:

Haematite Fe_2O_3 (red oxide of iron)

Limonite $Fe_2O_3 \times 3H_2O$ (hydrated oxide of iron)

Magnetite Fe_3O_4 (magnetic oxide of iron)

Varieties of Iron

Pig or Cast Iron	Wrought Iron	Steel
⇒ most impure form ⇒ 2.5 – 5% carbon and other impurities like Mn, Si, S and P ⇒ It is hard and Brittle and hence cannot be moulded by hammering	⇒ Purest form of iron ⇒ 0.1 – 0.25% carbon ⇒ Its is ductile, soft and malleable.	It is in between pig iron and wrought iron. ⇒ 0.25 to 2% carbon

Extraction of Cast Iron:

Reactions taking place in the blast furnace

Zone of combustion

$$\underset{(Coke)}{C} + O_2 \longrightarrow CO_2$$

Zone of reduction

$Fe_2O_3 + 3CO \longrightarrow Fe + CO_2$

Zone of reduction

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

$FeO + CO \longrightarrow Fe + CO_2$

Zone of slag formation

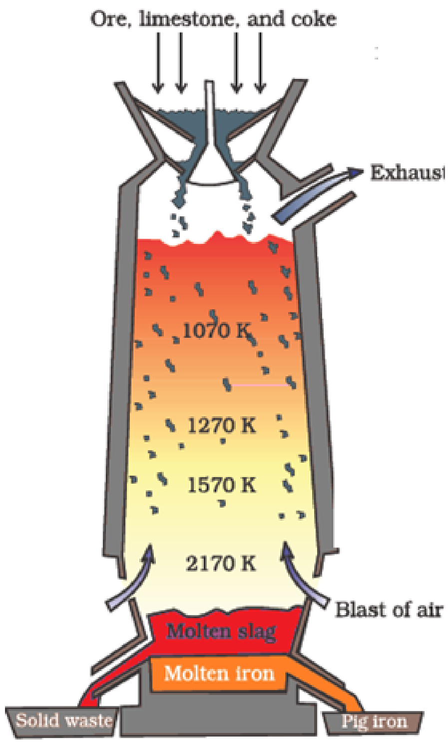
$$\underset{(lime\ stone)}{CaCO_3} \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow \underset{Fusible\ slag}{CaSiO_3};$$

Zone of fusion

lower part of furnace

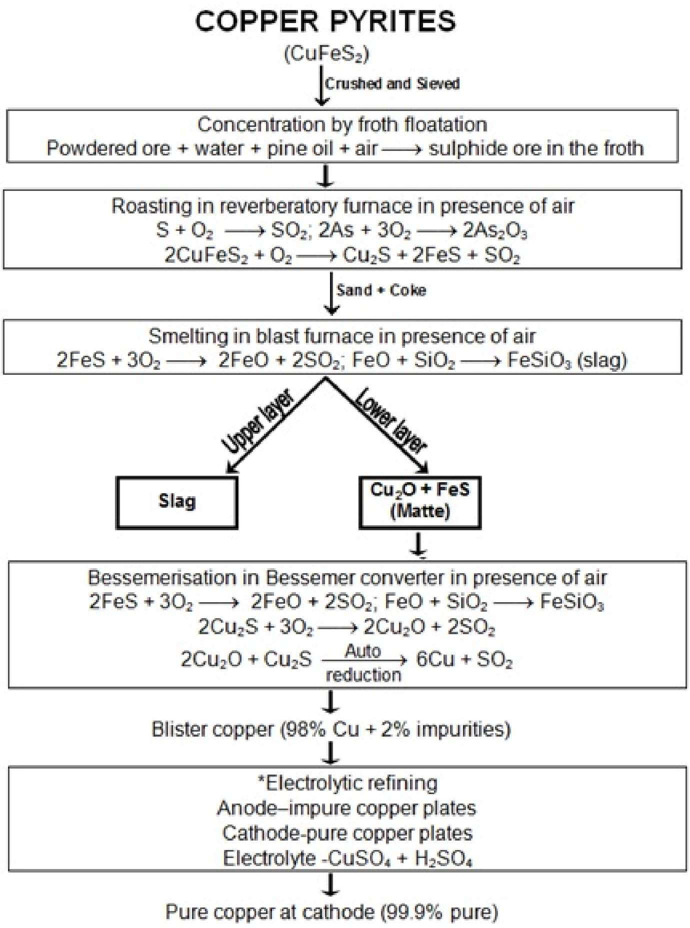
Molten iron is heavier than from molten slag. The two liquids are periodically tapped off. The molten iron tapped off from the furnace is solidifed into blocks called 'pigs'.



Extraction of Copper:

Ores of Copper:

- Copper glance (chalcocite) : Cu_2S
- Copper pyrites (Chalopyrites): $CuFeS_2$
- Malchite : $Cu(OH)_2 \times CuCO_3$
- Cuprite or Ruby copper: Cu_2O
- Azurite : $Cu(OH)_2 \times 2CuCO_3$



Refining of Metals:

Zone refining (Fractional crystallization): This method is employed for preparing extremely pure metals. This method is based upon the principle that when a molten solution of the impure metal is allowed to cool, the pure metal crystilises out while the impurities remain in the melt.

Electro-refining: In this method, the impure metal is converted into a block which forms the anode while cathode is a rod or plate of pure metal. These electrodes are suspended in an electrolyte which is the solution of a soluble salt of the metal usually a double salt of the metal. When electric current is passed, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ion. The soluble impurities present in the crude metal anode go into the solution while the insoluble impurities settle down below the anode as anode mud.

Van-Arkel Method: In this method, the metal is converted into it volatile unstable compound such as iodide leaving behind the impurities. The unstable compound thus formed is decomposed to get the pure metal.

$$Ti(s) + 2I_2(s) + \xrightarrow[540K]{} TiI_4(g) \xrightarrow[Ti(s)]{1700K} Ti + 2I_2(g)$$

Cupellation and Poling are used for refining of metals, cupellation is contain impurities of other metals with traces of lead are removed from silver by heating impure silver with a blast of air in a cupel (an oval shaped pan made up of bone ash) in which lead is oxidised to lead oxide (PbO) which being volatile escapes leaving behind pure silver.Poling is used for refining of such metals which contain impurities of its own oxide. In this process, the molten impure metal is stored with green wooden poles. At the high temperature of the molten metal, wood liberates methane which reduces the oxide of the metal to free metal.

$$3Cu_2O + CH_4 \longrightarrow 6Cu + 2H_2O + CO$$