General Principles and Processes of Isolation of Elements

Concentration of Ores

Overview

A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry.

A particular element may occur in a variety of compounds. The process of metallurgy and isolation should be such that it is chemically feasible and commercially viable. Still, some general principles are common to all the extraction processes of metals.

For obtaining a particular metal, first we look for minerals which are naturally occurring chemical substances in the earth's crust obtainable by mining. Out of many minerals in which a metal may be found, only a few are viable to be used as sources of that metal. Such minerals are known as **ores.**

Occurrence of Metals

Elements vary in abundance.

Among metals, aluminum is the most abundant.

It is the third most abundant element in earth's crust (8.3% approx. by weight).

It is a major component of many igneous minerals including mica and clays.

Many gemstones are impure forms of Al2O3 and the impurities range from Cr (in 'ruby') to Co (in 'sapphire').

Iron is the second most abundant metal in the earth's crust. It forms a variety of compounds and their various uses make it a very important element. It is one of the essential elements in biological systems as well.

Principal Ores of Some Important Metals

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[Al_2(OH)_4 Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

Concentration of Ores

Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as concentration, dressing or benefaction.

It involves several steps and selection of these steps depends upon the differences in physical properties of the compound of the metal present and that of the gangue.

The type of the metal, the available facilities and the environmental factors are also taken into consideration.

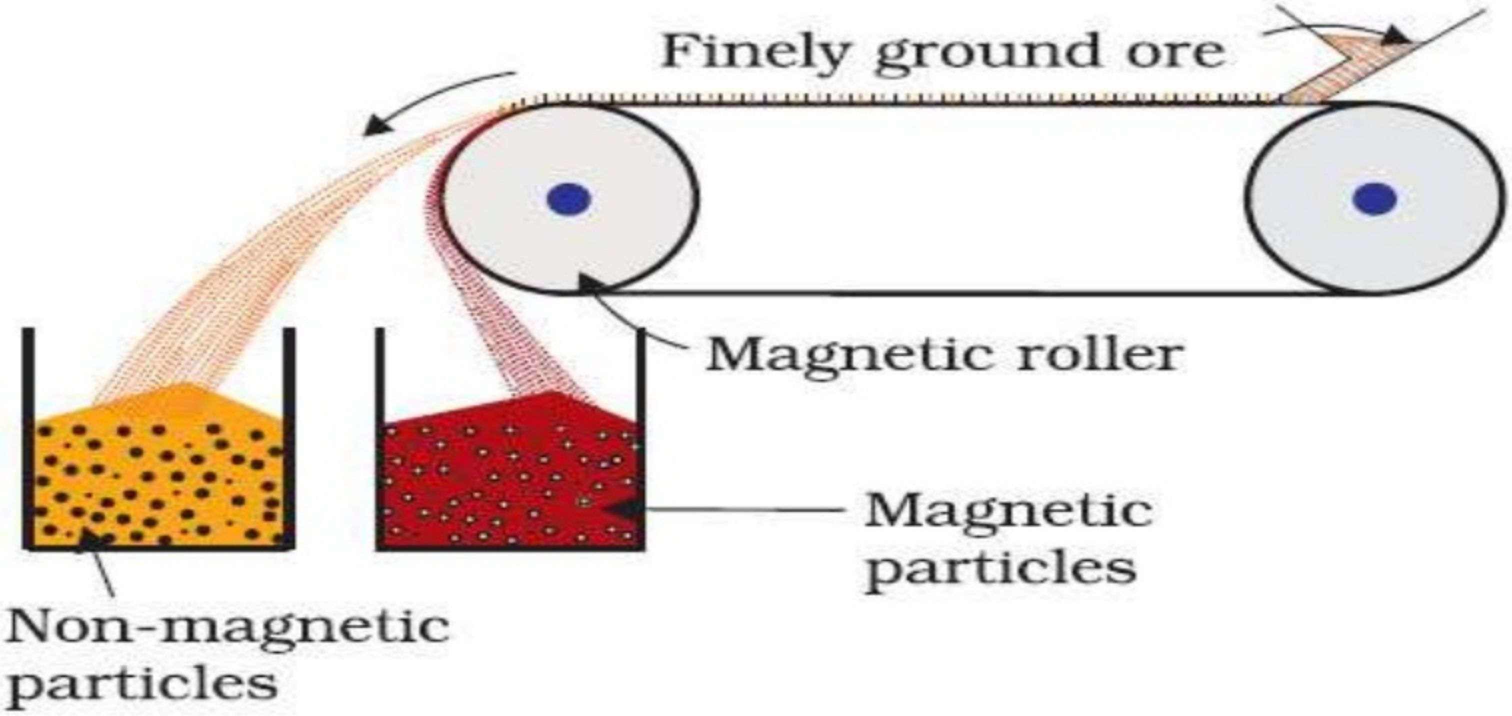
Magnetic Separation

This is based on differences in magnetic properties of the ore components.

If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out (e.g., in case of iron ores).

The ground ore is carried on a conveyer belt which passes over a magnetic roller

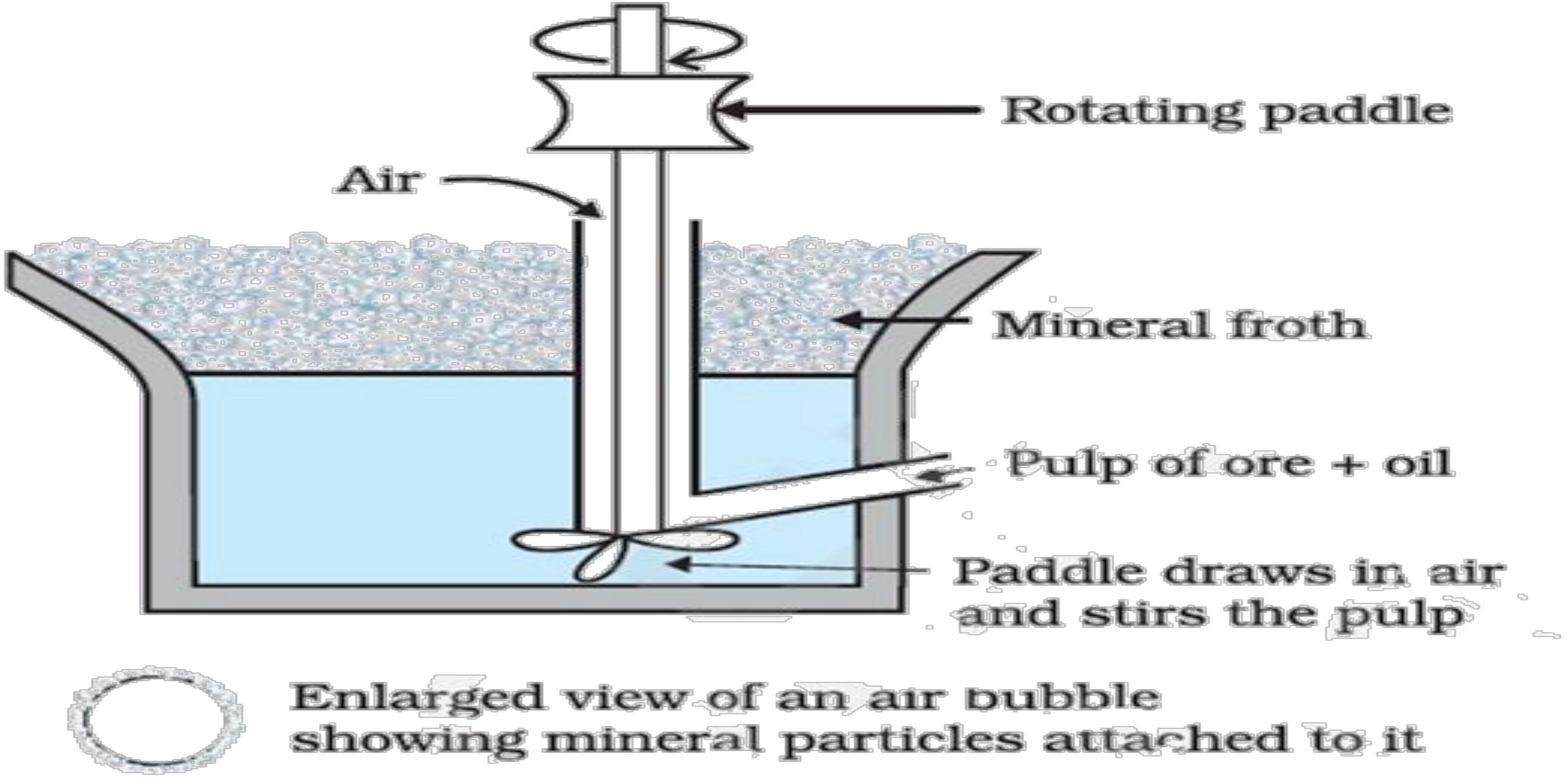
Magnetic Separation



Froth Floatation Method

This method has been in use for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it, *collectors and froth stabilizers are added. Collectors (e. g., pine oils, fatty* acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilisers (e. g., cresols, aniline .) stabilize the froth.

The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles



Froth floatation process

Extraction of Crude Metal from Concentrated Ore

The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Oxides are easier to reduce (for the reason see box). Thus isolation of metals from concentrated ore involves two major steps *viz.,*

i. Conversion to oxide

ii. Reduction of the oxide to metal.

A. Conversion to oxide

i. **Calcination :** Calcinaton involves heating when the volatile matter escapes leaving behind the metal oxide:

$$Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3\ (s) + xH_2O(g)$$

$$ZnCO_3\ (s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

$$CaCO_3.MgCO_3(s) \xrightarrow{\Delta} CaO(s) + MgO(s\ ) + 2CO_2(g)$$

Conversion to oxide

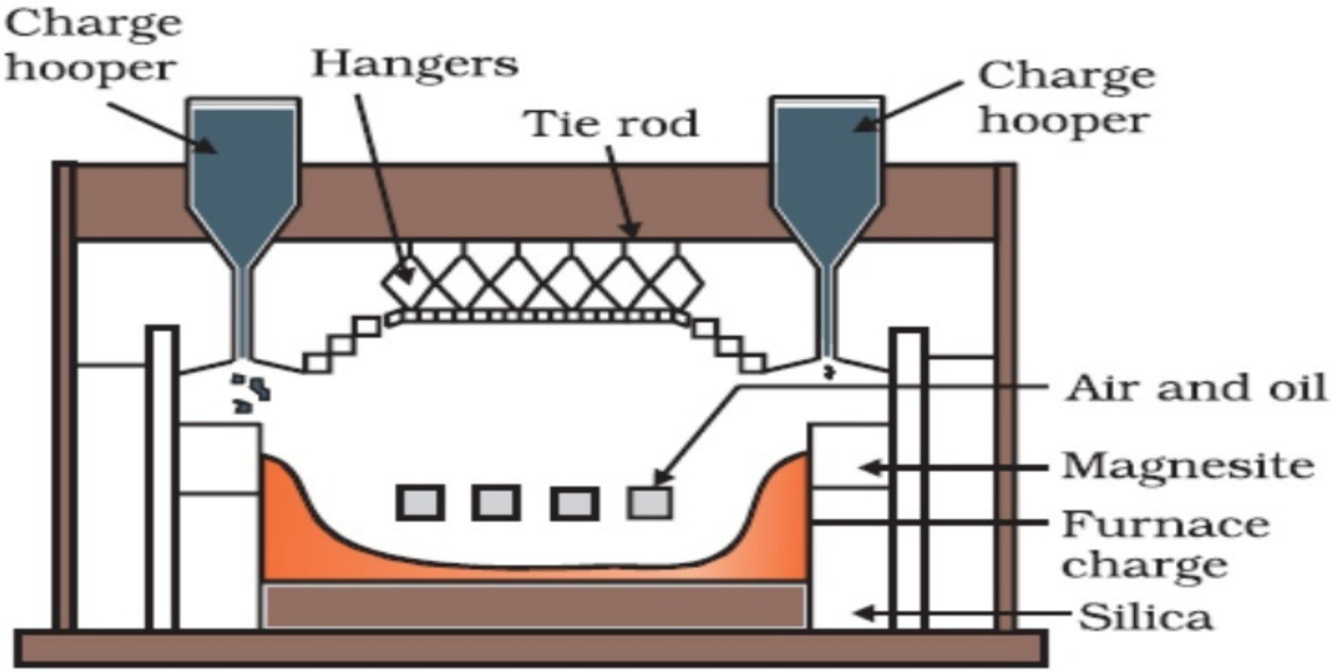
Roasting : In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. Some of the reactions involving sulphide ores are:

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

The sulphide ores of copper are heated in reverberatory furnace. If the ore contains iron, it is mixed with silica before heating. Iron oxide 'slags of ' **as iron silicate and** copper is produced in the form of *copper matte which contains Cu2S and FeS.*

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

A section of a modern reverberatory furnace



B. Reduction of oxide to the metal

Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent (C or CO or even another metal). The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.

Some metal oxides get reduced easily while others are very difficult to be reduced (reduction means electron gain or electronation). In any case, heating is required. To understand the variation in the temperature requirement for thermal reductions *(pyrometallurgy) and to predict which element will suit as the* reducing agent for a given metal oxide, Gibbs energy interpretations are made.

Blast furnace

In the Blast furnace, reduction of iron oxides takes place in different temperature ranges.

Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself.

The burning of coke therefore supplies most of the heat required in the process. The CO and heat moves to upper part of the furnace.

In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO. Thus, the reduction reactions taking place in the lower temperature range and in the higher temperature range, depend on the points of corresponding intersections in the Δ_rG^0 vs T plots.

Blast furnace

These reactions can be summarised as follows:

At 500 – 800 K (lower temperature range in the blast furnace) –

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$$

$$Fe_3O_4 + 4\ CO \rightarrow 3Fe + 4\ CO_2$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$

At 900 – 1500 K (higher temperature range in the blast furnace):

$$C + CO_2 \rightarrow 2\ CO$$

$$FeO + CO \rightarrow Fe + CO_2$$

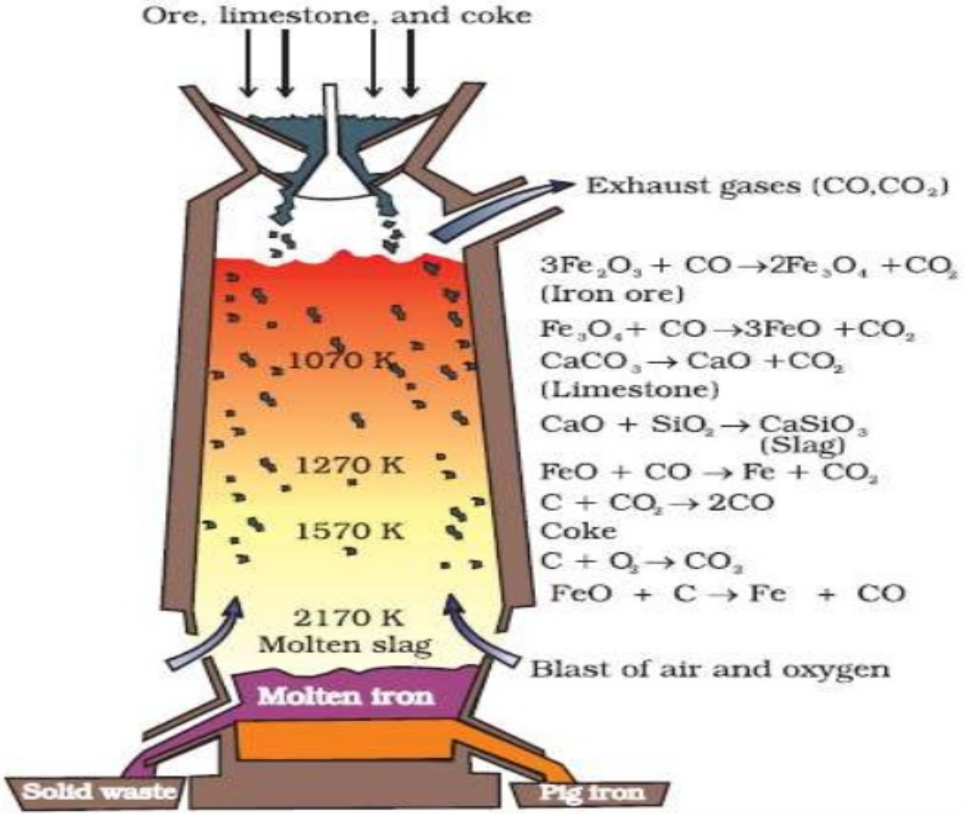
Blast furnace

Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

The iron obtained from Blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as *pig iron and cast into* variety of shapes. *Cast iron is different from pig iron and is made by melting pig iron* with scrap iron and coke using hot air blast.

It has slightly lower carbon content (about3%) and is extremely hard and brittle.

BLAST FURNACE



Extraction of iron from its oxides

Oxide ores of iron, after concentration through calcination/roasting (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with limestone and coke and fed into a *Blast furnace from* its top. Here, the oxide is reduced to the metal. Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is: $FeO(s) + C(s) \rightarrow Fe(s/l) + CO\ (g)$

It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO:

$$FeO(s) \rightarrow Fe(s) + \frac{1}{2}O_2(g) \qquad [\Delta G_{(FeO,\ Fe)}]$$

$$C(s) + \frac{1}{2}O_2\ (g) \rightarrow CO\ (g) \qquad [\Delta G_{(C,\ CO)}]$$

Metallurgy of Aluminium

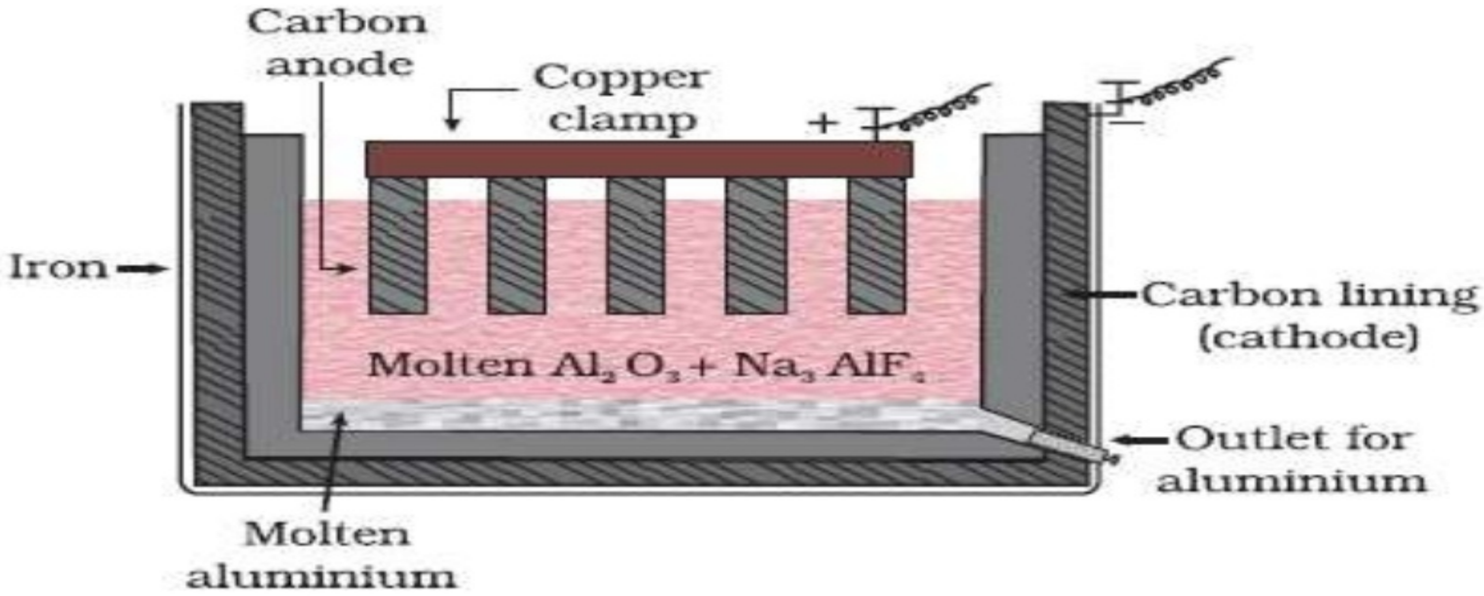
In the metallurgy of aluminium, purified Al2O3 is mixed with Na3AlF6 or CaF2 which lowers the melting point of the mix and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal.

The overall reaction may be taken as:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

This process of electrolysis is widely known as ***Hall-Heroult process.***

Electrolytic cell for the extraction of aluminum



Refining

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity.

Some of them are listed below :

i. **Distillation**
ii. **Liquation**
iii. **Electrolysis**
iv. **Zone refining**
v. **Chromatographic methods**

A. Distillation

This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

B. Liquation

In this method a low melting metal like tin can be made to flow on a sloping surface.

In this way it is separated from higher melting impurities.

C. Electrolytic refining

In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal.

The more basic metal remains in the solution and the less basic ones go to the anode mud. This process is also explained using the concept of electrode potential, over potential, and Gibbs energy. The reactions are:

$$\text{Anode:} \quad M \rightarrow M^{n+} + ne^-$$

$$\text{Cathode:} \quad M^{n+} + ne^- \rightarrow M$$

Electrolytic refining : Copper

Copper is refined using an **electrolytic** method : Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:

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

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

Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining.

D. Zone refining

This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal.

The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone.

The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off.

This is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

E. Chromatographic methods

This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

The mixture is put in a liquid or gaseous medium which is moved through the adsorbent.

Different components are adsorbed at different levels on the column.

Later the adsorbed components are removed (eluted) by using suitable solvents (eluant). Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method is given the name.

Chromatographic methods

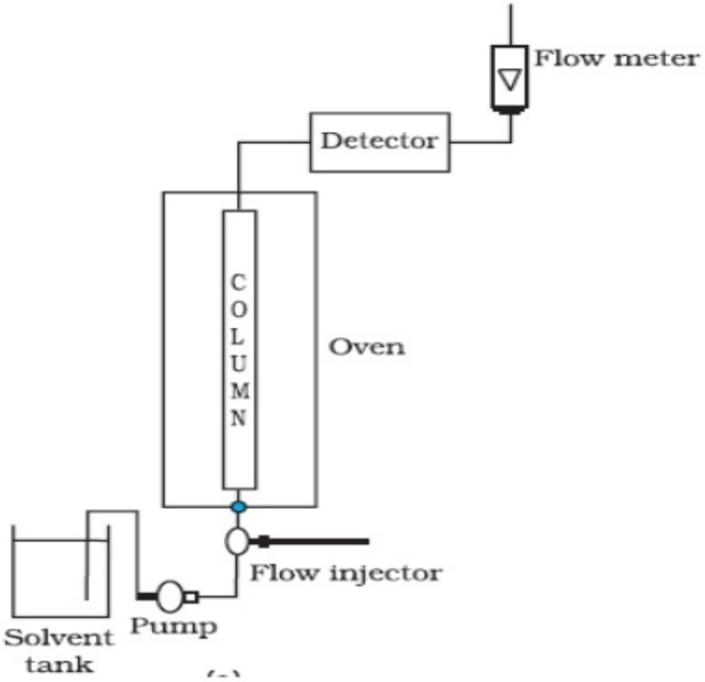
and the moving medium containing a solution of the components is in liquid form. This is an example of column chromatography.

This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

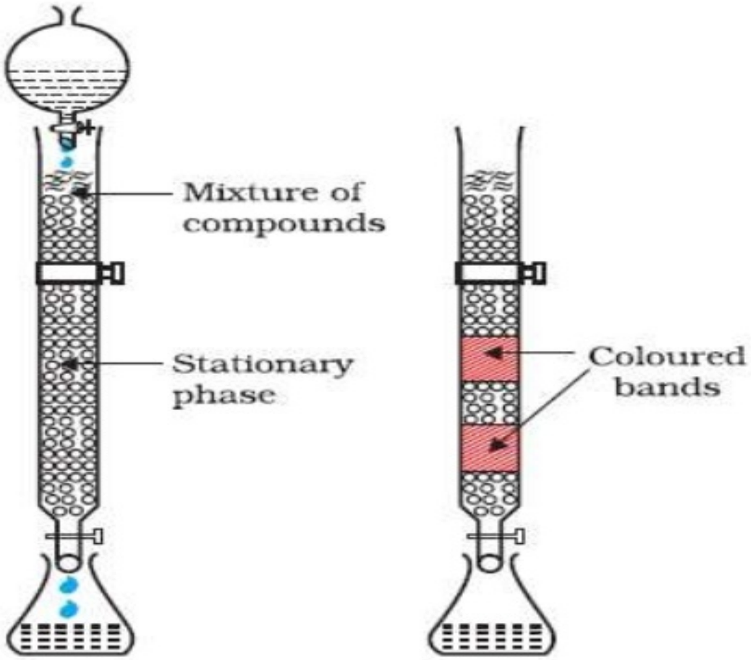
There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc.

Chromatographic methods

Industrial Method



Laboratory Method



Uses of Aluminium

i. Aluminium foils are used as wrappers for chocolates.

ii. The fine dust of the metal is used in paints and lacquers.

iii. Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides.

iv. Wires of aluminium are used as electricity conductors.

v. Alloys containing aluminium, being light, are very useful.

Uses of Copper

Copper is used for making wires used in electrical industry and for water and steam pipes.

It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin) and coinage alloy (with nickel).

Uses of Zinc

i. Zinc is used for galvanising iron.

ii. It is also used in large quantities in batteries, as a constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40–50%).

iii. Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

Uses of Iron

i. Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes , toys, etc.
ii. It is used in the manufacture of wrought iron and steel.
iii. Wrought iron is used in making anchors, wires, bolts, chains and agricultural implements.
iv. Steel finds a number of uses.
v. Alloy steel is obtained when other metals are added to it.
vi. Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes, chrome steel for cutting tools and crushing machines, and stainless steel for cycles, automobiles, utensils, pens, etc.