GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

Minerals are naturally occurring chemical substances in the earth's crust obtainable by mining.
Ores are only the few viable minerals from which the metal can be extracted.
Gangue is the contaminated or undesired part of the ore.
Metallurgy is the entire scientific and technological process used for isolation of the metal from its ores.

Aluminium	Bauxite
Iron	Kaolinite Haematite Magnetite Siderite Iron pyrites
Copper	Copper pyrites Malachite Cuprite Copper glance
Zinc	Zinc blende or sphalerite Calamine Zincite

Concentration, dressing or benefaction is the removal of the unwanted materials from the ore.

a) **Hydraulic washing** is based on the differences in gravities of the ore and the gangue particles.
b) **Magnetic separation** is based on differences in magnetic properties of the ore components.
c) **Froth flotation method** is used to remove gangue from sulphide ores. A suspension of the powdered ore is made with water and collectors (e.g. pine oils) and froth stabilizers (e.g. resols) are added. Mineral particles are wetted by oils and gangue by water. On agitation froth is formed carrying mineral particles and is skimmed from the top.
   (i) **Leaching** is used if the ore is soluble in some suitable solvent

The isolation of metals from concentrated ore involves two major steps *viz*.,
(a) Conversion to oxide
(b) Reduction of the oxide to metal.

(a) Conversion to oxide

(i) *Calcination*:

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

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

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

(ii) Roasting:

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

If the ore contains iron, it is mixed with silica before heating.

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

(b) Reduction of oxide to metal

$$M_xO_y + yC \rightarrow xM + y\,CO$$

Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations.
$\Delta G = \Delta H - T\Delta S$ .Where ΔG is the change in Gibbs energy, ΔH is the enthalpy change and ΔS is the entropy change.
$\Delta G^{\ominus} = -RT\ln K$
K is the equilibrium constant of the 'reactant – product' system at the temperature,T. A negative ΔG implies a positiive K in equation

1. When the value of ΔG is negative, only then the reaction will proceed. If ΔS is positive, on increasing the temperature (T), the value of T ΔS would increase ($\Delta H < T\,\Delta S$) and then ΔG will become negative.

2. If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is negative , the overall reaction will occur. So the process of interpretation involves coupling of the two reactions, getting the sum of their ΔG and looking for its magnitude and *sign*. Such coupling is easily understood through Gibbs energy (ΔG) vs T plots for formation of the oxides.

$$M_xO(s) \rightarrow xM\ (\text{solid or liq}) + \frac{1}{2}O_2\,(g)$$

$$xM(s \text{ or } l) + \frac{1}{2}O_2(g) \rightarrow M_xO(s) \qquad [\Delta G^{\ominus}_{(M,MxO)}]$$

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

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad [\Delta G_{(CO,\,CO_2)}]$$

$$\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g) \qquad [\frac{1}{2}\,\Delta G_{(C,\,CO_2)}]$$

$$M_xO(s) + C(s) \rightarrow xM(s \text{ or } l) + CO(g)$$

$$M_xO(s) + CO(g) \rightarrow xM(s \text{ or } l) + CO_2(g)$$

$$M_xO(s) + \frac{1}{2}C(s) \rightarrow xM(s \text{ or } l) + \frac{1}{2}CO_2(g)$$

Applications

(a) Extraction of iron from its oxides

(b) Extraction of copper from cuprous oxide [copper(I) oxide]

(c) Extraction of zinc from zinc oxide

Electro chemical principles of metallurgy

$$\Delta G^{\ominus} = -nE^{\ominus}F$$

here n is the number of electrons and E is the electrode potential of the redox couple formed in the system.

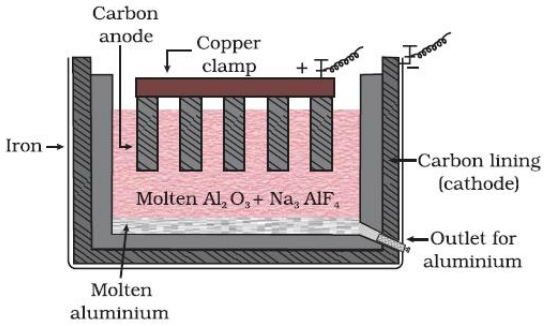
$$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$$

ALUMINIUM

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

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

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.



Electrolytic cell for the extraction of aluminium

Cathode: $Al^{3+}(melt) + 3e^- \rightarrow Al(l)$

Anode: $C(s) + O^{2-}(melt) \rightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}(melt) \rightarrow CO_2(g) + 4e^-$

Copper from Low Grade Ores and Scraps

Copper is extracted by *hydrometallurgy* from low grade ores.

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

Oxidation Reduction

$$2Cl^-(aq) + 2H_2O(l) \longrightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$$

The G0 for this reaction is + 422 kJ. When it is converted to E0, we get E0 = – 2.2 V. Naturally, it will require an external e.m.f. that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions. Thus, Cl2 is obtained by electrolysis giving out H2 and aqueous NaOH as byproducts. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.

Extraction of gold and silver involves leaching the metal with CN–.

$$4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \longrightarrow 4[Au(CN)_2]^- + 4OH^-(aq)$$
$$2[Au(CN)_2]^-(aq) + Zn(s) \longrightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$$

Refining

(a) Distillation

(b) Liquation

(c) Electrolysis

(d) Zone refining

(e) Vapour phase refining

(f) Chromatographic methods

These are described in detail here.

(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 which you have seen in previous sections. The reactions are:

$$Anode: M \longrightarrow M^{n+} + ne^{-}$$

$$Cathode: M^{n+} + ne^{-} \longrightarrow M$$

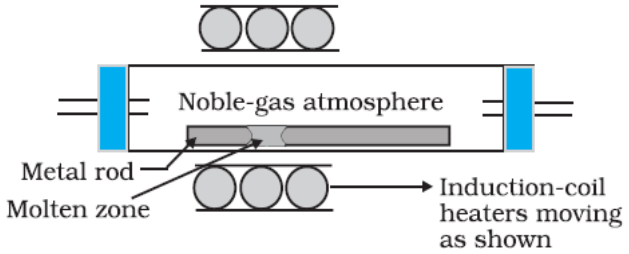
Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:

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

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. Zinc may also be refined this way.

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



Zone refining process

(e) Vapour phase refining

In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal. So, the two requirements are:

(i) the metal should form a volatile compound with an available reagent,

(ii) the volatile compound should be easily decomposable, so that the recovery is easy.

Following examples will illustrate this technique.

Mond Process for Refining Nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:

$$Ni + 4CO \longrightarrow (330 - 350K)\ Ni(CO)_4$$

The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal:

$$Ni(CO)_4 \longrightarrow (450 - 470K) Ni + 4CO$$

vanArkel Method for Refining Zirconium or Titanium: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent,volatilizes:

$$Zr + 2I_2 \longrightarrow ZrI_4$$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI_4 \longrightarrow Zr + 2I_2$$

(f) 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 methodis given the name. In one such method the column of Al2O3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form. This is an example of *column chromatography*. There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc.

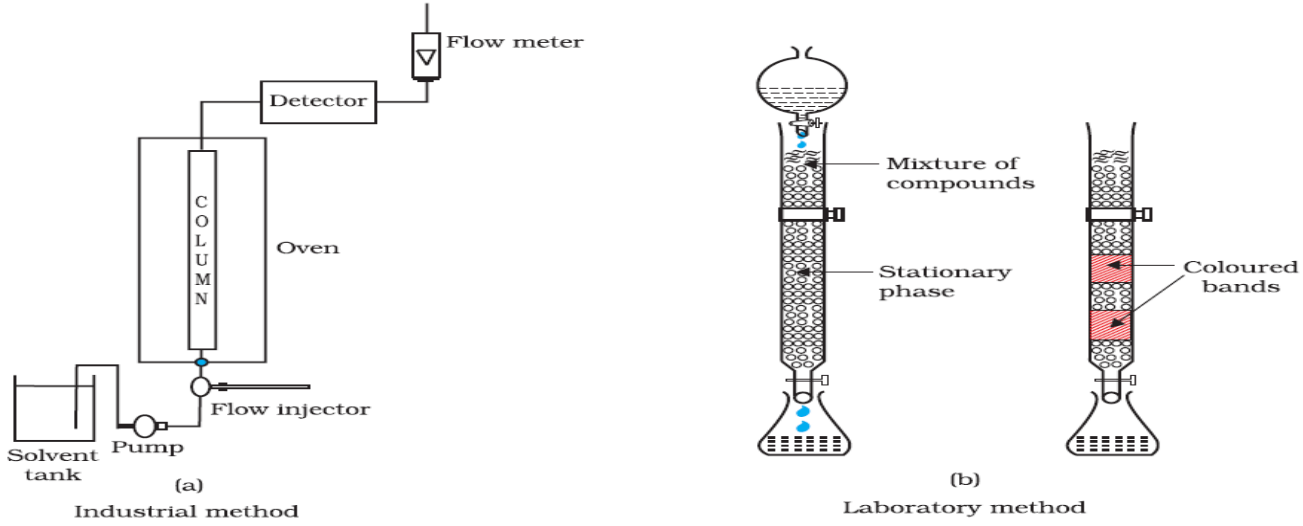


Fig. 6.8: Schematic diagrams showing column chromatography

Aluminium	Electrolysis of bauxite dissolved in molten cyolite	For the extraction, a good source of electricity is required.
Iron	Reduction of the oxide with CO and coke in a blast furnace	Temperature approaching 2170K is required.
Copper	Roasting of sulphide partially and reduction	Its self reduction in a specially designed converter. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc	Roasting followed by reduction with coke	The metal may be purified by fractional distillation