

General Principles and Processes of Isolation of Elements

MINERALS AND ORES

- **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**.
- **All ores are Minerals but all Minerals are not ores**

METALLURGY

- Rarely, an ore contains only a desired substance.
- It is usually contaminated with earthly or undesired materials known as **gangue**.
- **The extraction and isolation** of metals from ores involve the following major steps:
 - **Concentration of the ore,**
 - **Isolation of the metal from its concentrated ore, and**
 - **Purification of the metal.**
- The entire scientific and technological process used for isolation of the metal from its ores is known as **metallurgy**.

OCCURRENCE OF METALS

Table 6.1: Principal Ores of Some Important Metals

Metal	Ores	Composition
Aluminium	Bauxite	$\text{AlO}_x(\text{OH})_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[\text{Al}_2(\text{OH})_4 \text{Si}_2\text{O}_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	FeCO_3
	Iron pyrites	FeS_2
Copper	Copper pyrites	CuFeS_2
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	ZnCO_3
	Zincite	ZnO

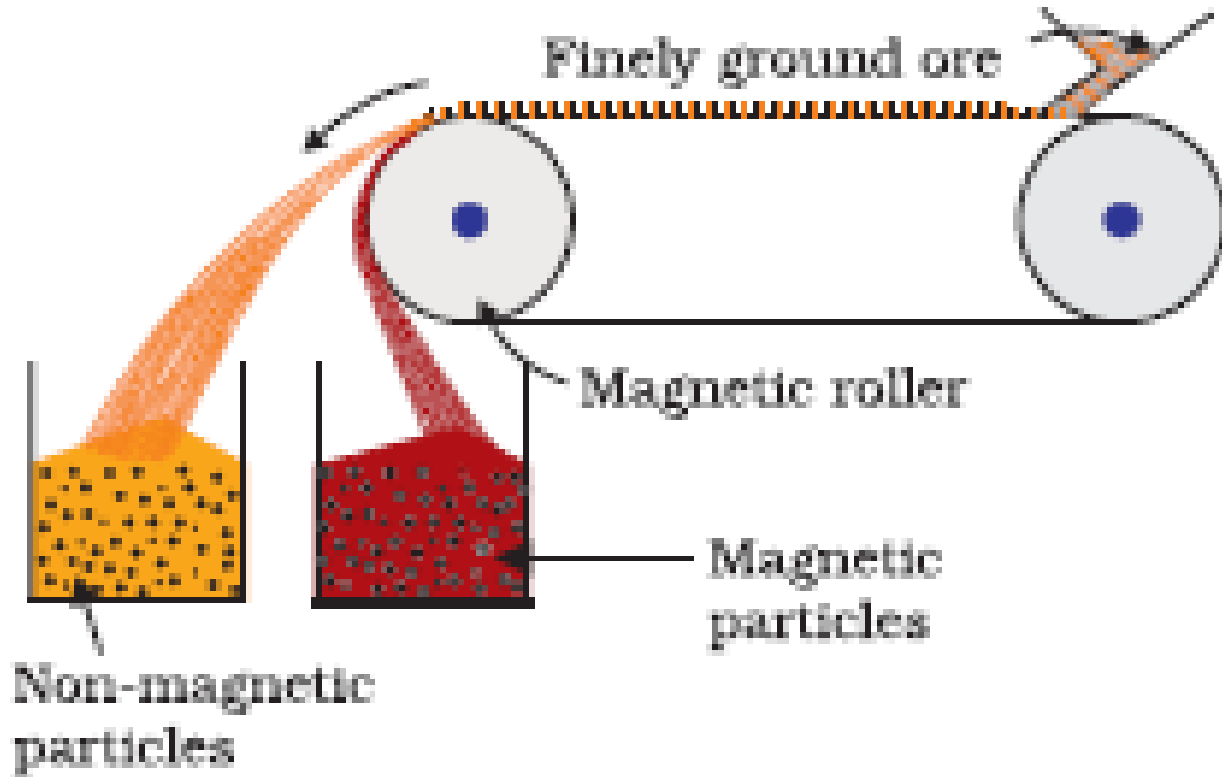
CONCENTRATION OF ORES

- 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
 1. differences in physical properties of the compound of the metal present and
 2. that of the *gangue.*
 3. *The type of the metal,*
 4. *the available facilities and*
 5. *the environmental factors are also taken into consideration.*

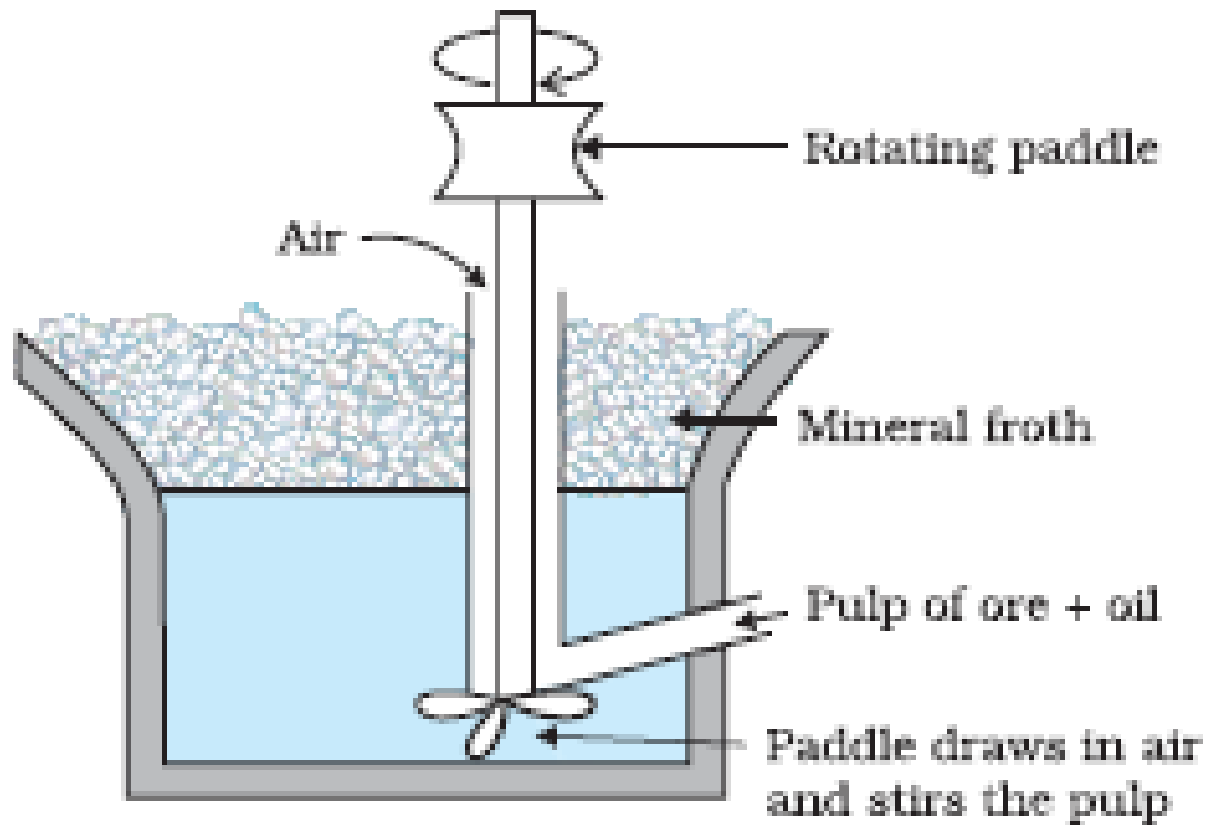
HYDRAULIC WASHING

- This is based on the differences in gravities of the ore and the *gangue* particles.
- It is therefore a type of *gravity separation*.
- *In one such process*, an upward stream of running water is used to wash the powdered ore.
- The lighter gangue particles are washed away and the heavier ores are left behind.

MAGNETIC SEPARATION



FROTH FLOATATION METHOD



Enlarged view of an air bubble showing mineral particles attached to it

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 stabilisers 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) stabilise 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 METHOD

- Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using '*depressants*'.
- *For* example, in case of an ore containing ZnS and PbS, the depressant used is NaCN.
- It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

LEACHING

- Leaching is often used if the ore is soluble in some suitable solvent.

(a) Leaching of alumina from bauxite

The principal ore of aluminium, bauxite, usually contains SiO_2 , iron oxides and titanium oxide (TiO_2) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473 – 523 K and 35 – 36 bar pressure. This way, Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving the impurities behind:



The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation:

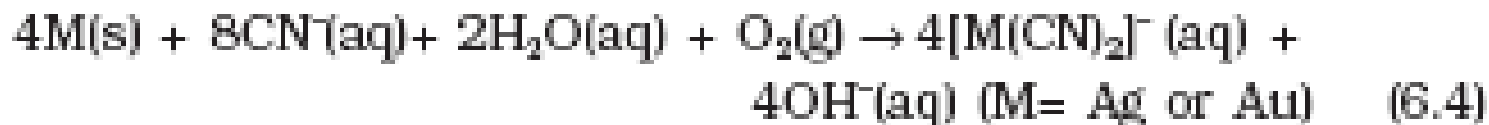


The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3 :



(b) Other examples

In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement:



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
- Thus isolation of metals from concentrated ore involves two major steps *viz.*,
 - (a) conversion to oxide, and**
 - (b) reduction of the oxide to metal.**

(a) Conversion to oxide

(i) **Calcination:** Calcination involves heating when the volatile matter escapes leaving behind the metal oxide:



(ii) **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:



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 off' as iron silicate and copper is produced in the form of *copper matte* which contains Cu_2S and FeS .

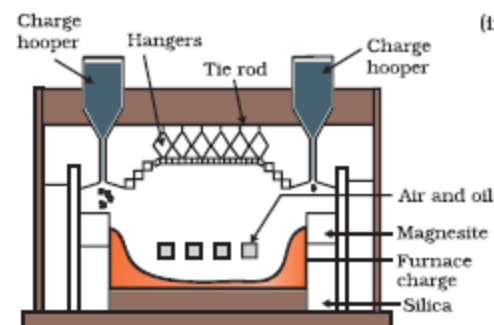


Fig. 6.3: A section of a modern reverberatory furnace

REVERBERATORY FURNACE.

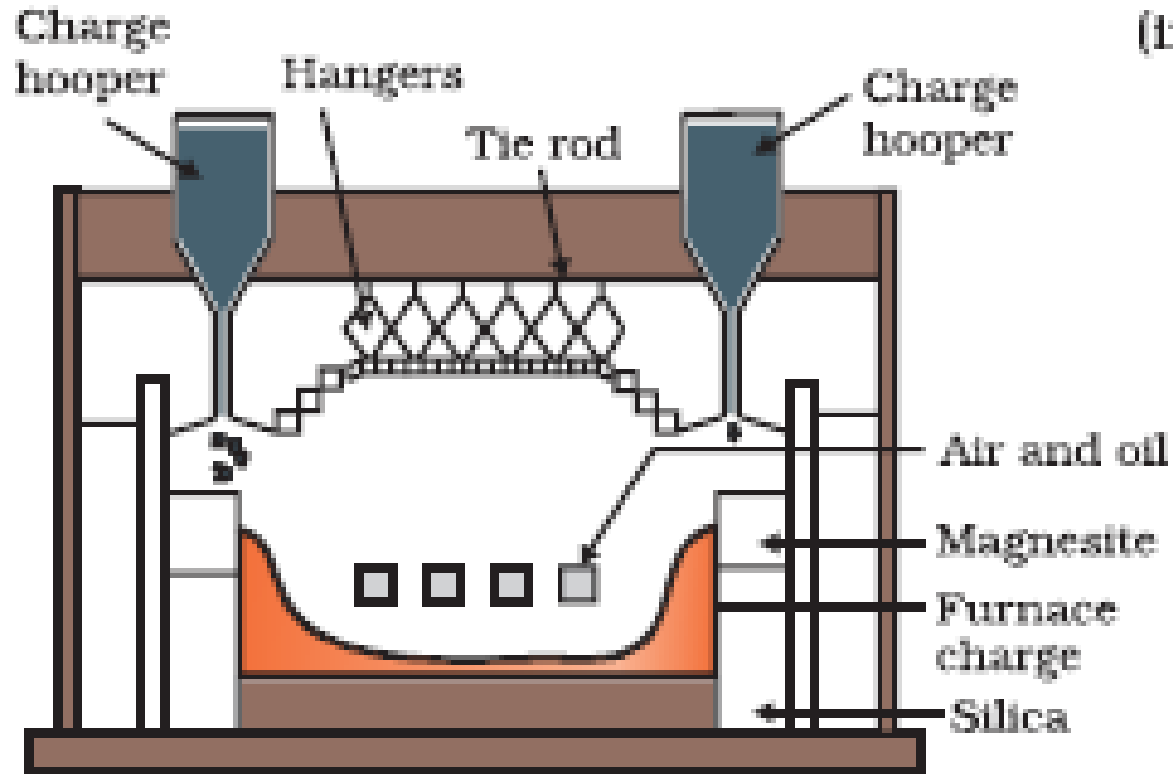


Fig. 6.3: A section of a modern reverberatory furnace

The SO_2 produced is utilised for manufacturing H_2SO_4

(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 (M_xO_y), Gibbs energy interpretations are made.

THERMODYNAMIC PRINCIPLES OF METALLURGY

- Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations.
- **Gibbs energy** is the most significant term here.
- The change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

$$\Delta G = \Delta H - T\Delta S \text{ —————(6.14)}$$

- where, ΔH is the enthalpy change and ΔS is the entropy change for the process.
- For any reaction, this change could also be explained through the equation:

$$\Delta G^0 = - RT\ln K \text{ —————(6.15)}$$

- where, K is the equilibrium constant of the 'reactant – product' system at the temperature, T .
- A negative ΔG implies a +ve K in equation 6.15.
- And this can happen only when reaction proceeds towards products.
- **From these facts we can make the following conclusions:**

THERMODYNAMIC PRINCIPLES OF METALLURGY

1. **When the value of ΔG is negative in equation 6.14, only then the reaction will proceed.**

If ΔS is positive, on increasing the temperature (T), the value of $T\Delta S$ would increase ($\Delta H < T\Delta S$) and then ΔG will become –ve.

2. **If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is –ve, 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^0) vs T plots for formation of the oxides.

APPLICATIONS

(a) 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:



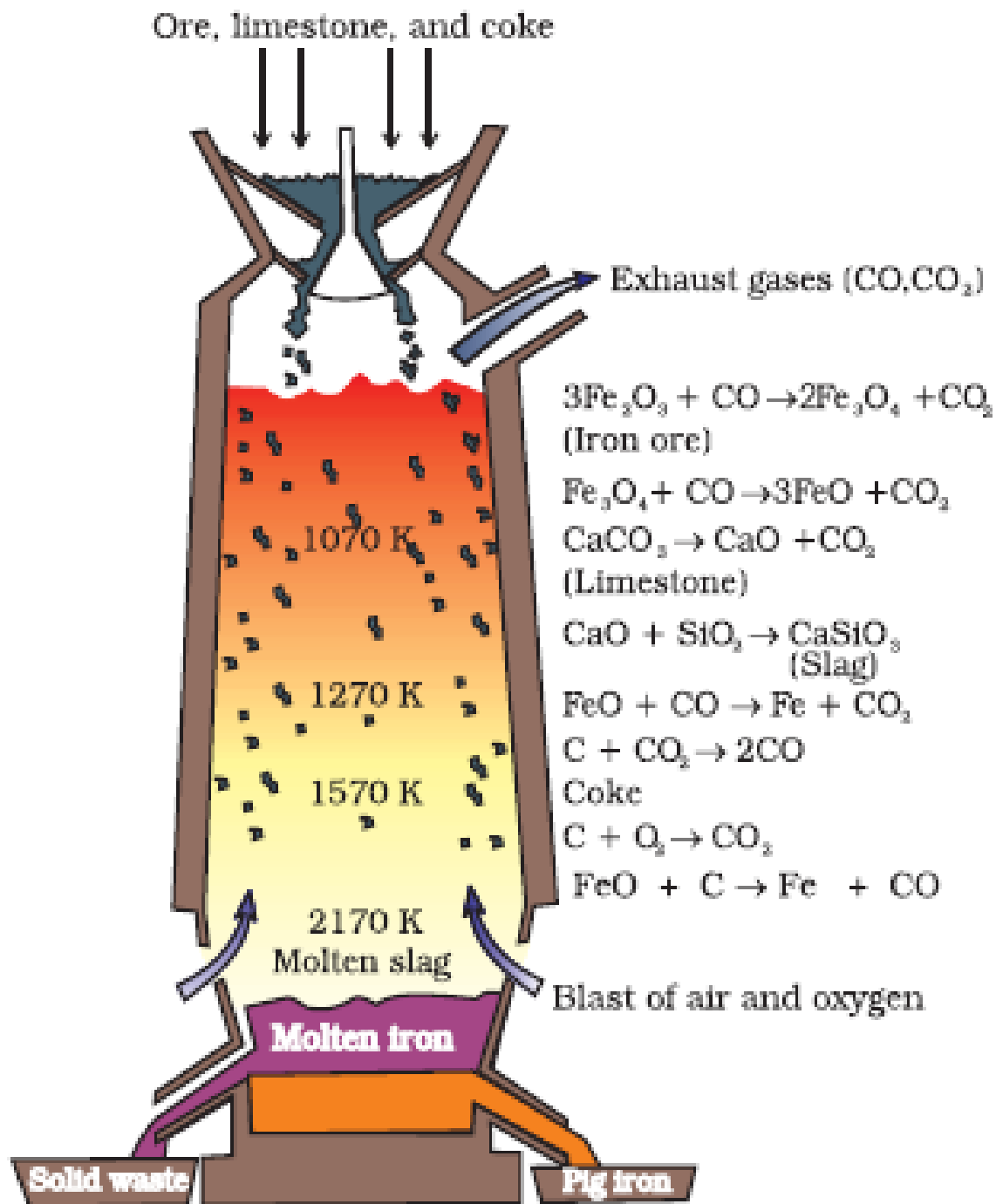
It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO:



When both the reactions take place to yield the equation (6.23), the net Gibbs energy change becomes:

$$\Delta G_{(\text{C}, \text{CO})} + \Delta G_{(\text{FeO}, \text{Fe})} = \Delta_r G \quad (6.27)$$

Naturally, the resultant reaction will take place when the right hand side in equation 6.27 is negative.



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



At 900 – 1500 K (higher temperature range in the 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 (about 3%) and is extremely hard and brittle.

FURTHER REDUCTIONS

- *Wrought iron or malleable iron is the purest form* of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite.
- This haematite oxidises carbon to carbon monoxide:
$$\text{Fe}_2\text{O}_3 + 3 \text{C} \rightarrow 2 \text{Fe} + 3 \text{CO}$$
- Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag.
- The metal is removed and freed from the slag by passing through rollers

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

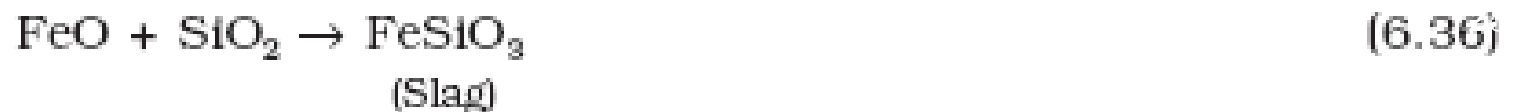
In the graph of $\Delta_r G^\ominus$ vs T for formation of oxides (Fig. 6.4), the Cu_2O line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO_2 are at much lower positions in the graph particularly after 500 – 600K). However most of the ores are sulphide and some may also contain iron. The sulphide ores are roasted/smelted to give oxides:



The oxide can then be easily reduced to metallic copper using coke:



In actual process, the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags off' as iron silicate and copper is produced in the form of *copper matte*. This contains Cu_2S and FeS .



- Copper matte is then charged into silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining FeS_2 , FeO and $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$ to the metallic copper. Following reactions take place:



The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called ***blister copper***.

(c) Extraction of zinc from zinc oxide

- The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.



- The metal is distilled off and collected by rapid chilling.

ELECTROCHEMICAL PRINCIPLES OF METALLURGY

In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^{\ominus} = - nE^{\ominus}F \quad (6.42)$$

here n is the number of electrons and E^{\ominus} is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E^{\ominus} values corresponds to a positive E^{\ominus} and consequently negative ΔG^{\ominus} in equation 6.42, then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,



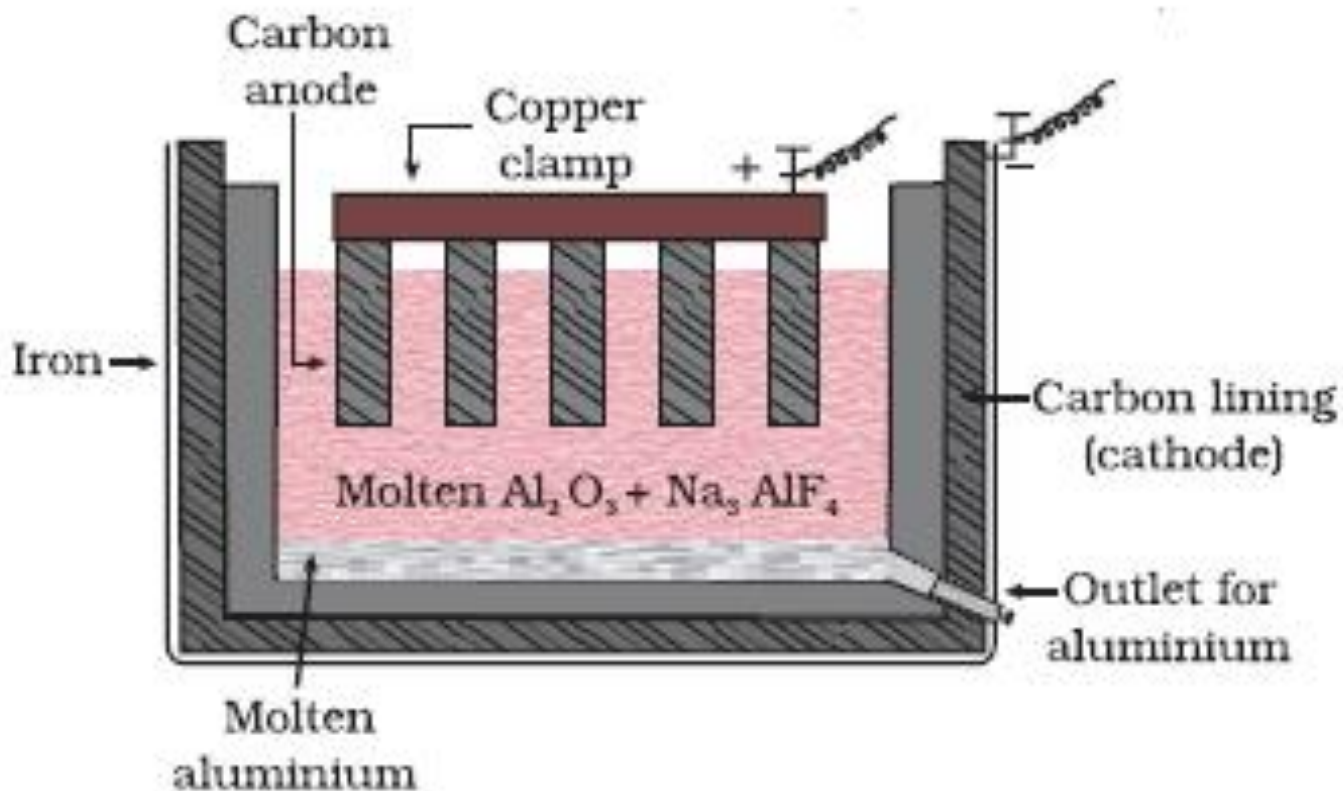
- In simple electrolysis, the M^{n+} ions are discharged at negative electrodes (cathodes) and deposited there.
- Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes.
- Sometimes a flux is added for making the molten mass more conducting.

EXTRACTION OF ALUMINIUM

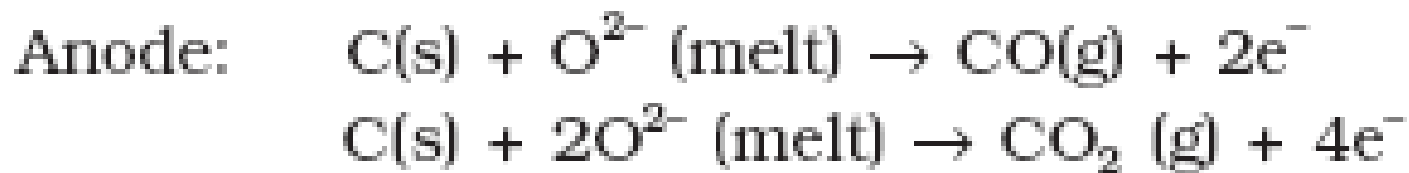
Hall-Heroult process

- In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 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:
$$2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$$
- This process of electrolysis is widely known as *Hall-Heroult process*.

ELECTROLYTIC CELL FOR THE EXTRACTION OF ALUMINIUM

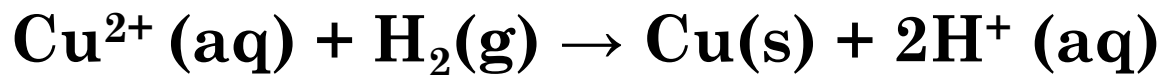


- The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes.
- The oxygen liberated at anode reacts with the carbon of anode producing CO and CO₂.
- This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away.
- The electrolytic reactions are:



Copper from Low Grade Ores and Scraps

- Copper is extracted by *hydrometallurgy* from low grade ores.
- *It is leached* out using acid or bacteria.
- The solution containing Cu^{2+} is treated with scrap iron or H_2



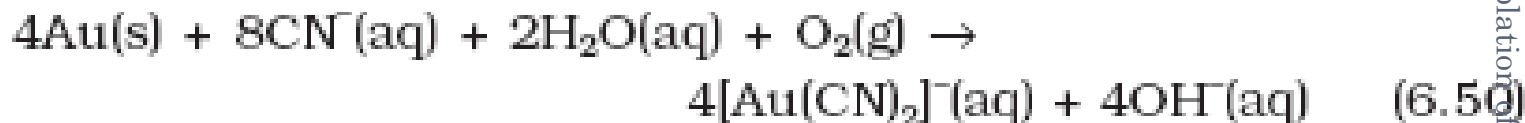
OXIDATION REDUCTION

Besides reductions, some extractions are based on oxidation particularly for non-metals. A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is abundant in sea water as common salt) .



The ΔG^\ominus for this reaction is + 422 kJ. When it is converted to E^\ominus (using $\Delta G^\ominus = - nE^\ominus F$), we get $E^\ominus = - 2.2$ 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, Cl_2 is obtained by electrolysis giving out H_2 and aqueous NaOH as by-products. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.

As studied earlier, extraction of gold and silver involves leaching the metal with CN^- . This is also an oxidation reaction ($\text{Ag} \rightarrow \text{Ag}^+$ or $\text{Au} \rightarrow \text{Au}^+$). The metal is later recovered by displacement method.



In this reaction zinc acts as a reducing agent.

REFINING

- (a) Distillation
- (b) Liqutation
- (c) Electrolysis
- (d) Zone refining
- (e) Vapour phase refining
- (f) 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*

- **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:**

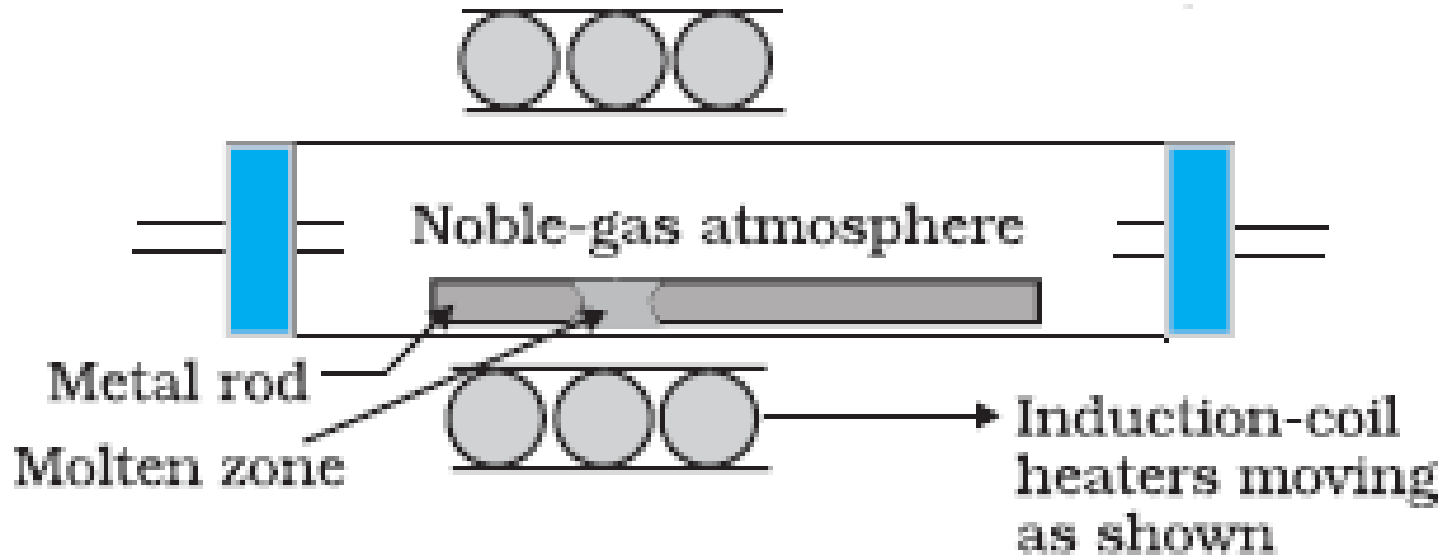


- Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining.
- Zinc may also be refined this way.

(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.

ZONE REFINING



- 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.

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



VAN ARKEL 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, volatilises:



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

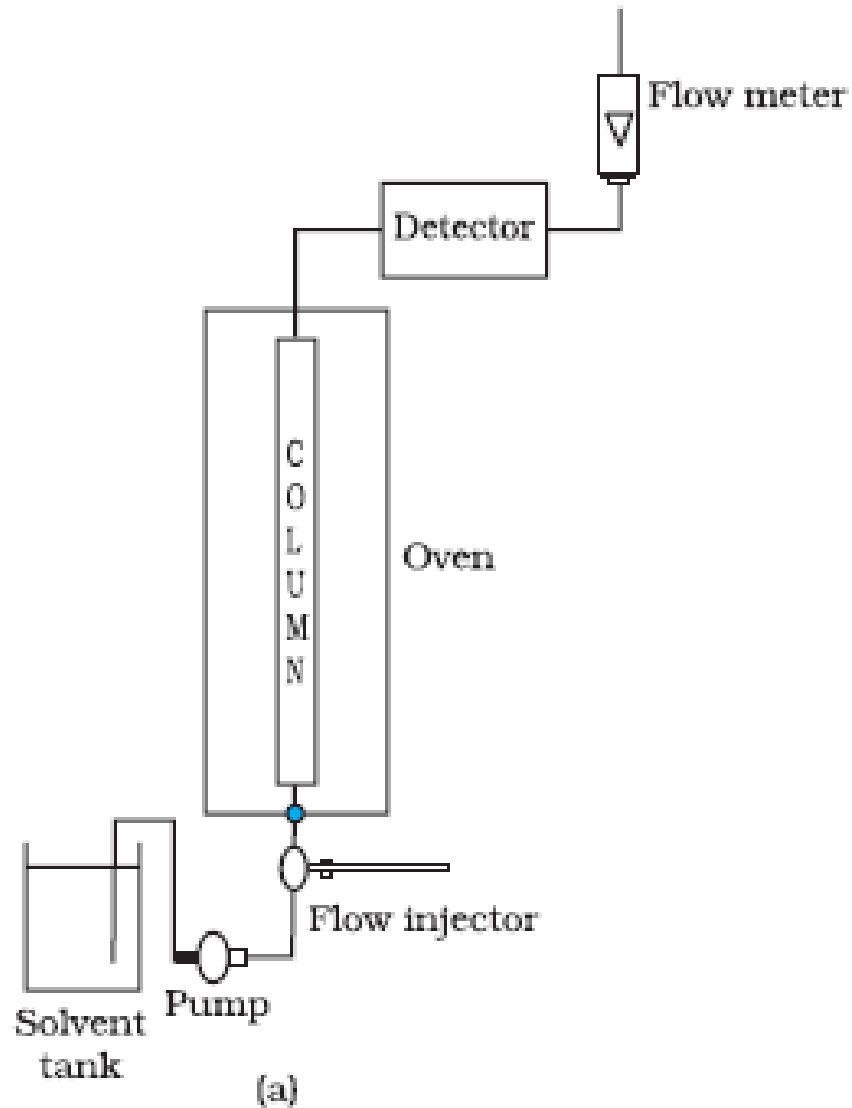


(F) CHROMATOGRAPHIC METHODS

- 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 method* **is given the name.**

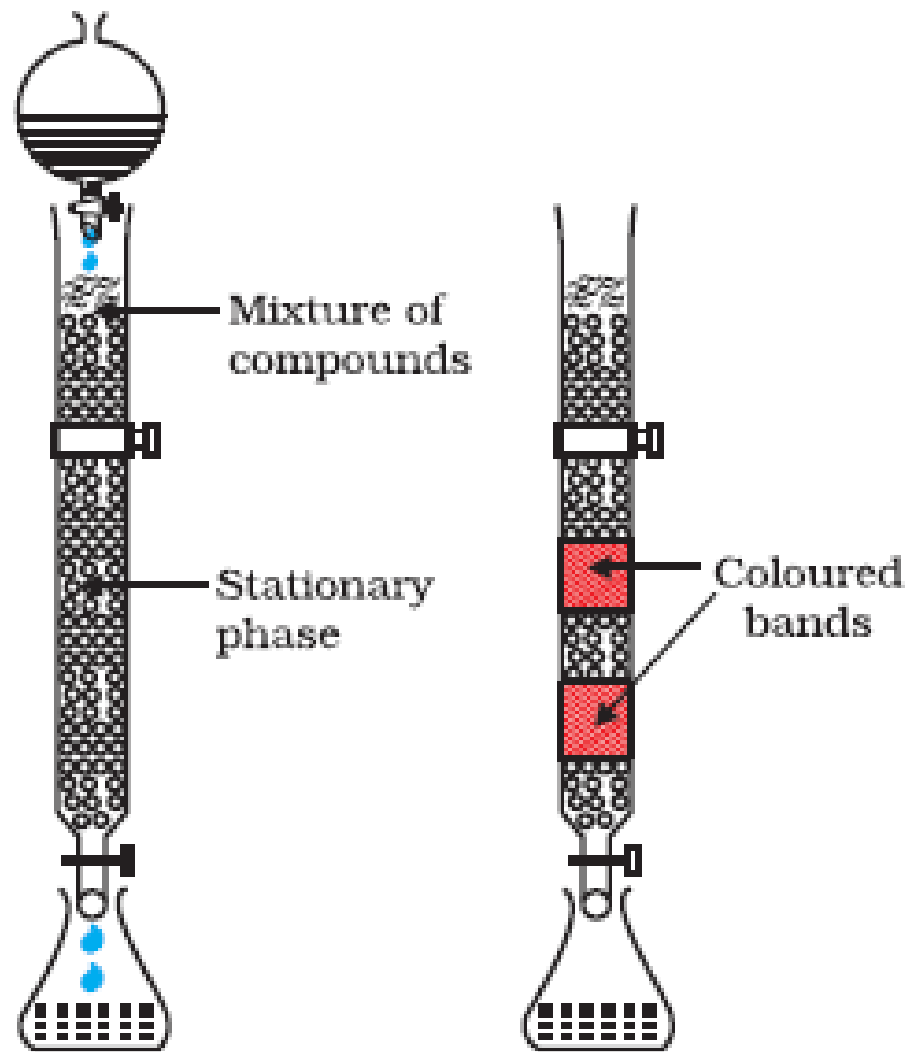
- In one such method the column of Al_2O_3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form.
- This is an example of ***column chromatography***.
- *This is very* useful for purification of the elements which are available in minute quantities 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.

COLUMN CHROMATOGRAPHY (INDUSTRIAL METHOD)



Industrial method

COLUMN CHROMATOGRAPHY (LABORATORY METHOD)



USES OF ALUMINIUM, COPPER, ZINC AND IRON

- Aluminium foils are used as wrappers for chocolates.
- The fine dust of the metal is used in paints and lacquers.
- Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides.
- Wires of aluminium are used as electricity conductors.
- Alloys containing aluminium, being light, are very useful.

○ **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).

Zinc

- Zinc is used for galvanising iron.
- 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%).
- Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

USES OF IRON

- Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc.
- It is used in the manufacture of wrought iron and steel.
- Wrought iron is used in making anchors, wires, bolts, chains and agricultural implements.
- Steel finds a number of uses.
- Alloy steel is obtained when other metals are added to it. 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.

THANK YOU