

METALLURGY

1. INTRODUCTION

The Compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called ores. An ore is usually contaminated with earthy or undesired materials known as gangue. So all minerals are not ores but all ores are minerals.

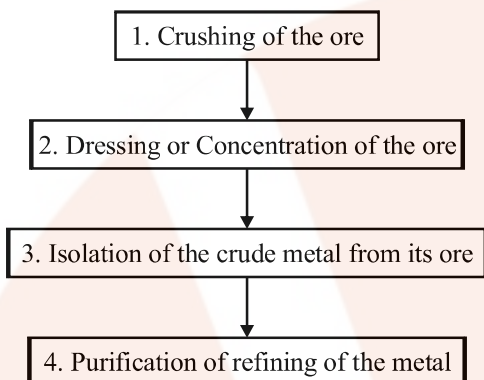
SOME IMPORTANT ORES OF METALS

Metal	Ores	Composition
Aluminium	Bauxite Diaspore Corundum	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ Al_2O_3
Iron	Haematite Magnetite Siderite Iron pyrite Limonite	Fe_2O_3 Fe_3O_4 FeCO_3 FeS_2 $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Copper	Copper pyrite Copper glance Cuprite Malachite Azurite	CuFeS_2 Cu_2S Cu_2O $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$
Zinc	Zinc blende or Sphalerite Calamine Zincite	ZnS ZnCO_3 ZnO
Lead	Galena Anglesite Cerrusite	PbS PbSO_4 PbCO_3
Magnesium	Carnallite Magnesite Dolomite Epsomsalt (Epsomite) Langbeinite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ($\text{K}_2\text{MgCl}_4 \cdot 6\text{H}_2\text{O}$) MgCO_3 $\text{MgCO}_3 \cdot \text{CaCO}_3$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$
Tin	Cassiterite (Tin Stone)	SnO_2
Silver	Silver glance (Argentite) Pyrargyrite (Ruby Silver) Chlorargyrite (Horn silver) Stefinite Proustite	Ag_2S Ag_3SbS_3 AgCl Ag_3SbS_4 Ag_3AsS_3

2. METALLURGY

The scientific and technological process used for extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps :



2.1 Crushing and Grinding

The ore is first crushed by jaw crushers and ground to a powder (pulverisation of the ore) in equipments like ball mills and stamp mills.

2.2 Concentration

The removal of unwanted useless impurities from the ore is called dressing, concentration or benefaction of ore.

2.2.1 Hydraulic washing or Gravity separation :

It is based on the difference in the densities of the gangue and ore particles. In this, the powdered ore is agitated with water or washed with an upward stream of running water, the lighter particles of sand, clay etc are washed away leaving behind heavier ore particles.

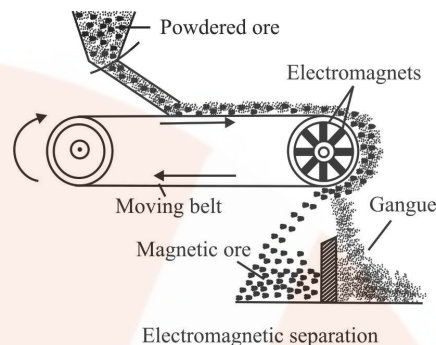
2.2.2 Electromagnetic separation :

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

It is used when either the ore or the impurities associated with it are magnetic in nature. A magnetic separator consists of a belt (of leather or brass) moving over two rollers, one of which is magnetic. When the powdered ore is dropped on the belt at the other end, magnetic component of the ore is attracted by the magnetic roller and falls nearer to the roller while the non-magnetic impurities fall away from it.

EXAMPLE

Chromite ore ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) is separated from non-magnetic silicious impurities and **cassiterite ore** (SnO_2) is separated from magnetic **Wolframite** ($\text{FeWO}_4 + \text{MnWO}_4$).



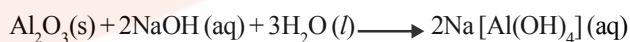
2.2.3 Froth floatation process :

This method is commonly used for the **concentration of the low grade sulphide** ores like galena, PbS (ore of Pb) ; copper iron pyrites $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ or CuFeS_2 (ore of copper); zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wet ability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process one or more chemical frothing agents are added.

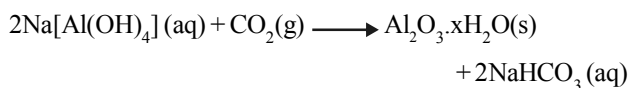
When a mineral contains other minerals as impurities. The addition of these agents activates or depresses the flotation property of other minerals present as impurities and thus helps in separating the impurities. For example galena (PbS) usually contains the minerals namely zinc blende (ZnS) and pyrites (FeS_2) as impurities. Flotation is carried out by using potassium ethyl xanthate (used as a collector) along with NaCN and Na_2CO_3 (used as depressing agent).

2.2.4 Leaching of alumina from bauxite :

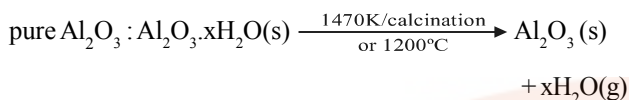
The principal ore of aluminium, bauxite, usually contains SiO_2 , iron oxides and titanium oxide (TiO_2) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35 - 36 bar pressure. This way, Al_2O_3 is leached out as sodium aluminate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



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 of $\text{Al}(\text{OH})_3$.



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



These steps comprises the **Bayer's process**.

In the **metallurgy of silver and that of gold**, the respective metal/ore is leached with a dilute solution of NaCN or KCN in the presence of air (or O_2) from which the metal is obtained later by displacement with zinc scrap. This is also known as **Mac-Arthur Forest Cyanide process**.

2.3 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 as given below.

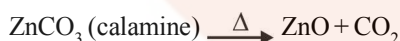
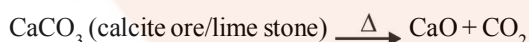
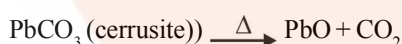
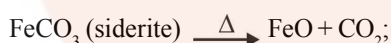
- Conversion to oxide
- Reduction of the oxide to metal.

2.3.1 Conversion to oxide :

Conversion of ore into oxide is carried out in two ways depending upon the nature of ore.

2.3.1.1 Calcination : It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes :

- (a) The carbonate ore gets decomposed to form the oxide of the metal, e.g.,



- (b) Water of crystallisation present in the hydrated oxide ore gets lost as moisture, e.g.,



- (c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

2.3.1.2 Roasting :

It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point. Roasting and exothermic process once started it does not require additional heating. Some of the reactions involving sulphide ores are :



* Some times roasting may not bring about complete oxidation.



The reduction of the sulphide ore directly into metal by heating it in air or O_2 is called by various names like self-reduction, auto-reduction, air-reduction etc. The SO_2 produced is utilised for manufacturing of H_2SO_4 .

2.3.2 Reduction of metal oxide to the metal :

The calcined or roasted ore is then reduced to the metallic state in either of the following ways.

2.3.2.1 Reduction by carbon (Smelting) :

"Reduction of the oxide with carbon at high temperature is known as smelting".

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced by strongly heating them with coal or coke, in the blast furnace.

Slag : Fusible material during reduction process.

Slag : Gangue + substance (for remove gangue)

Fluxes : Substance used for removing gangue

Fluxes acidic : Borax, SiO_2 (remove basic impurity)

Fluxes basic : MgO , MgCO_3 , CaCO_3 (remove acidic impurity)

Smelting :

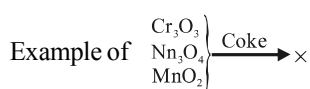
Concentration + gangue + R_A (carbon) + Flux



Metal + Slag + gases

When melting point of compound is too high then Al powder used as reducing agent **Al powder + ore** is called thermite and this process is called **Gold-Schmidt Alumino Thermite process**.

Coke is not used for s-block oxide, Al_2O_3 some d-block oxide (due to of metal carbides $\text{CaO} + 2\text{C} \rightarrow \text{CaC}_2 + \text{CO}$)



Some reaction are :

- (a) $\text{CuO} + \text{CO} \rightarrow \text{CO}_2 + \text{Cu}$
- (b) $\text{PbO} + \text{C} \rightarrow \text{Pb} + \text{CO}$
- (c) $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow \text{Fe} + 3\text{CO}$
- (d) $\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$
- (e) $\text{ZnO} + \text{CO} \rightarrow \text{Zn} + \text{CO}_2$

(gangue) Acidic impurity + flux \rightarrow slag

- (a) $\text{SiO}_2 + \text{CaCO}_3 \rightarrow \text{CaSiO}_3 + \text{CO}_2 \downarrow$
- (b) $\text{P}_2\text{O}_5 + 3\text{CaO} \rightarrow \text{Ca}_3(\text{PO}_4)_2$

Basic impurity + Flux \rightarrow slag

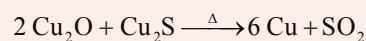
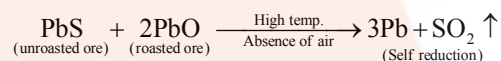
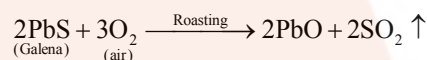
- (a) $\text{MgCO}_3 + \text{SiO}_2 \rightarrow \text{MgSiO}_3 + \text{CO}_3 \downarrow$
- (b) $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$

2.3.2.2 Self reduction

Compounds of certain metals are reduced to metal without using additional reducing agent ores of Cu, Pb, Hg etc.

Their sulphide ores are partially roasted to give some oxide. This oxide is now reduced to the metal by the remaining sulphide ore at elevated temperatures in the absence of air. The process is known as self reduction. or auto reduction

Self reduction for Pb :-

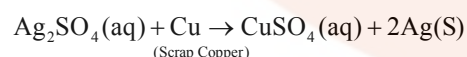
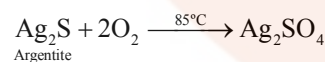


2.3.2.3 Metal displacement method

In this method, a water soluble compound is obtained from the ore. The aqueous solution of the compound is reacted with a more electropositive metal which displaces, the metal from the solution.

EXAMPLE

(i) Zairvogel process for silver.

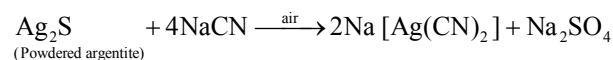


(ii) Separation of Ag by Complex formation

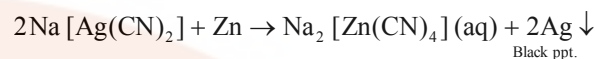
Silver and gold are extracted by a method involving complex formation.

Powdered argentite is reacted with a dilute solution of sodium cyanide in the presence of air. The silver from the

ore is dissolved in the cyanide solution forming sodium argentocyanide.



Now metallic zinc is added to the complex salt solution which being more electropositive element than silver, displaces it form the solution.



2.3.2.4 Electrolytic reduction

This process is mainly used for the extraction of highly electropositive metals.

Electrolysis is carried out in a large cells and a small amount of **another suitable electrolyte is added** which :

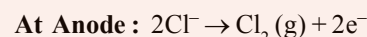
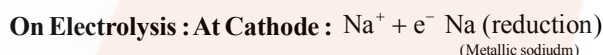
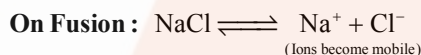
- (a) Lowers the melting point of the main electrolyte
- (b) Enhances its conductivity
- (c) Reduces corrosion troubles

EXAMPLE

Na, K, Mg, Ca, Al, etc.

(a) Manufacture of metallic sodium (Down's process)

Molten NaCl containing a little CaCl_2 is electrolyzed between graphite anode and iron cathode. The various reactions that take place are :

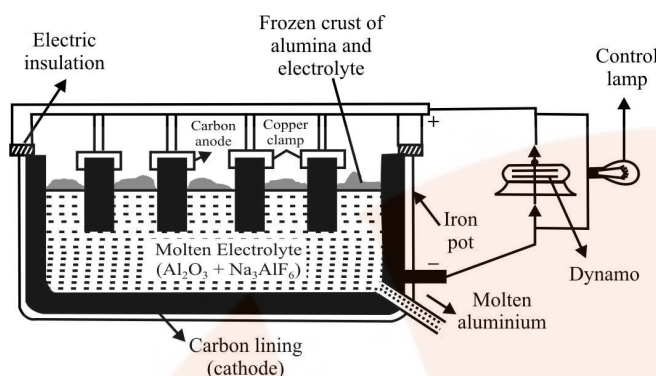
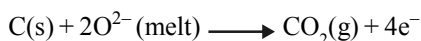
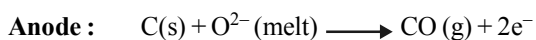


(b) Electrolytic reduction (Hall-Heroult process) :

The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful for reduction to the metal. The overall reaction may be taken as :



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 CO_2 . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are :



2.4 Purification or Refining of metals

Metals obtained by reducing processes still contains some objectionable impurities and have to be refined. Refining techniques vary widely from metal to metal and also depend on the use to which a metal has to be put.

2.4.1 Liquations process :

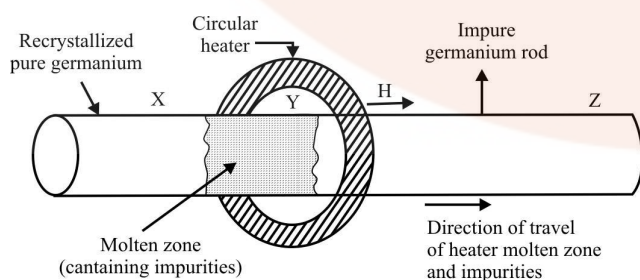
This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not, i.e., the impurities are infusible. In other words, we can say that the melting point of the metal to be purified should be lower than than of each of the impurities associated with the metal. This process is used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy, which is obtained at the end of Parke's process and contains Pb as impurity.

2.4.2 Distillation process :

This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.

2.4.3 Zone refining method (Fractional crystallisation method):

This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.



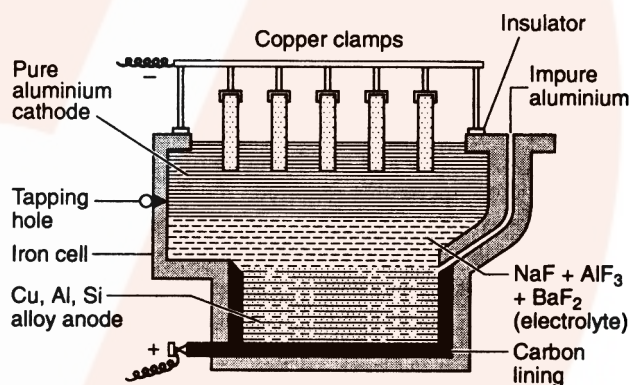
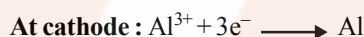
Zone refining of germanium metal

2.4.4 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 solvent (eluant).

2.4.5 Electrolytic Refining :

Some metals such as Cu, Ni, and Al are refined electrolytically. The **Hoope's process** is a process for the **electrolytic refining of aluminum**. Impure Al forms the anode and pure Al forms the cathode of the Hooper's cell which contains three liquid layers. The bottom layer is molten impure Al, the middle is a fused salt layer containing aluminum fluoride, and the top layer is pure Al. At the anode (bottom layer), Al passes with solution as aluminum ion (Al^{3+}), and at the cathode (top layer), these ions are reduced to the pure metal. In operation, molten metal is added to the bottom of the cell and pure aluminum is drawn off the top. Aluminium obtained is 99.98% pure.



2.4.6 Vapour Phase Refining :

In this method, the metal is converted into its volatile compound and then collected. It is then heated so that it gets decomposed to give pure metal. So, following two requirements are essential for vapour phase refining.

- The metal should form a volatile compound with an available reagent.
- The volatile compound should be easily decomposable, so that the recovery is easy.

SOME IMPORTANT COMPOUNDS, MINERALS, MIXTURES & THE FORMULA'S

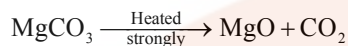
1. Epsom salt	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	25. Nitrolium	CaCN_2
2. Gypsum salt	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	26. Hydrolith	CaH_2
3. Glauber's salt	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	27. Fusion mixture	$\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$
4. Lime water	Ca(OH)_2 (slaked lime)	28. Gun powder	$\text{KNO}_3 + \text{K}_2\text{CO}_3$
5. Quick lime	CaO	29. Pink salt	$(\text{NH}_4)_2\text{SnCl}_6$
6. Washing Soda	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	30. Laughing gas	N_2O (nitrous oxide)
7. Crystal carbonate	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	31. Red Lead	Pb_3O_4
8. Soda ash	Na_2CO_3	32. Blue vitriol	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
9. Baking Soda	NaHCO_3	33. Green vitriol	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
10. Turnbull's blue	$\text{Fe}_3[\text{Fe(CN)}_6]_2$	34. Chiense white	ZnO
11. Chile salt petre	NaNO_3	35. Philospher's wool	ZnO
12. Indian salt petre	KNO_3	36. Potash alum	$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
13. Brine or Table salt	NaCl	37. Chrome alum	$\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
or Rock salt		38. Ferric alum	$\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$
14. Potash ash or Pearl ash	K_2CO_3	39. Chrome lemon (or)	PbCrO_4
15. Nitre or Indian salt petre	KNO_3	Yellow chrome	
or Chemical refrigerant		40. Pyrolusite	MnO_2
16. Norwegian salt petre	$\text{Ca(NO}_3)_2$	41. Rochelle salt	CH(OH)COONa CH(OH)COOK
17. Salt Cake	K_2SO_4	42. Sorel's cement	$\text{MgCl}_2 \cdot 5\text{HgO} \cdot \text{H}_2\text{O}$
18. Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	43. Lithopone	$\text{BaSO}_4 + \text{ZnS}$
19. Hypo	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	44. Aqua regia	$\text{Conc. HNO}_3 + \text{Conc. HCl (1 : 3)}$
20. Borax or Tincal	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	45. Ammonium alum	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
21. Barytes of Heavy spar	BaSO_4	46. Sodium Alum	$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
or Barium meal		47. Killed salt (or Butter of Zinc)	$\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$
22. Baryta water	Ba(OH)_2	48. Oxymuriate (or) Butter of Tin	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$
23. Magnesia	MgO		
24. Microcosmic salt	$\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$		

EXTRACTION OF SOME METALS

MAGNESIUM (Mg)

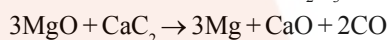
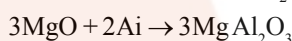
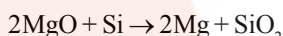
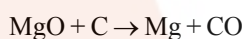
Extraction : It is usually extracted by the electrolysis of fused oxide of fused anhydrous magnesium chloride.

- (i) **From magnesite :** The magnesite ore (MgCO_3) is calcined into magnesium oxide (magnesia).



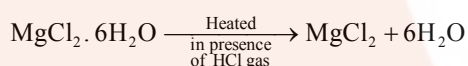
Magnesium may be obtained either by electrolysis or by thermal reduction of magnesium oxide. The oxide is dissolved in a mixture of molten fluorides of magnesium, barium and sodium. The electrolysis of molten mixture is done by using carbon rods as anodes which suspend in molten mass and cast iron rods as cathodes at 650°C . On electrolysis magnesium is obtained in molten state.

The thermal reduction of magnesium oxide can be done by using reducing agents like carbon, silicon, aluminium or calcium carbide.

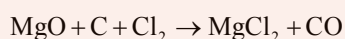


The reduction is done at 2000°C in vacuum. The vapours of magnesium are condensed.

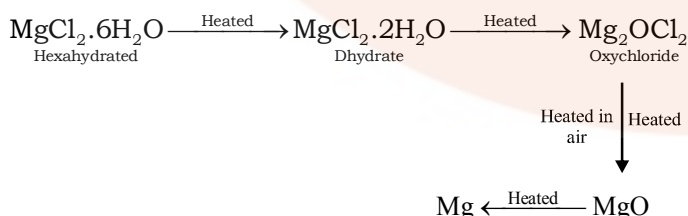
- (ii) **Electrolysis of anhydrous magnesium chloride :** **Carnallite** is a hydrated compound. To make it anhydrous, it is first heated in air and then in current of HCl gas.



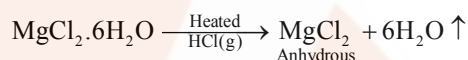
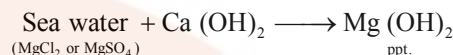
Anhydrous magnesium chloride can also be obtained from MgO or sea water. Chlorine is passed over red hot mixture of MgO and carbon



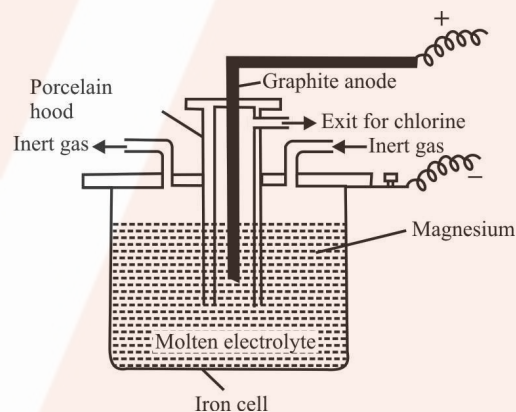
It cannot be dehydrated by heating because the water of crystallization reacts chemically with magnesium chloride to form magnesium oxychloride and finally magnesium oxide.



Sea water contains magnesium compounds. It is treated with calcium hydroxide when magnesium hydroxide gets precipitated. It is dissolved in dilute HCl. The solution then concentrated when hydrated magnesium chloride crystallizes out. It is dehydrated as described above.



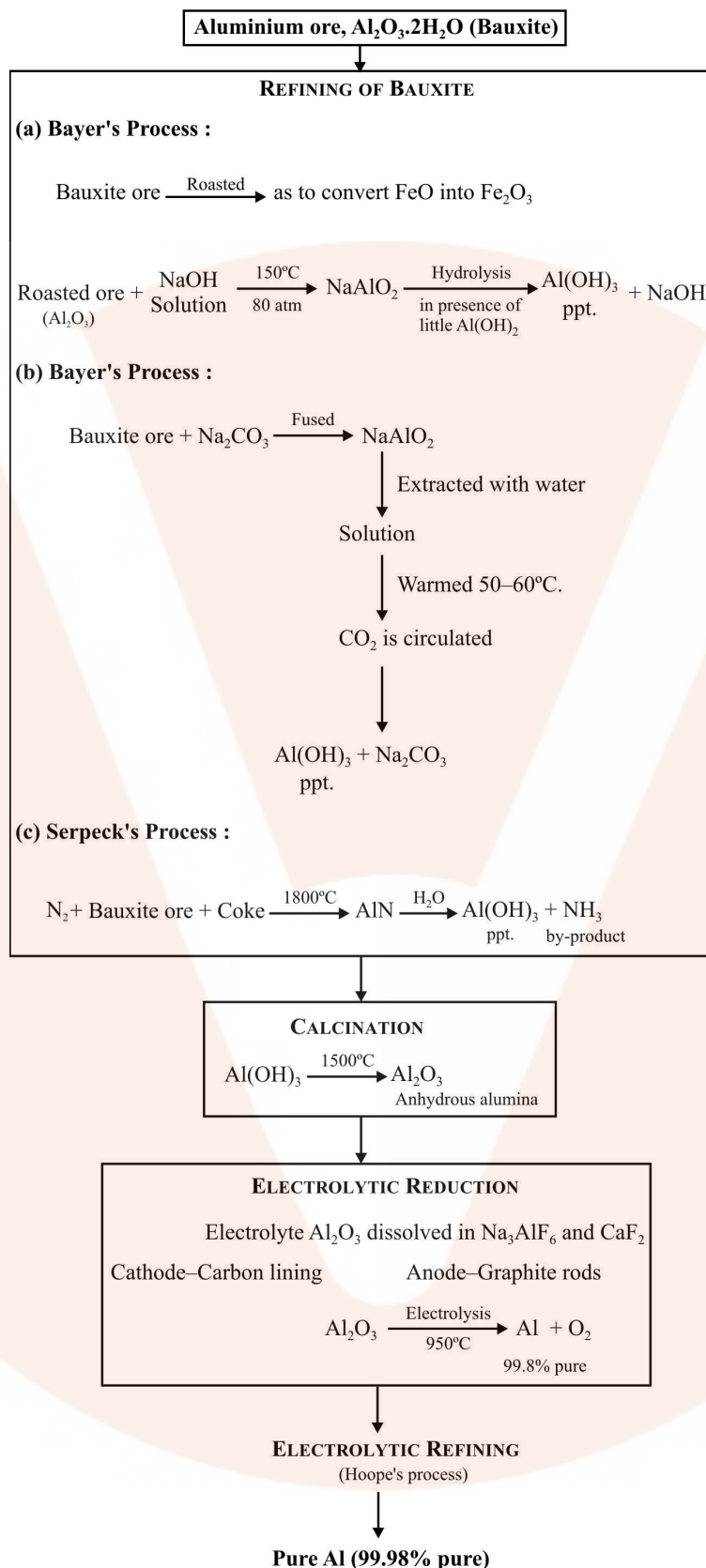
The anhydrous magnesium chloride is fused with NaCl and anhydrous calcium chloride in the ratio of 35% (MgCl_2); 50% (NaCl) and 15% (CaCl_2). The purpose of addition of NaCl and CaCl_2 to anhydrous MgCl_2 is to lower the fusion temperature and make the fused mass good conductor of electricity. The mixture is electrolysed at 700°C in presence of an inert gas in electrolytic cell as shown in figure



ALUMINIUM (Al)

Extraction : Aluminium is mainly isolated from bauxite ore which is generally contaminated with ferric oxide and silica. The removal of ferric oxide and silica from bauxite ore is essential before it is subjected to electrolysis. Thus, the extraction of aluminium from bauxite ore involves the following three steps.

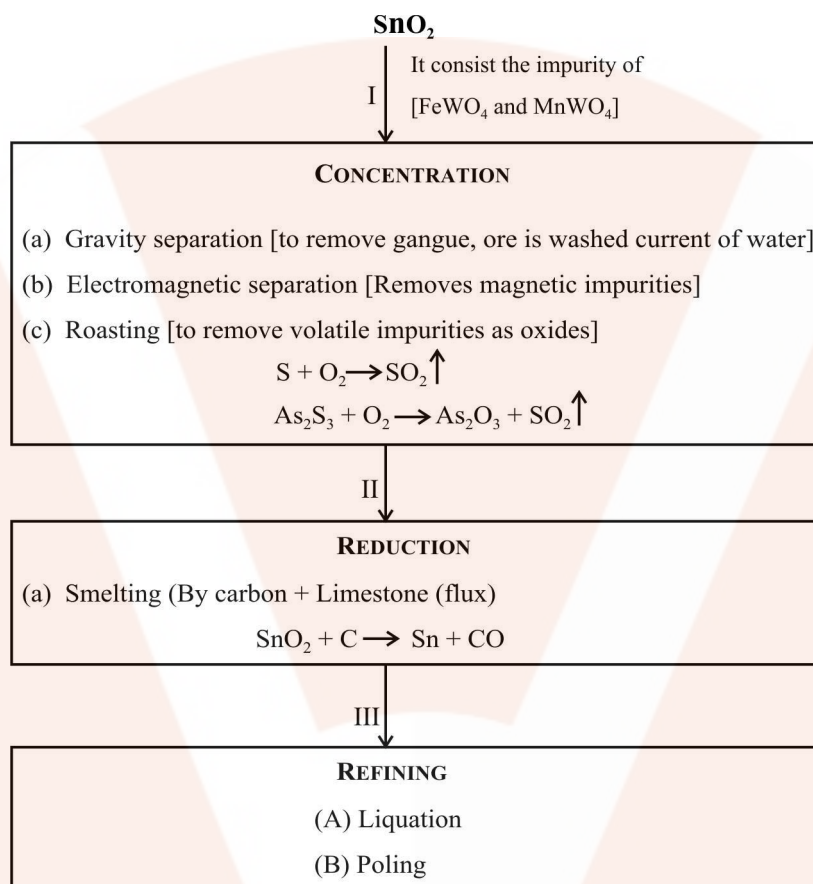
- (i) Purification of bauxite ore, i.e., removal of ferric oxide and silica.
- (a) **Baeyer's process :** This process is mainly applied to bauxite ore containing ferric oxide as chief impurity.
- (b) **Hall's process :** This process is mainly applied to bauxite ore containing ferric oxide as a chief impurity.
- (c) **Serpeck's process :** This process is mainly applied to bauxite ore containing silica as a chief impurity.



FLOW SHEET FOR THE EXTRACTION OF ALUMINIUM

TIN (Sn)

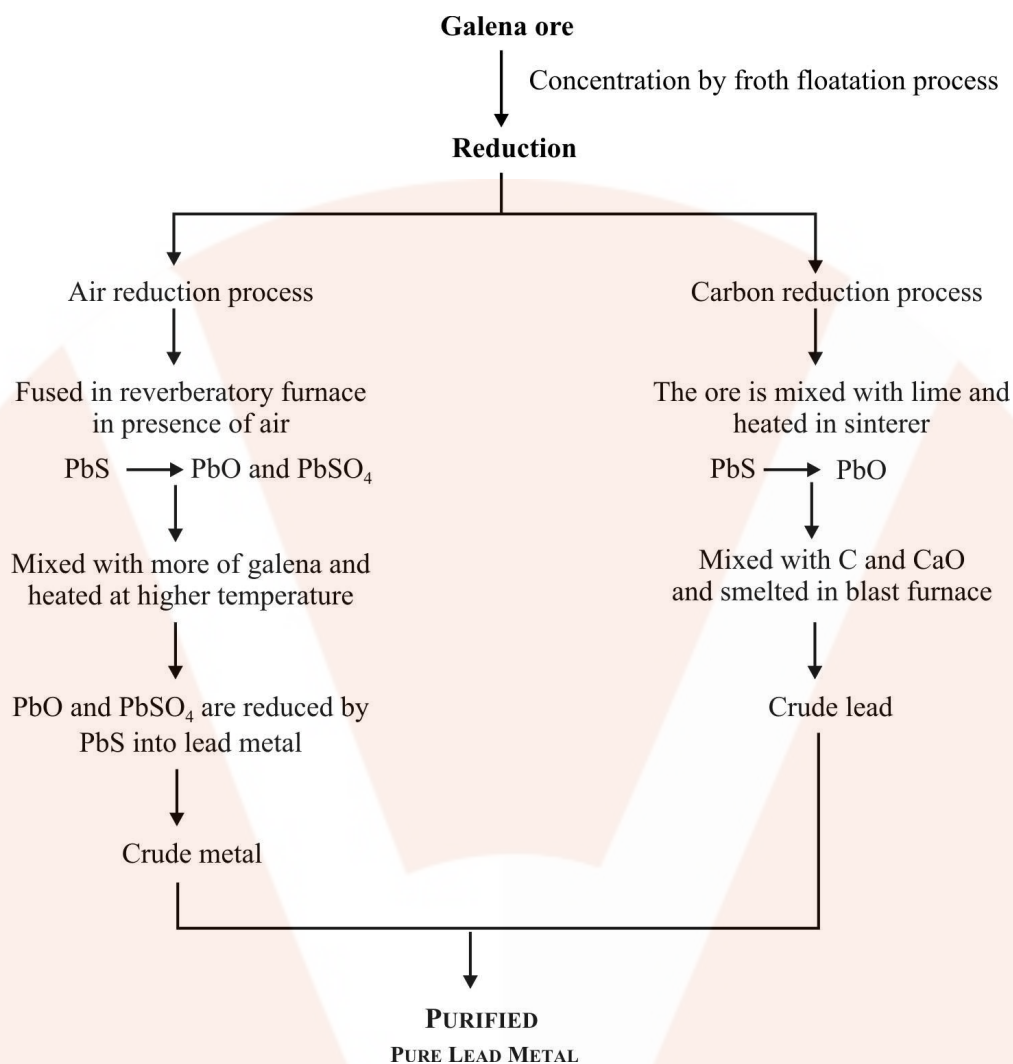
Extraction : Tin is extracted from **cassiterite ore**. The ore is usually associated with siliceous matter, tungstates of iron (FeWO_4) and manganese (MnWO_4).

**LEAD OR PLUMBUM (Pb)**

Extraction : Lead is mainly extracted, from **galena ore**. (PbS)

The extraction involves the following steps :

- (i) Concentration of the ore
- (ii) Reduction
- (iii) Purification



Flow Sheet for the Extraction of Lead and Formation of Various Compounds

IRON (Fe)

Extraction : Iron is extracted from its oxide ores especially from the **magnetite, haematite and limonite** ores. The extraction involve the following steps given in flow sheet :

IRON ORE

I ↓

CONCENTRATION

Gravity process followed by electromagnetic separation

II ↓

CALCINATION AND ROASTING

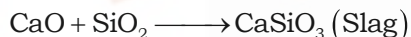
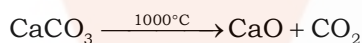
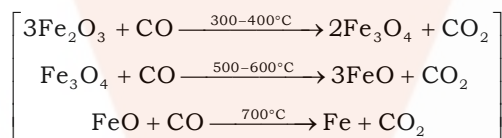
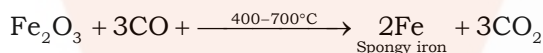
Ore + air $\xrightarrow{\text{Heat}}$ moisture, CO_2 , SO_2 , As_2O_3 removed

FeO is Oxidised to ferric oxide

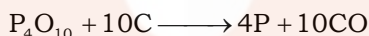
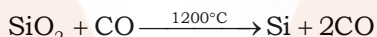
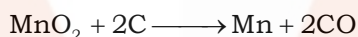
III ↓

REDUCTION

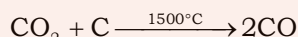
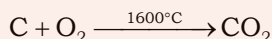
Smelting in a blast furnace (ore + coke + limestone). The following reactions occur



Silicates, phosphates and manganates present as impurities in ore, are reduced to Si, P and Mn, respectively



Spongy iron + C, Mn, Si, etc. \longrightarrow Impure iron



IV ↓

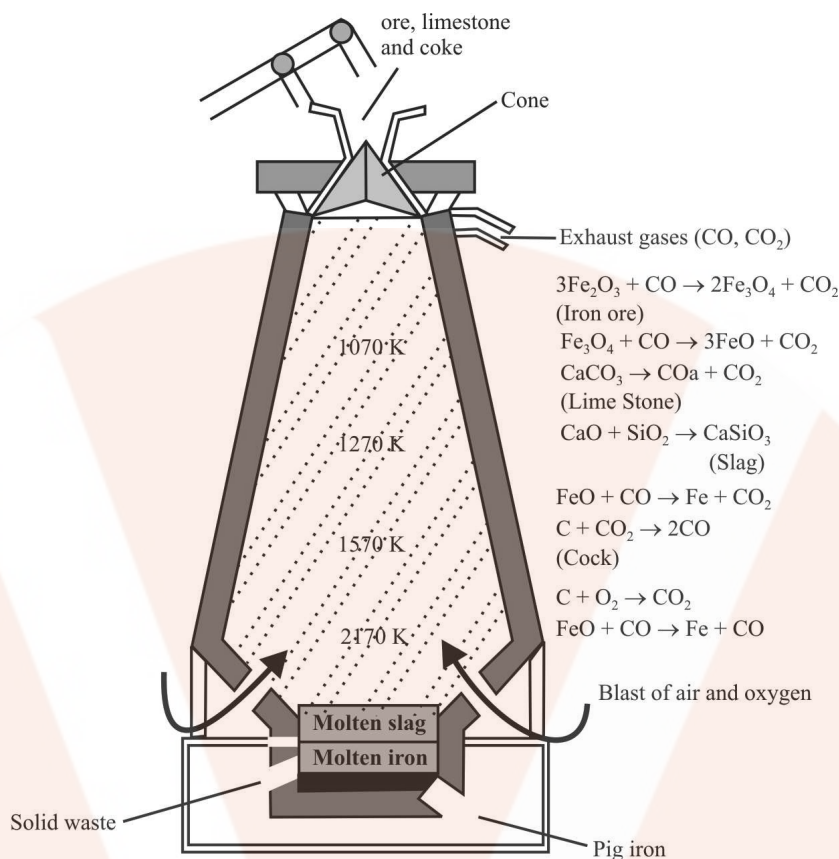
PIG IRON

V ↓

REMELTED AND COOLED : CAST IRON

(Fe = 93%; C = 5% and impurities of Mn, P, Si, etc. = 2%)

FLOW SHEET FOR EXTRACTION OF IRON



When the molten pig iron is cooled at once, the iron is called white cast iron, which contains carbon in the form of cementite, Fe₃C and when the molten pig iron is cooled slowly and slowly, the iron is called as grey cast iron, which contains carbon in the form of graphite.

1. Cost Iron or Pig Iron :

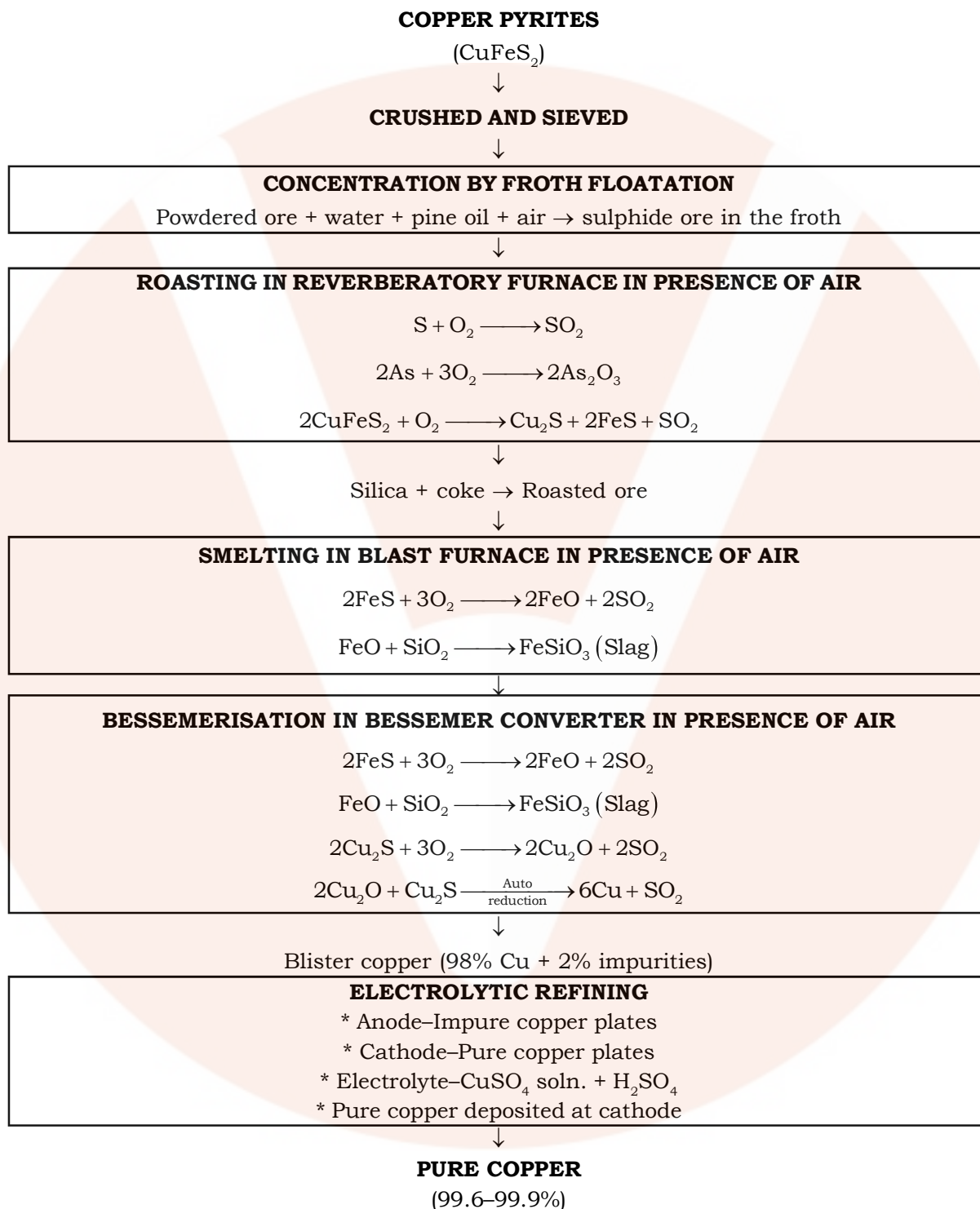
This is the least pure form of commercial iron and contains the highest percentage of carbon viz., 2.5 to 4.5% and traces of impurities like S, P, Mn and Si. The average composition of cast iron is : Fe = 93 – 95%, C = 2.5 – 4.5%, Si = 0.6 – 2.8%, P = 0.4 – 1.0%, S = 0.1 – 0.3%, Mn = 0.3 – 1.2%.

2. Wrought Iron :

It is the purest form of commercial iron and contains the lowest percentage of carbon viz. 0.12 to 0.25% and 0.3% of impurities like S, P, Si and Mn.

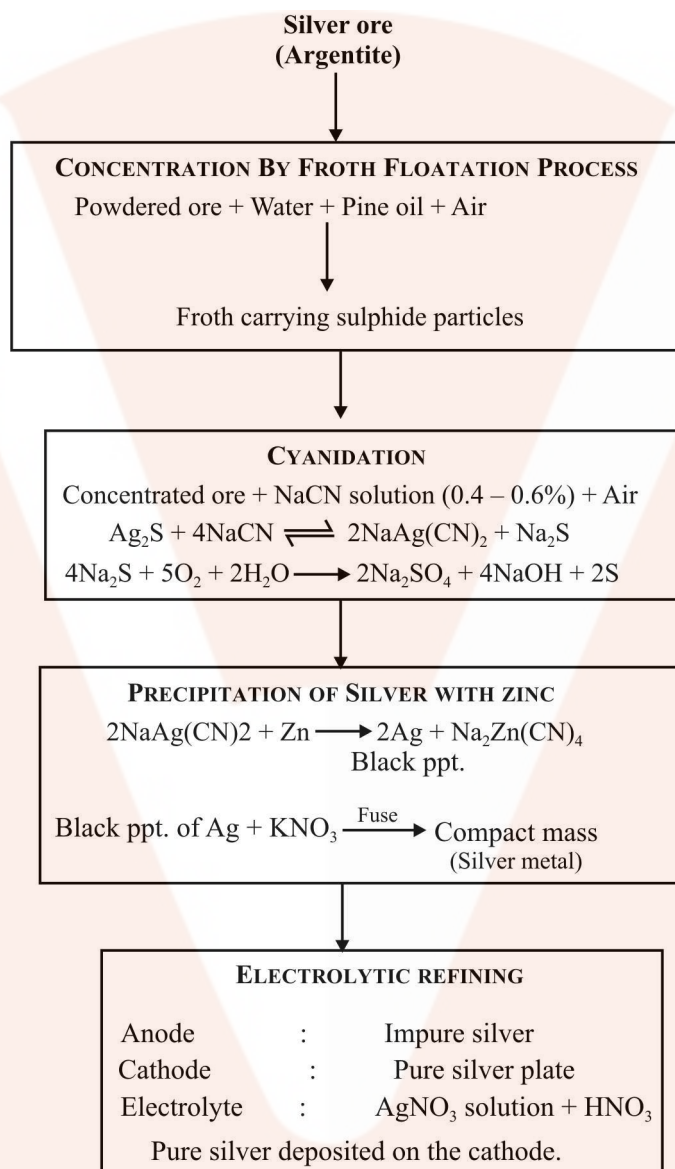
COPPER (Cu)

Extraction : Copper is extracted mainly from **copper pyrites (Cu Fe S₂)**. The extraction involve the following steps given in flow sheet.

**FLOW SHEET FOR THE EXTRACTION OF COPPER**

SILVER (Ag)

Silver is also associated in the form of **Ag₂S** in the lead ore, **galena (PbS)**. The lead extracted usually contains silver and called argentiferous lead. Silver is recovered before lead is put into use.

FLOW SHEET FOR THE EXTRACTION OF SILVER

Same process is employed for the extraction of gold (Au)

STEEL

Composition of Steel :

Steel is an alloy of iron (as ferrite) containing 0.25 to 2.5% of carbon (as cementite, Fe_3C) and traces of S, P, Si and Mn. Thus, we see that the percentage of carbon in steel is intermediate between that in wrought iron and cast iron. S and P are objectionable impurities. The percentage of S and P are usually below 0.05%, depending on the method used for the manufacture of steel. Si is usually between 0.15 to 0.35% and is present as iron silicide, FeSi which is soluble in ferrite. High content of Si gives a fibrous structure to steel. Mn is added to steel during its manufacture to serve as a deoxidiser and to neutralise the harmful effect of sulphur by forming MnS which is inert, while FeS makes steel brittle in hot working.

Varieties of Steel :

There are many varieties of steel depending on the amount of carbon present in it.

Some of the alloy steels along with their composition, properties and uses are listed in Table given below :

Some important alloy steels

	Name	Percentage composition	Properties	Uses
1.	Stainless	Fe = 73 Cr = 18 Ni = 8 and carbon	Hard and rust-proof	Utensils, cycle and automobile parts, cutlery.
2.	Nickel Steel	Fe = 98 – 96 Ni = 2 – 4	Hard, elastic and rust-proof	Cables, automobile and aeroplane parts, armour plates, gears
3.	Invar	Fe = 64, C = 0.3 Ni = 36	Low expansion on heating	Metre scales, measuring instruments, clock pendulums.
4.	Tungsten steel	Fe = 83 – 72 W = 14 – 20 Cr = 3 – 8	Hard, resistant to corrosion	High speed cutting tools, springs
5.	Silicon steel	Fe = 84 Si = 15	Hard, and resistant to acid	Pumps and pipes for carrying acids.
6.	Manganese steel	Fe = 88 – 85 Mn = 12 – 15	Extremely hard, high m.pt.	Rock crushers, burglar proof safes, rail tracks.
7.	Perma alloy	Fe = 21 Ni = 78 and carbon	Strongly magnetised by electric current and demagnetised upon cutting off current.	Electromagnets, cables for oceans.
8.	Alnico	Fe = 63, Ni = 20 Al = 12, Co = 5	Highly magnetic	Permanent magnets.

1. Mild and quenched steels :

Mild steel is a variety which contains lower percentage of carbon. It possesses the properties of wrought iron along with elasticity and hardness of steel. If mild steel is heated to a high temperature (i.e., to bright redness) and then suddenly cooled by plunging in oil or water, it becomes as hard and brittle as glass. This is called quenched steel and process is called quenching or hardening.

2. Hard Steel :

This variety contains higher percentage of carbon. It is hard and brittle like glass.

3. Special Steels or alloy Steels :

Addition of small amounts of nickel, cobalt, chromium, tungsten, molybdenum, manganese and silicon confer special properties on steel considerably altering its hardness, tenacity, resistance to corrosion and coefficient of expansion. Such products are called special steels or alloy steels and find extensive use in industry.

4. **Steel containing S and P.** Iron or steel containing excess of S is brittle when hot (hot short) and that containing excess of P is also brittle when cold (cold short).

Manufacture of steel

We have already said that the amount of carbon in steel is mid-way between that of cast iron and in wrought iron so that steel can be obtained either by removing a part of carbon from cast iron or by adding some carbon to wrought iron. Thus steel is prepared either from cast iron or from wrought iron. Following methods are used :

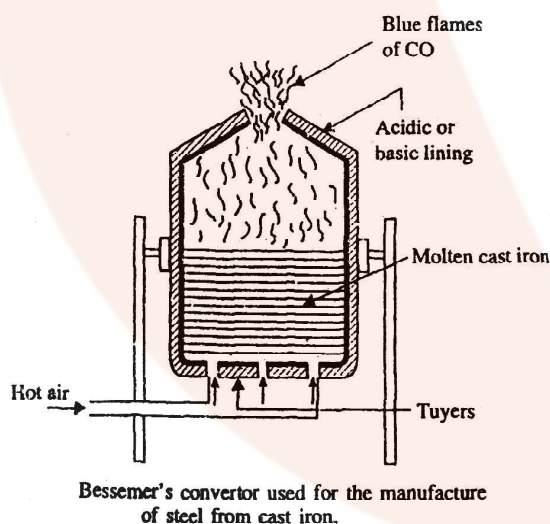
1. Bessemer's process

This process was discovered by Sir Henry Bessemer of England in 1856.

Principle of the process. This process is based on the fact that the impurities present in cast iron are completely oxidised in presence of hot air blast, i.e., virtually wrought iron is obtained. This is then mixed with known amount of spiegeleisen, an alloy of Fe, Mn and C to obtain steel.

In this process molten cast iron is taken directly from the blast furnace and is put into Bessemer's converter.

Construction of Bessemer's converter. Bessemer's converter is a pear-shaped furnace, about 20m high and 10m in diameter. It is made of steel plates and has a number of holes (called tuyers) at its base through which a blast of hot air can be admitted into the converter. The converter is rotated on its horizontal central axis fig.



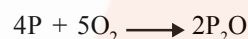
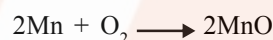
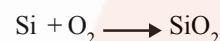
Depending on the nature of the impurities present in the cast iron, the converter is lined on its inside with silica, SiO_2 (acidic lining) or lime (CaO)/magnesia (MgO) (basic lining). If the cast iron contains C, S, Si and Mn as impurities silica lining is used and the process is called acid Bessemer's

process. On the other hand, if the cast iron contains P as impurity, CaO/MgO lining is used and the process is known as basic Bessemer's process. In actual practice, basic lining is obtained by using a mixture of CaO and MgO mixed with tar to bind them. The materials (SiO_2 , CaO and MgO) used for lining the converter act as flux as will be evident from the following discussion.

Working. To start with, the converter is brought into the horizontal position, molten cast iron is put into it and then a blast of hot air or O_2 is blown into the converter through its tuyers. The converter is then rotated so that its mouth comes in vertically upwards position. The blowing of hot air is continued.

Reaction taking place in Bessemer's converter

- (i) In the beginning Si, Mn and P (impurities) get oxidised by O_2 to their respective oxides.



MnO produced as above combines with SiO_2 lining (acidic lining) of the Bessemer's converter to form the slag of MnSiO_3 and is thus removed.

MnO (basic impurity) + SiO_2 (acidic lining acting as an acidic flux) $\rightarrow \text{MnSiO}_3$ (slag)

P_2O_5 and SiO_2 produced react with CaO lining (basic lining) of the Bessemer's converter to form the slags of $\text{Ca}_3(\text{PO}_4)_2$ and CaSiO_3 and are thus removed.

P_2O_5 (acidic impurity) + 3CaO (basic lining acting as a basic flux) $\rightarrow \text{Ca}_3(\text{PO}_4)_2$ (slag)

SiO_2 (acidic impurity) + CaO (basic lining acting as a basic flux) $\rightarrow \text{CaSiO}_3$ (slag)

The mixture of the three slags viz. MnSiO_3 , $\text{Ca}_3(\text{PO}_4)_2$ and CaSiO_3 is called basic slag which is used as a fertiliser. The present discussion makes it evident that SiO_2 , CaO and MgO which are used for lining the converter act as fluxes.

- (i) Later on C and S are oxidised to CO and SO_2 respectively by the blast of air. SO_2 escapes from the mouth of the converter and CO burns with a blue flame at the mouth of the Bessemer converter (Bessemer's condes). When the whole of carbon present in the cast iron has been oxidised to CO , the burning of CO at the mouth of the converter stops. At this state, the blowing of O_2 into the converter is stopped. Here it should be noted that the formation of slags. After all the impurities

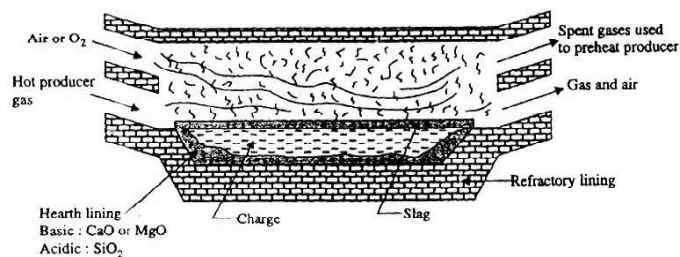
have been removed, the calculated quantity of spiegeleisen alloy (an alloy of iron and manganese having Mn = 20–30%, C = 5%, Fe = remaining quantity) is added to the molten cast iron into the converter and blast of hot O_2 is again allowed to enter into the converter so that carbon and Mn present in spiegeleisen alloy get mixed with cast iron and steel is obtained which is taken out of the converter in the molten state. Steel obtained in this way is called manganese steel. Spiegeleisen alloy being added does the following functions :

- It acts as a scavenger (i.e., cleaning agent), since Mn present in the alloy removes O_2 , N_2 , P and S, if dissolved in the molten steel, in the form of its oxide (MnO), nitride (Mn_3N_2), phosphide (Mn_3P_2) and sulphide (MnS). If O_2 and N_2 are not removed, these gases, on cooling, become less soluble and form bubbles (called blow holes) in steel. These bubbles weaken the strength of the steel. Thus Mn prevents the formation of blow holes. Some Al or ferro-silicon may also be added to remove blow holes. Due to the formation of Mns, the harmful effects of sulphur are neutralised.
- It acts as a de-oxidiser, since Mn present in the alloy reduces oxidised iron, if present.
- The alloy supplies the required quantity of carbon, Mn and Fe to get the steel of the required composition. Note that carbon is an essential constituent of all types of steel. Mn makes the steel hard and increases its tensile strength. If more quantity of Mn (upto 14%) is added in the form of spiegelcisen alloy, manganese steel obtained is very hard, tough for making steel helmets, safes, cross overs etc.

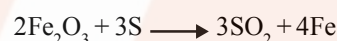
Requisite quantity of other metals like Cr, Ni etc. along with carbon are also added to get the steel of a particular composition.

2. Open-hearth process of Siemens-Martin process

This is the modern process and the furnace used in this process is called open-hearth furnace. Since this furnace works on the regenerative principle of heat economy, it is also called regenerative furnace. In this process steel is prepared from cast iron. Open-hearth furnace consists of an open hearth. The hearth is lined with silica or calcined dolomite ($CaO.MgO$) depending upon the nature of impurities present in pig or cast iron. Silica lining is used if the impurities are manganese, silicon, etc., and calcined dolomite lining is used if much of phosphorus is present. A high temperature of about $1500^\circ C$ is generated by burning producer gas which works on regenerative system of heat economy (fig.)



The charge consists of pig or cast iron, scraps, iron ore (haematite) and lime. The charge is heated on the hearth of the furnace. The impurities are oxidised by iron ore.



Samples of steel are drawn from time to time and tested for carbon content. Finally spiegleisen (an alloy of iron, manganese and carbon) is added to the molten mass and obtain desired steel. The process takes about 8 to 10 hours for completion. The process takes longer time than Bessemer process.

Advantages of open-hearth process over Bessemer's process.

Open-hearth process has the following advantages over the Bessemer's process.

- The temperature can be controlled as the heating is done externally.
- As it is a slower process, it can be controlled in better way. The composition and quality can be well controlled.
- The loss of iron in this process is only 4% while the loss is about 15% in Bessemer's process.
- In this process scrap iron is re-used.
- This yields better quality of steel.
- A considerable economy of the fuel is achieved by using the regenerative system.

3. Duplex process

Now-a-days Duplex process is being used for the manufacture of large quantities of steel. This process is a combination of Bessemer's process and open-hearth process. In this process the molten pig iron is first treated in an acid Bessemer's converter to remove Si, Mn and a part of

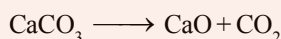
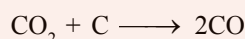
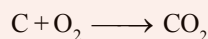
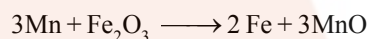
C. The molten pig iron is then transferred to open-hearth furnace with a basic lining to remove P and remaining C and is finished off as usual. Tata Iron and Steel Works as using Duplex process for the manufacture of steel.

4. Electric process

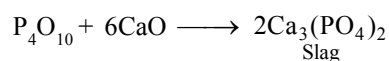
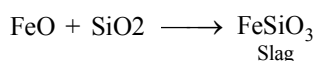
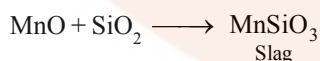
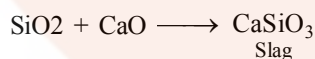
In this process steel is prepared in arc furnace (also called Heroult's furnace). This is a crucible-shaped furnace and consists of steel shell which is lined inside with magnesite of dolomite and is covered with heat resisting bricks. The furnace is provided with movable and water jacketed graphite electrodes coming in from the roof or from the sides (fig.). Each electrode can be raised or lowered independently by a rack or pinion arrangement. The electrodes are held vertically and the charge which consists of Bessemer's steel, iron ore haematite and calculated quantity of lime is run into the arc furnace and the current is switched on to produce electric arc between the electrodes. This electric arc produces a temperature of 3000–3500°C.

Reactions : Reactions taking place in this process are :

(a) Oxidation and formation of slag. At the temperature of the electric arc, the charge melts and vigorous reaction starts. In this reaction Si, Mn, C and P are oxidised to SiO_2 , MnO , CO and P_4O_{10} respectively and CaCO_3 gets decomposed.

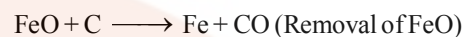


The oxides viz. SiO_2 , MnO , CO and P_4O_{10} are removed as slags.



This slag being lighter floats over the metallic portion. As soon as the oxidation and formation of slag is complete, the furnace is carefully tilted and the slag is pured out of it.

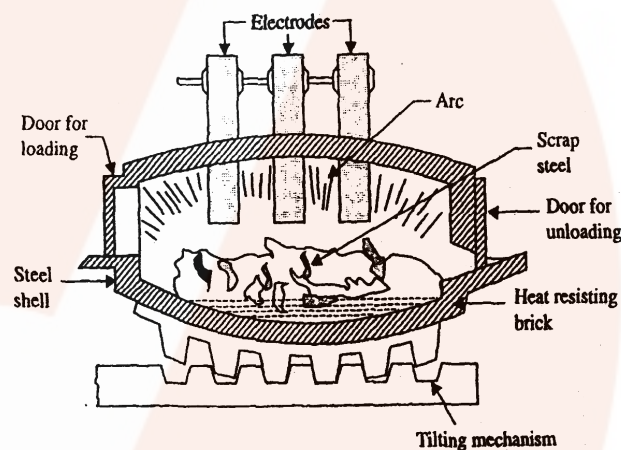
- (b) Deoxidation and desulphurization. After the slag is poured out of the furnace, a charge consisting of lime, sand, fluorspar and some coke and ferro-silicon is added to the furnace. Any FeO present in the steel is removed as Fe by reducing it with the added coke.



Sulphur present as FeS is removed as CaS by treating it with CaO



FeO thus produced is at once reduced to Fe as before while CaS goes into the slag. When desulphurization (i.e., removal of sulphur) is complete, the steel is poured out into moulds.



Arc furnace (Heroult's furnace) for the manufacture of steel.

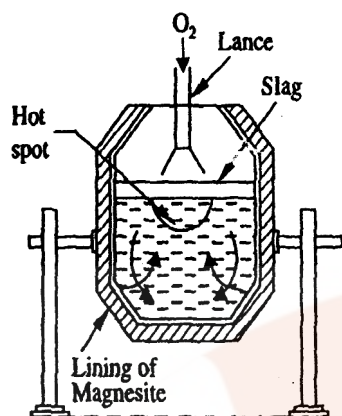
This method is also used for the manufacture of alloy steels, tool steels, stainless steels and special quality steels.

5. L.D. process :

This process has recently been developed in Lintz and Dusenverfahren in Austria and is in use at the Rourkela steel plant. The main advantages of the process are :

- (i) Less capital expenditure and more productivity.
- (ii) It takes only 45 minutes to treat one lot.
- (iii) Even scrap iron can be used.
- (iv) Less operating cost and better quality of steel.

The process is carried out in a converter lined with magnesite which differs from the Bessemer converter in not having the perforated base but a solid bottom. Pure O_2 is blown from the top through a copper lance (fig.)



Converter for L.D. process.

Properties of steel

1. **Mechanical properties.** Steel combines the useful properties of cast iron and wrought iron, being both hard and elastic and provided the proportion of carbon is not high, it can be forged and welded.
2. **Action of Heat : Heat treatment of steel.** A characteristic behaviour of steel which distinguishes it from other commercial forms of iron is that its hardness and elasticity can be varied by proper heat treatment of steel. For example :
 - (a) **Annealing.** When hard steel is heated to bright redness and then allowed to cool slowly, hardness of steel is considerably decreased and it gets softened. This process is called annealing.
 - (b) **Quenching or hardening.** When mild steel is heated to a high temperature (i.e., to bright redness) and then suddenly cooled by plunging it in oil or water, it becomes as hard and brittle as glass. This process is called quenching or hardening

and the steel obtained by this method is called quenched steel.

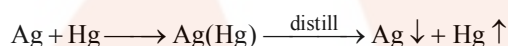
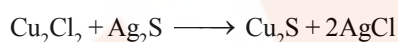
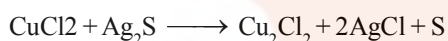
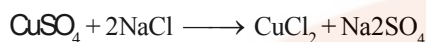
- (c) **Tempering.** The quenched steel can be made to lose its brittleness by heating it to varying temperatures for varying periods. The process is called tempering and is employed for bringing the steel into a suitable state of hardness and elasticity. The temperature is generally judged from the colour of a thin film of oxide which is formed on the surface and varies from yellow (200–230°C) to brown (225–270°C) to blue (300°C) as the temperature rises. Steel for cutting blades and tools is made yellow but that required for springs, saws, etc., is tempered blue.
3. **Surface treatment of steel.** The surface treatment of the steel is done by the following process :
 - (a) **Case hardening.** The process of producing a thin coating of hardened steel on the surface of the mild steel is called case hardening. This is done by heating the mild steel with charcoal and then plunging into oil. This produces a thin coating of hardened steel on the surface. Such a steel becomes resistant to wear and tear.
 - (b) **Nitriding.** The process of producing a hard coating of iron nitride on the surface of steel is called nitriding. Steel is heated in the atmosphere of dry ammonia at 500–600°C for about 3 to 4 days when a hard coating of iron nitride is produced on the surface.

Comparison between cast iron, wrought iron and steel

Property	Cast iron	Wrought iron	Steel
Chemical composition	Iron 93–95%, Carbon 2.5–5% Impurities about 2%	Iron 99.5–99.8%, Carbon 0.1–0.25% Impurities about 0.3%	Iron 99.5–98.0%, Carbon 0.25 to 2.0%

SOME SPECIAL PROCESSES FOR SILVER**Mexican Amalgamation Process**

Mercury and magistral (burnt pyrites-sulphates and oxides of copper and iron) are added to the powdered mineral containing H_2O and $NaCl$. The mixture is kept for several days. Silver is formed in the amalgam form. On washing, drying and subsequent distillation, silver is obtained.



Desilverisation of Lead : When lead-silver alloy is poor in silver (such as argentiferous lead or galena), desilverisation of lead is affected by **Parke's process**. It depends upon the fact that :

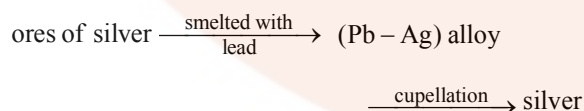
- (i) when zinc is added to a melted alloy of silver and lead, zinc takes away silver from the alloy and itself forms an alloy with silver and not with lead
- (ii) alloy of zinc and silver melts at a higher temperature than lead
- (iii) the alloy of silver and zinc is lighter than lead and forms two separate layers
- (iv) on distillation of silver and zinc, zinc separates

Pattinson's Process

It depends upon the fact that the alloy of lead and silver containing less than 1.8 percent of silver, melts at a low temperature than pure lead. If this type of alloy is melted, and the melted alloy is allowed to cool, lead first separates and repeating the process, one becomes richer in silver. Further recovery is done by cupellation process.

Lead Process

This process depends upon the fact that when ores of silver are smelted down with lead, and alloy of lead and silver is formed; from this alloy lead is removed by oxidation.



- * (Pb-Ag) alloy rich in silver : Cupellation process is used
- * (Pb-Ag) alloy poor in silver : Parke's or Pattinson's process is used

3. THERMODYNAMIC PRINCIPLES OF METALLURGY

The basic concepts of thermodynamics are quite helpful in selecting which element will be the most suitable reducing agent for a particular oxide during a metallurgical operation. It can also predict the optimum temperature at which the reduction can occur smoothly.

For any reaction or process, Gibb's Helmholtz free energy change (ΔG) is given by the equation,

$$\Delta G = \Delta H - T\Delta S \quad \dots\dots (i)$$

where ΔH is the enthalpy change and ΔS is the entropy change and T is the absolute temperature at which the reaction is carried out. For the feasibility of any reaction at any temperature the value of ΔG must be negative at the temperature. The free energy change is also related to the equilibrium constant ' K ' of the reaction at temperature T by the following equation,

$$\Delta G = -RT \ln K \quad \dots\dots (ii)$$

A negative ΔG implies a +ve K in the equation. This can happen only if the reaction proceeds towards the products. The following conclusions can be drawn :

- (i) **Greater the negative value of free energy change (ΔG), more spontaneous is the reaction.**

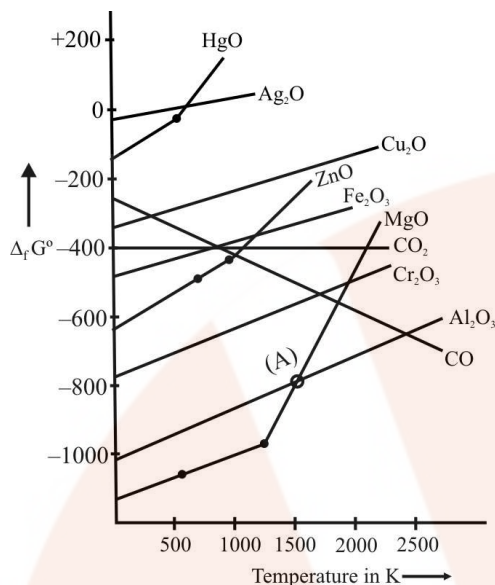
ΔG	$T\Delta S$	Favourable conditions
-ve	+ve	Any temperature
-ve	-ve	$\Delta H > T\Delta S$ (Temp. should be low)
+ve	+ve	$T\Delta S > \Delta H$ (Temp. should be high)

- (ii) If two reactions are put together in a system and the net ΔG of both the reactions is -ve, the overall reaction will occur, i.e., a reaction with ΔG positive can be made to occur if it is coupled with another reaction having a large negative ΔG so that the net ΔG of both the reactions is negative.

Such coupling reactions can be easily understood through **Ellingham diagram**.

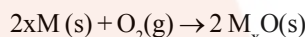
Ellingham diagram : Ellingham diagram consists of graphs which represent the variation of standard free energy with temperature of the formation of oxides of various elements, i.e., of $\Delta_f G^\circ$ vs T . Similar plots can also

be plotted for sulphides and halides. These were first plotted by H.J.T. Ellingham. These diagrams help us in predicting the feasibility of thermal reduction of an ore.



Ellingham diagrams for oxides of some elements

Consider the formation of a metal oxide (M_xO).



In this reaction, there is decrease in the value of ΔS° as M_xO is solid and O_2 is a gas, i.e., ΔS is negative. Thus, if temperature is increased, $T\Delta S^\circ$ becomes more negative.

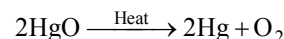
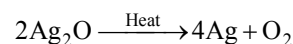
As in the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

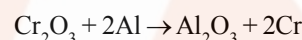
$T\Delta S^\circ$ is subtracted, therefore, ΔG° becomes less negative, i.e., ΔG° is likely to increase with rise in temperature and this trend is confirmed from the curves.

- The slope of the curves of the formation of metal oxides is +ve because ΔG° becomes less negative or increases with the rise in temperature.
- Each curve is a straight line except when some change takes place in phase ($s \rightarrow l$ or $l \rightarrow g$). The temperature at which such a change occurs is indicated by an increase in the slope on the +ve side. For example, in the Zn–ZnO curve, the melting of zinc is indicated by an abrupt increase in the +ve slope at temperature 692 K.
- In the case of less reactive metals like silver and mercury, ΔG° becomes positive at high temperatures. It indicates that both silver oxide (Ag_2O) and mercury oxide (HgO) are unstable and decompose

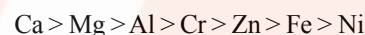
at high temperature.



- In the curve of CO, ΔG° decreases as ΔS° increases. This is indicated by the downward trend.
- Any metal oxide with lower value of ΔG° is more stable than a metal oxide with higher ΔG° . This implies that the metal oxide placed higher in the diagram can be reduced by the metal involved in the formation of the oxide placed lower in the diagram. For example, Cr_2O_3 can be reduced by Al metal but Al_2O_3 cannot be reduced by Cr.



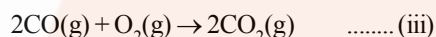
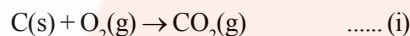
Thus, the relative tendency of the various metals to act as reducing agents is :



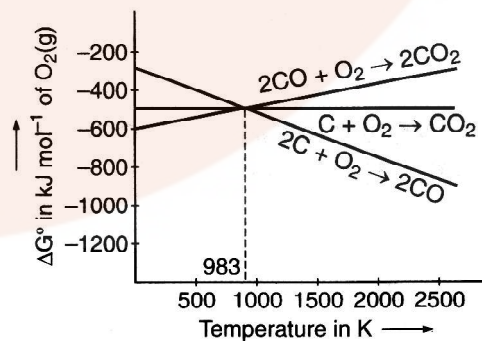
3.1 Reducing Nature of Carbon

Carbon in the form of coke, charcoal or carbon monoxide is used as a reducing agent in pyrometallurgical operations. Such a reduction process used in the extraction of a metal is termed **smelting**.

When carbon is to act as a reducing agent, the following three reactions are possible :



In the first reaction (formation of CO_2) there is hardly any change in entropy, i.e., $\Delta S^\circ \approx 0$ and therefore, ΔG° remains nearly the same with rise in temperature, i.e., ΔG° is independent of temperature.



Ellingham diagram for the reducing nature of carbon

In the second reaction (formation of CO), there is increase in entropy (ΔS° is positive) and therefore, ΔG° becomes more negative with increase in temperature.

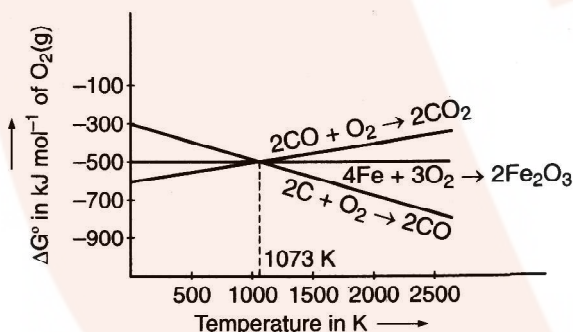
However, in third reaction, there is decrease in entropy (ΔS° is negative) and therefore, ΔG° becomes less negative with increase in temperature.

The above observations can be seen in Fig. The three curves have been found to intersect at 983 K. It implies that above this temperature, the reaction (ii) is most suitable. It means that carbon can reduce any metal oxide at very high temperatures and is then itself oxidised to CO. However, the reduction with carbon at high temperatures is not preferred in all cases due to the following reasons :

- It involves high cost.
- Some metals react with carbon at high temperatures and form carbides.
- There are many practical difficulties in the maintenance of high temperature.

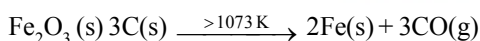
(A) Theory of reduction of Haematite

In the Ellingham diagram, there are three curves which illustrate the formation of ferric oxide from Iron, formation of CO from carbon and formation of CO_2 from CO. The curves cross each other at 1073 K.



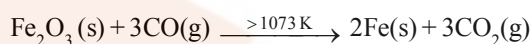
Ellingham diagram for the reduction of haematite

Above 1073 K, ΔG° for the formation of Fe_2O_3 is less negative than ΔG° for the formation of carbon monoxide from carbon. Thus, above 1073 K, carbon (coke) can reduce Fe_2O_3 , i.e., $\Delta_r G^\circ$ for the reaction,



is negative.

Below 1073 K, ΔG° for formation of CO from carbon is less negative than ΔG° for the formation of Fe_2O_3 . $\Delta_r G^\circ$ for the reduction of Fe_2O_3 with carbon will be positive and hence, reduction is not possible. However, it is observed from the diagram that ΔG° of formation of CO_2 from CO is more negative than ΔG° of formation of Fe_2O_3 . This means that Fe_2O_3 can be reduced by CO below 1073 K, i.e., $\Delta_r G^\circ$ for the reaction,

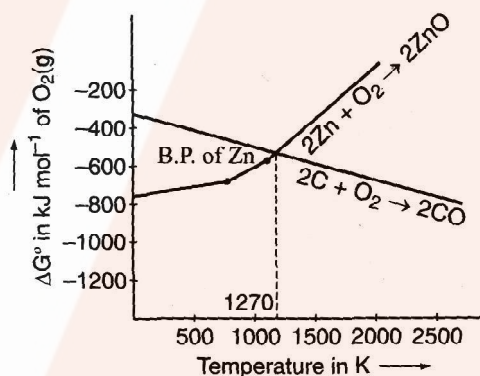


is negative.

Thus, in the blast furnace, reduction of Fe_2O_3 occurs in different temperature ranges either below 1073 K by carbon monoxide or above 1073 K by carbon (coke).

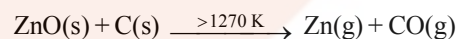
(B) Theory of reduction of ZnO

Ellingham diagram reveals that the curves involving the formation of ZnO and carbon monoxide cross each other at about 1270 K.



Ellingham diagram for formation of ZnO and CO

There is sudden increase in the value of ΔG° for the formation of ZnO above 1180 K. This is due to the fact that zinc begins to boil at this temperature. Above 1270 K, $\Delta_r G^\circ$ of the following equation,



is considerable negative and thus, reduction of ZnO with coke occurs easily.