

9. METALLURGY

SYNOPSIS:

- Generally metals occur as compounds in the earth crust. The compounds of metals which occur in earth crust, along with the earthy impurities associated with them are called minerals.
- The impurities present in the mineral are called Gangue (or) Matrix.
- The mineral from which the metal can be extracted very easily and economically is known as an ore.
- All ores are minerals, but all minerals are not ores.
- The selection of a mineral as an ore depends on following factors
 - i) The percentage of metal in the mineral
 - ii) Nature and magnitude of impurities in the mineral.
 - iii) The expenditure involved in the extraction of metal from the mineral.
 - iv) The industrial utility of by-products produced in the separation of metal from the mineral.
- Metals generally occur as their oxides, carbonates, sulphides, chlorides, silicate minerals.

Nature of the Mineral	Name of the Mineral	Important constituent metal
Oxide minerals	Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)	Al
	Cuprite (Cu_2O)	Cu
	Magnetite (Fe_3O_4)	Fe
	Haematite (Fe_2O_3)	Fe
	Zincite (ZnO)	Zn
	Cassiterite (SnO_2)	Sn
	Chromite ($\text{Cr}_2\text{O}_3 \cdot \text{FeO}$)	Cr
	Pitch blende (U_3O_8)	U
Carbonate minerals	Malachite $\{\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2\}$	Cu
	Azurite $\{2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2\}$	Cu
	Calamine (ZnCO_3)	Zn
	Siderite (FeCO_3)	Fe
	Magnesite (MgCO_3)	Mg
	Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$)	Mg Ca
	Lime Stone (CaCO_3)	Ca
Sulphide minerals	Copper pyrites ($\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$)	Cu
	Iron pyrites (FeS_2)	Fe
	Zinc blende (ZnS)	Zn
	Pentlandite (Ni,FeS)	Ni
	Argentite (Ag_2S)	Ag
Halide minerals	Common salt (NaCl)	Na
	Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)	Mg
	Horn Silver (AgCl)	Ag
	Cryolite (Na_3AlF_6)	Al

	Sylvine (KCl)	K
Sulphate minerals	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Ca
	Anglesite (PbSO_4)	Pb
	Barytes (BaSO_4)	Ba
Phosphate minerals	Monazite (a mixture of rare earths)	Th
	Monite ($\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$)	Ca
Silicate minerals	Thorite (ThSiO_4)	Th
	Zircon(Zr-SiO_4)	Zr

PRINCIPLES OF EXTRACTION

- The term metallurgy includes
 - concentration of the ore
 - reduction of the ore
 - refining of metal
- The removal of the gangue from the ore is called ore dressing (or) concentration of the ore.
- The separating of metal in crude form (impure form) from the ore is called reduction of the ore.
- The separation of a metal in pure state from the crude metal is called refining of metal.
- The concentration of the ore can be done by
 - Hand picking
 - Gravity method (washing with water)
 - Froth floatation
 - Magnetic separation
 - Liquation
 - Leaching
- The minerals available in nature contains various impurities which are combined with mineral physically or chemically.
- The substances which do not melt or become soft even on strong heating are called refractory substances.
Eg: Silica, quartz, calcia, magnesia, graphite, chromite, bone ash etc.,
- Silica is an acidic refractory material. Calcia and magnesia are basic refractory materials Graphite, silicon carbide are neutral refractory materials.
- The substance used to remove the gangue from the ore in the form of easily fusible mass is called a flux.
- The flux is added to the ore during the metallurgical process and heated.
- The flux combines with the gangue and forms a easily fusible mass called **slag**. The slag can be very easily removed from the contents.
Gangue + flux = slag
- Fluxes are of two types
 - Acidic flux. Eg: Silica
 - Basic flux. Eg: Calcia, magnesia.
- Acidic flux is used to remove gangue having basic nature.
- Basic flux is used to remove gangue having acidic nature.
- Haematite ore contains silica as impurity (gangue). This impurity is removed by using lime stone as flux.

$$\begin{array}{ccccccc} \text{CaCO}_3 & + & \text{SiO}_2 & \rightarrow & \text{CaSiO}_3 & + & \text{CO}_2 \\ \text{Flux} & & \text{Gangue} & & \text{Slag} & & (\text{Flue gas}) \end{array}$$
- In the extraction of copper from copper iron pyrites, FeO is gangue. This is removed by using silica as flux.

$$\begin{array}{ccccccc} \text{FeO} & + & \text{SiO}_2 & \rightarrow & \text{FeSiO}_3 & & \\ \text{Gangue} & & \text{Flux} & & \text{Slag} & & \end{array}$$
- The waste gases produced during the metallurgical process are called **flue gases**.

(Eg: CO_2, SO_2)

- Sand and small stones are removed by hand picking method
- Haematite ore occurs as lumps. So it can be very easily separated from the impurities like sand, stone pieces present along with it by Hand picking.
- In washing method ore is made into fine powder by using ball mills
- Ores like cassiterite and alluvial sand (contains Gold) are concentrated by washing with water.
- Gravity method is based on the difference between the densities of the ore particle and gangue.
- Gravity process is used for the concentration of denser ores from the water soluble and lighter impurities (Gangue). Oxide ores and carbonate ores are concentrated by this method.

FROTH FLOATATION PROCESS

- This method is used when a higher ore contains impurities having higher density.
- This method is used for the concentration of Sulphide ores. (Eg: Copper pyrites, iron pyrites, Galena, Zinc blende etc.,)
- In this process collectors and froth stabilisers are added.
- Collectors (e.g., pine oils, fatty acids, xanthates, etc.)
Froth Stabilisers (e.g., cresols, aniline)
- 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.
- Sometimes it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using 'depressants'.

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.

ELECTROMAGNETIC PROCESS

- This method is used if the ore (or) gangue particles are magnetic in nature.
- Tin stone ore is non magnetic. It contains wolframite as impurity. The **wolframite** is magnetic. The formula of wolframite is $FeWO_4$.
- Haematite (or) Magnetite ore is magnetic. It contains silica as impurity. The silica is non magnetic.

LIQUATION PROCESS:

- This method is used if the ore contains high melting gangue and easily fusible mineral particles.
- Stibnite, an ore of antimony is placed on the height of a slant surface and heated slowly. The ore melts at $500 - 600^\circ C$ and flows down leaving behind the gangue.

TYPES OF FURNACES

- The important parts in a furnace are
i) Hearth ii) Fire place (fire box) iii) Chimney
- The different types of furnaces used are
i) Reverberatory furnace ii) Retort furnace
iii) Blast furnace iv) Shaft furnace
v) Open hearth furnace vi) Muffle furnace
vii) Electrical furnace viii) Arc furnace
ix) Bessemer converter.
- The ore along with the substances added to it (if any) is known as charge.
- The charge is placed on the hearth of a furnace.

REVERBERATORY FURNACE

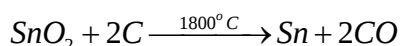
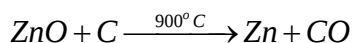
- The principle involved in reverberatory furnace is indirect heating.
- The hot gases and flames produced by the burning of fuel in the fire box, reach the top of the furnace and then reflected on to the hearth. The charge gets heated.
- The efficiency of the furnace is less because the heat content of waste gases cannot be used repeatedly.
- This furnace is used in the metallurgy of Cu, Pb, steel etc.,

BLAST FURNACE

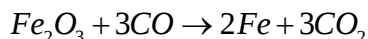
- The principle involved in blast furnace is direct heating.
- The charge is introduced into the furnace from the top by a special arrangement known as double cup and cone arrangement.
- Hot air is blown through a series of pipes called **tuyeres** to heat the charge.
- Molten mass (products) which collects at the bottom of the furnace (i.e. hearth) is called **smelt**.
- The temperature of furnace at the top (near cup and cone) is 400 - 500°C and at tuyere's region is 1500°C.

EXTRACTION OF METAL REDUCTION OF THE ORES

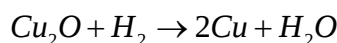
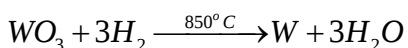
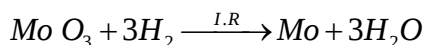
- Generally oxide and halide ores are reduced.
- The reduction of the ore can be done by
 - i) chemical methods
 - ii) electrolytical methods.
- The commonly used reducing agents in metallurgy are H_2 gas, CO gas, water gas, Al, Mg, Ca metals, Coke.
- The electrolysis methods are used from the extraction of highly electropositive metals from their ores.
- The metals generally obtained by the electrolysis of their ores are Na, K, Ca, Mg, Al etc.,
- The metals obtained by the reduction of their ores with suitable reducing agent are Zn, Sn, Cu, Fe etc.,
- Metal oxide ore on reduction with carbon or coke gives metal. This method is used for the extraction of metals like Zn, Sn etc.,



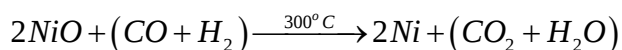
- Haematite (Fe_2O_3) is reduced to iron mainly by carbon monoxide.



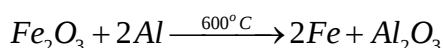
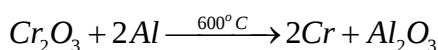
- Metal oxide on reduction with hydrogen gas gives metal. This method is used for the extraction of metals like Cu, W, Mo etc.,

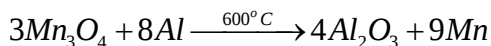


- NiO is reduced to nickel by water gas.

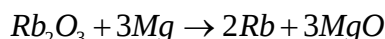


- Metal oxide on reduction with aluminium powder gives metal. This is known as Gold Schmidt aluminothermic process. This method is for the extraction of metals like Cr, Fe, Mn etc.,

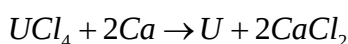
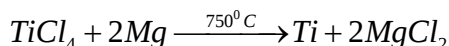




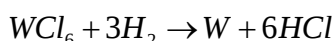
- The temperature of mixture in Aluminothermic process increases to 2500 - 3000°C due to the exothermic nature of reaction. So the metal is obtained in molten state in the reaction.
- Rubidium oxide on reduction with magnesium gives rubidium.



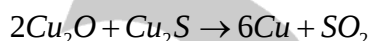
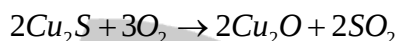
- 'Al' can be extracted by passing current through a molten solution of and Al_2O_3 cryolite
- The alkali metals, Titanium, Tungsten, Uranium are generally extracted by reducing their halides with Mg, Ca, or by electrolysis.
- TiCl_4 on reduction with Mg gives titanium. on reduction with calcium gives uranium.



- UCl_4 on reduction with hydrogen gives tungsten



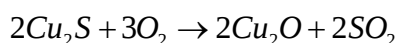
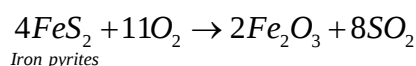
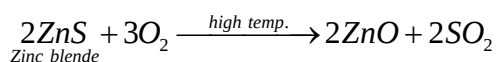
- Self reduction method is used for the extraction of metals like Cu, Hg, Pb etc.,



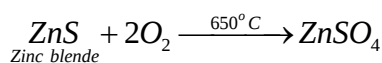
- More electropositive metal can displace less electropositive metal from the aqueous solution of its salt. This is known as Hydro metallurgy.
- Copper can be obtained by adding iron to aqueous CuSO_4 solution. This is an example for hydro metallurgy.

ROASTING

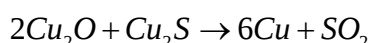
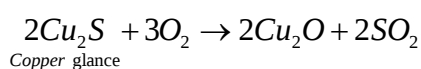
- The process of heating an ore alone (or) mixed with other substances in air below its melting point is known as roasting.
- The roasting process removes volatile impurities from the ore.
- The roasting process is used for sulphide ores.
- In roasting process air acts as oxidant.
- Some sulphide ores on roasting gives metal oxide and sulphur dioxide. This is known as **oxidizing roasting**.



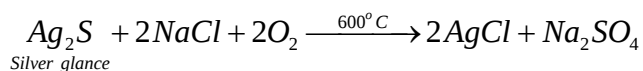
- Some Sulphide ores on roasting gives metal sulphate. This known as **sulphatizing roasting**.



- Some sulphide ores on roasting gives metal and sulphur dioxide. This is known as **auto-reduction** (self-reduction).

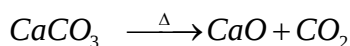


- Some sulphide ores are mixed with a chloride salt and roasted. The sulphide ore changes to chloride ore. This is known as chloridizing roasting.

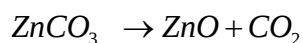


CALCINATION

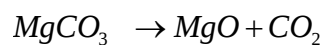
- The process of heating an ore in the absence of air below its melting point is known as Calcination.
- The calcination process removes volatile impurities from the ore.
- The calcination process is used for oxide, carbonate and bicarbonate ores.
- Carbonate ores on calcination decomposes giving metal oxide and CO_2 .



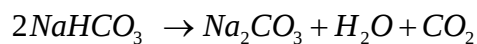
Limestone



Calamine



Magnesite



baking soda



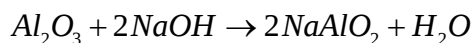
SMEETING

- The process of separating molten metal in crude form (or) mixture of metal sulphides in molten form from the ore is called smelting.
- A mixture of haematite, coke and limestone on heating in a blast furnace gives **molten iron**.
- A mixture of copper iron pyrites, coke and sand on heating in blast furnace gives **Matte**. The matte is molten Cu_2S containing a little FeS .

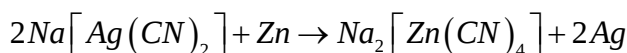
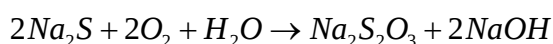
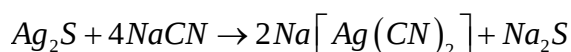


LEACHING PROCESS

- The ore is treated with a suitable solution. The ore dissolves in solution leaving behind the gangue. The solution is separated from the gangue.
- From the solution the ore is separated in a different chemical form.
- In leaching process mineral acids or aqueous solution of reagent are used as leaching agent
- Bauxite on leaching with aqueous NaOH solution gives NaAlO_2 solution. $\text{Al}(\text{OH})_3$ is separated from the solution at 473-523K and 35-36 bar pressure



- Silver ore on leaching with aqueous gives $\text{Na}[\text{Ag}(\text{CN})_2]$ solution. Ag metal is separated from this solution directly.



ELECTROLYTIC REDUCTION

- This method is used for the isolation of most reactive metals and non metals like Na, K, Al, Ca and F_2, Cl_2
- Sodium is obtained by the electrolysis of
 - molten NaCl (Down's method)
 - fused NaOH (Castner's method)
- Magnesium is obtained by the electrolysis of fused MgCl_2 .
- Aluminium is obtained by the electrolysis of Al_2O_3 dissolved in molten cryolite. This is known as Hall-Heroult's method.

REFINING (OR) PURIFICATION

METHODS OF METALS

- The removal of impurities from crude metal is called refining of metal.
- The methods used for refining of metals are liquation, distillation, cupellation, poling electrolysis, zone refining.
- Liquation method is used to refine metals having low melting points. Eg. Tin, Lead, Bismuth.
- In liquation method crude metal is placed on the height of a sloping hearth and heated slowly. The metal melts and flows down, leaving behind the impurity. The impurity left behind is called **dross**.
- Distillation method is used to refine metals having low boiling points. Eg: Zn, Cd, Hg.
- Metals containing non volatile impurities can also be purified by distillation
- In distillation method the crude metal is heated in a retort. The metal distills over leaving the impurity in the retort.
- Cupellation method is used to refine metals having easily oxidisable impurities. Eg. Ag.
- Ag metal contains lead as impurity. The crude silver metal is heated in a cupel (a small bowl type vessel) made of bone ash in free supply of air. Lead gets oxidised to PbO and goes out of the cupel leaving silver in pure state.
- Poling method is used to refine metals having metal oxide as impurity. Eg. Cu, Sn

- In poling method, carbon powder is sprinkled over the surface of molten crude metal and the mixture is stirred with poles of green wood. The reducing gases formed from wood and carbon reduces the metal oxide impurity to metal.
- Electrolysis method is used to refine metals like Cu, Ag, Au, Al.
- In electrorefining method, impure metal is taken as anode and pure metal is made cathode. The electrodes are placed in acidified aqueous solution of metal salt (or) molten metal salt. On electrolysis, the metal in anode dissolves into the solution and gets deposited over the cathode.
- The residue left below anode in the electro refining of metal is called **anode mud**.

ZONE REFINING (OR) FRACTIONAL

CRYSTALLIATION

- This method is used to refine elements like Si, Ge, Ga etc.,
- This method is used to produce ultra pure elements.
- This method is based on the difference in the solubilities of impurities in the molten and solid state of metal .
- In this method a movable heater is fitted around a rod of impure metal. As the heater moves from one end to other end of the metal rod, the metal and impurities are separated.
- The process is be repeated a number of times in the same direction.

EXTRACTION OF COPPER

- The important minerals of copper as oxides & sulphides are

Cuprite (or) ruby copper Cu_2O

Copper glance Cu_2S

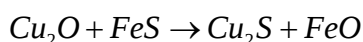
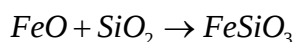
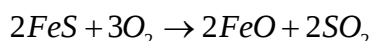
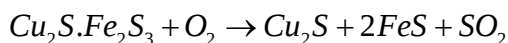
Copper pyrites $CuFeS_2$

$(Cu_2S.Fe_2S_3)$

Malachite $CuCO_3 \cdot Cu(OH)_2$

Azurite $2CuCO_3 \cdot Cu(OH)_2$

- Copper is extracted from sulphide minerals (Copper iron pyrites).
- The $CuFeS_2$ ore is concentrated by froth flotation process.
- The concentrated ore is roasted in a reverberatory furnace.
- The roasting process removes volatile impurities like As or Sb from the ore.
- The roasted ore contains Cu_2S , FeS and small quantities of Cu_2O and FeO.
- The roasted ore is mixed with a little coke and sand and smelted in blast furnace.



- The slag formed in the blast furnace is $FeSiO_3$ (Ferrous silicate).
- The smelt formed in the blast furnace contains Cu_2S and a little FeS. This mixture is called **copper matte**.
- The copper matte is heated in Bessemer converter lined inside with basic oxides such as lime (or) magnesia in presence of air and sand.

- In Bessemer converter all iron is removed as $FeSiO_3$ slag.
- In Bessemer converter Cu_2S undergoes self reduction giving Blister copper.
- Blister copper is 98% pure copper.
- Blister copper contains Cu_2O as impurity.
- The molten blister copper is refined first by poling method and then by electrolysis.
Thin plates of pure copper serves as cathode which are coated with graphite and impure copper plates act as anode. Electrolyte is copper (II) Sulphate solution.
- The copper metal obtained by electro refining is 100% pure.
- Copper has more affinity for sulphur and iron has more affinity for oxygen. So smelt of blast furnace contains more and a little FeS, because FeO formed in blast furnace is removed as .

EXTRACTION OF ZINC

- The zinc metal is called Yashada in Ayurvedic medicine.
- Zinc metal does not occur in native state.
- The minerals of zinc are

Zinc blende	ZnS
Zincite	ZnO
Calamine	$ZnCO_3$
Franklinite	$ZnO.Fe_2O_3$
Willemite	$Zn_2SiO_4 (2ZnO.SiO_2)$

- Zinc blende ore is crushed , washed with water and then concentrated by
 - i) Gravity process using Wilfley's table.
 - ii) Froth floatation process.
- The zinc blende ore is subjected to electromagnetic separation to remove iron oxide impurity.
- Zinc blende ore on roasting in free supply of air gives ZnO, in rotary shelf burner.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$ZnS + 2O_2 \rightarrow ZnSO_4, \quad 2ZnSO_4 \rightarrow 2ZnO + 2SO_2 + O_2$$
- The calamine ore on calcination gives zinc oxide

$$ZnCO_3 \rightarrow ZnO + CO_2$$
- The zinc oxide on reduction with carbon powder gives zinc metal. This is known as Belgian process

$$ZnO + C \xrightarrow{1100^\circ C} Zn + CO$$

$$ZnO + CO \rightarrow Zn + CO_2$$

- The mixture of ZnO and coke is heated in fire clay (or) earthen ware retorts, to which long bent iron devices are attached. The long bent iron devices are called prolongs. The fire clay retorts and the prolong are as shown below.
- The fuel used in Belgian process is producer gas.
- The zinc powder collected in the condensers and prolongs is mixed with some zinc oxide. This mixture is called zinc dust.
- The zinc metal collected in fused state is solidified in moulds. This zinc is called Spelter.
- The spelter is nearly 98% pure zinc.
- The impurities present in spelter are Cd, Pb.

- Zinc metal is refined by electrolysis.
- Roasted ZnS is digested in dilute H_2SO_4 . Upon electrolysis it gives Zn at anode. Impurities removed are As, Sb, Fe, Cu etc.
- In the electro refining of zinc
 - i) Anode - impure zinc ii) Cathode - Pure zinc iii) Electrolyte - aqueous $ZnSO_4$ containing .
- Commercial zinc contains 1.3% of lead, 0.1% of Fe and traces of Cd and As.
- Commercial zinc is purified by liquation (or) fractional distillation process.

EXTRACTION OF IRON AND TYPES OF IRON

- Iron occurs in native state in meteorites.
- The minerals of iron are
 - Haematite (reddish brown coloured) - Fe_2O_3
 - Magnetite (magnetic oxide) - Fe_3O_4
 - Limonite (hydrated oxide) - $2Fe_2O_3 \cdot 3H_2O$
 - Siderite (Spathic ore) - $FeCO_3$
 - Iron pyrites - FeS_2
 - Copper pyrites - $CuFeS_2$
- Iron can be obtained in three different forms. They are
 - i) cast iron (or) pig iron H_2O, CO_2, S & As.
 - ii) wrought iron iii) steel

MANUFACTURING OF CAST IRON

- This is the most impure form of iron.
It contains Fe = 93%, C = 4 - 5% and rest Mn, P, Si etc.,
- Haematite or magnetite ore is washed with water, mixed with a small amount of coal and heated in free supply of air. The following changes occur
 - i) The ore loses volatile impurities like H_2O, CO_2, S & As.
 - ii) Siderite present in ore changes to FeO
 - iii) The FeO in the ore is oxidised to Fe_2O_3
 - iv) The ore becomes porous
- The heated ore, coke and limestone are mixed in 8 : 4 : 1 ratio by weights. This mixture is called charge.
- The charge is heated in the blast furnace.
- In the blast furnace spongy iron is formed in the zone of reduction (400 - 700°C)

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO; \quad Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$
- In the blast furnace is converted to CO in the zone of heat absorption (800 - 1000°C)

$$CO_2 + C \rightarrow 2CO; \quad CaCO_3 \rightarrow CaO + CO_2$$
- In the blast furnace slag is formed in the zone of heat absorption .

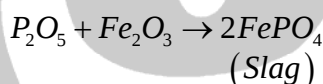
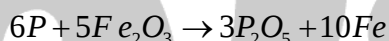
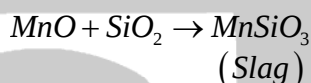
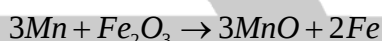
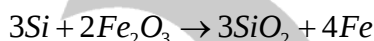
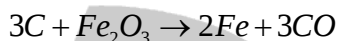
$$CaO + SiO_2 \rightarrow CaSiO_3$$
- In the blast furnace coke is oxidised to in the zone of fusion (1200 - 1300°C)

$$C + O_2 \rightarrow CO_2$$

- In the blast furnace complete reduction of Fe_2O_3 to iron takes place, in the zone of fusion.
- In the blast furnace molten iron collects in the bottom of the hearth and slag floats over it. ($> 1300^\circ C$)
- The molten iron obtained from blast furnace is called pig iron.
- The waste gases known as "blast furnace gas" escape from the top of the furnace.
- The pig iron on solidification is called cast iron.
- The slag formed in blast furnace is $CaSiO_3$.
- The pig iron on sudden cooling gives white cast iron which contains carbon impurity in the form of cementite (Fe_3C).
- The pig iron on slow cooling gives grey cast iron which contains carbon impurity in the form of graphite.

MANUFACTURING OF WROUGHT IRON .

- It is the purest form of iron. It contains Fe = 99.5%, C = 0.1 - 0.25% and rest Mn, P, Si etc.,
- It is manufactured from cast iron by puddling process.
- Cast iron is heated in a reverberatory furnace, the hearth of which is lined with basic lining of Fe_2O_3 .
- The impurities in cast iron are oxidised by Fe_2O_3 .



- The oxidised impurities form slags like $MnSiO_3$, $FePO_4$ etc.,
- The CO formed escapes and burns with blue flames. The flames are known as Puddler's candles.
- The molten mass on the hearth of the furnace is taken out in the form of balls with the help of long iron rods.
- The iron balls are beaten under steam hammers to squeeze out as much of slag as possible.
- The fibrous nature of wrought iron is due to small amount of slag present in it.

MANUFACTURING OF STEEL

- It is the most important commercial form of iron. It contains 0.25 to 2% of carbon.
- It is manufactured from cast iron mainly by two methods . They are
 - i) Bessemer converter process
 - ii) Open hearth process.

BESSEMER CONVERTER PROCESS

- If cast iron contains phosphorus as impurity, the Bessemer converter is lined inside with basic material like CaO (or) MgO.
- If cast iron contains Mn as impurity the Bessemer converter is lined inside with acidic material like silica.
- The molten cast iron is taken in Bessemer converter and air is blown in to it. The impurities in the iron are oxidised and finally form slags like etc.,



- The carbon monoxide formed burns at the mouth of the furnace with blue flame. If the blue flame suddenly dies out, it indicates completion of oxidation of impurity and formation of wrought iron.
- Calculated quantity of spiegeleisen is added to the wrought iron formed to get manganese steel.
- Spiegeleisen is an alloy of Fe, Mn (15-20%) and carbon (60%).
- In this there is a loss of iron due to slag formation and Mn reduces the loss of iron.
- Ferromanganese unites with O_2 in the steel after Bessemerization process.
- The $Ca_3(PO_4)_2$ formed as slag is known as Thomas slag. it is used as a fertilizer.
- The quality of steel produced in this process is not high.

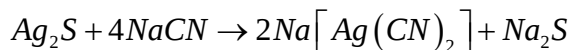
OPEN HEARTH PROCESS

(SIEMENS - MARTIN PROCESS)

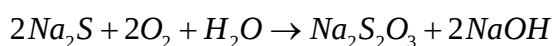
- This process is used to produce high quality steel.
- The open hearth process works on the principle of heat regeneration.
- The fuel in open hearth process is producer gas or coal gas.
- The charge introduced into the open hearth process consists of pig iron, iron ore (Fe_2O_3 -haematite) scrap iron, scrap steel and lime stone.
- In open hearth process the quality of steel produced can be analysed at desired intervals of time.
- There is no loss of iron due to slag formation in this process, as blast of air is not used.

EXTRACTION OF SILVER

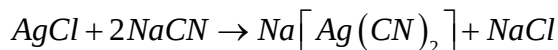
- Silver occurs in native state associated with Cu and Au in alluvial sands.
- The minerals of silver are
Argentite (or) Silver glance - Ag_2S
Horn silver (or) Chlorargyrite - $AgCl$
Pyrargyrite (or) Ruby silver - Ag_3SbS_3 ($3Ag_2S.Sb_2S_3$)
- Argentiferous lead also contains silver.
- The anode mud obtained in the electrorefining of copper also contains silver.
- The silver is generally extracted from its sulphide ores (or) halide ore by Mac Arthur - Forrest process (or) Cyanide process.
- The argentite is concentrated by froth floatation process.
- The concentrated ore is digested with a dilute solution (1%) of sodium cyanide to get sodium argento cyanide.



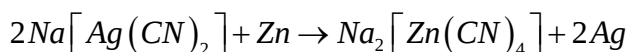
- Air is blown into the solution to oxidise to .



- The oxidation of Na_2S to Na_2SO_4 helps the completion of reaction.
- Horn silver on leaching with dilute NaCN solution gives sodium argento cyanide



- Silver is precipitated from sodium argento cyanide solution by adding zinc dust.



- Any metal which is more reactive or more electro positive than silver can be used in place of zinc in this process.
- The silver precipitated is fused with KNO_3 to oxidise any zinc present in it.
- The silver metal is purified by electrorefining. In this method
Anode - impure silver (contains Zn, Cu, Au, as impurities).
Cathode - pure silver
Electrolyte - aqueous $AgNO_3$ containing HNO_3
- The silver metal can be obtained from argentiferous lead by
i) Parke's process ii) Pattinson's process

EXTRACTION OF ALUMINIUM

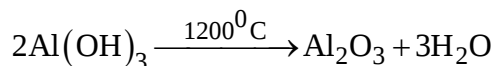
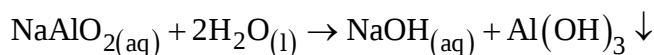
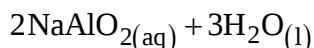
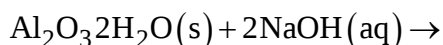
- Aluminium is the third most abundant element found in nature next to oxygen and Si.

PURIFICATION OF BAUXITE

- Aluminium is extracted from Bauxite Ore.
- White Bauxite contains silica (SiO_2) as impurity and purified by Serpeck's process.
- Red Bauxite contains FeO as impurity
- Concentration of Red Bauxite is done by
1. Baeyer's process 2. Hall's process

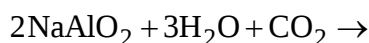
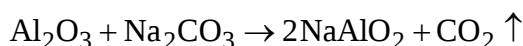
BAEYER'S PROCESS:

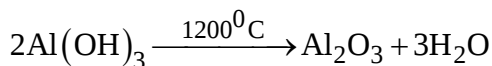
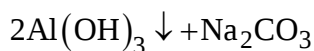
- Powdered Bauxite is first roasted to convert ferrous oxide impurity present in it into ferric oxide
- The roasted bauxite ore is dissolved in Conc. NaOH solution at 423 K giving sodium meta aluminate
- The clear aqueous solution of $NaAlO_2$ is diluted with water and pinch of $Al(OH)_3$ is added to it. The solution is agitated well. $Al(OH)_3$ added act as seeding agent. $NaAlO_2$ undergoes hydrolysis giving $Al(OH)_3$.
- The $Al(OH)_3$ is ignited at $1200^\circ C$ gives pure Al_2O_3 .
- The pure Al_2O_3 is known as Alumina.



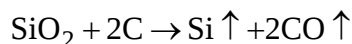
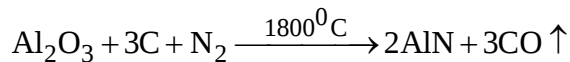
HALL'S PROCESS:

- Bauxite is fused with Na_2CO_3 to get $NaAlO_2$ which is extracted with water.
- CO_2 gas is passed into the aqueous solution of $NaAlO_2$ to get $Al(OH)_3$.
- The $Al(OH)_3$ on strong heating at $1200^\circ C$ gives alumina.



**SERPECK'S PROCESS:**

- Powdered Bauxite and Coke is heated in N_2 at 1800°C .
- AlN , Silicon vapor and CO gas are formed due to following reactions.



- AlN on hydrolysis gives $\text{Al}(\text{OH})_3$ and NH_3 gas. (bye product)
- $\text{Al}(\text{OH})_3$ on ignition gives Al_2O_3 .
- Pure Al_2O_3 is a bad conductor of electricity and its fusion temperature is very high

HALL-HEROULT PROCESS:

- Al metal is obtained by the electrolysis of Al_2O_3 dissolved in molten cryolite.
- **ELECTROLYTE:** Al_2O_3 dissolved in molten cryolite to which a small quantity of CaF_2 is also added.
- Cryolite increases the conductivity and CaF_2 reduces the fusion temperature of Al_2O_3 .
- **CATHODE:** The carbon lining present inside the electrolytic cell (an iron tank)
 - a) Gas liberated - oxygen
 - b) Cathode reaction: $4\text{Al}^{+3} + 12\text{e}^- \rightarrow 4\text{Al}$
- **ANODE:** Bunch of graphite rods suspended in the electrolyte.
 - a) Gas liberated - Fluorine
 - b) Anode reaction: $12\text{F}^- \rightarrow 6\text{F}_2 + 12\text{e}^-$
- F_2 gas liberated at anode reacts with Al_2O_3 present in the electrolyte.

$$2\text{Al}_2\text{O}_3 + 6\text{F}_2 \rightarrow 4\text{AlF}_3 + 3\text{O}_2$$
- The oxygen gas evolved reacts with carbon powder, sprinkled on the surface of the electrolyte giving CO and CO_2 . Some of the oxygen escapes.

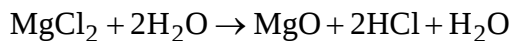
HOOPE'S PROCESS:

- **ELECTROLYTE:** Fused mixture of Fluorides of sodium, Barium and Aluminium saturated with Al_2O_3
- **CATHODE:** Pure Aluminium layer in which graphite rods are suspended.
- **Anode:** Impure Aluminium layer having contact with carbon plate fixed at the bottom of the electrolytic cell.
- The aluminium metal obtained in Hoopes process is 99.98% pure.

EXTRACTION OF MAGNESIUM

Magnesium metal is industrially prepared from carnallite, magnesite or sea water.

- **FROM CARNALLITE:**
 - a) Carnallite must be dehydrated to get anhydrous mineral.
 - b) The removal of first four water molecules is easier but the removal of the remaining two water molecules is difficult because they react chemically with MgCl_2 to form Magnesium oxide, which is an insulator.



c) Carnallite is dehydrated in an atmosphere of HCl gas. Excess of hydrochloric acid prevents the hydrolysis of MgCl_2 by its own water of crystallisation.

d) The anhydrous carnallite is mixed with an equal amount of NaCl and heated to 700°C . The presence of KCl and NaCl in anhydrous MgCl_2 prevents the hydrolysis giving Magnesium at cathode and chlorine at anode.

at cathode : $\text{Mg}^{++} + 2\text{e}^- \rightarrow \text{Mg}$

at anode : $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

e) In the electrolysis of carnallite:

CATHODE-Iron tank

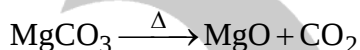
ANODE-Graphite rod coated with Lead.

f) In the electrolysis of carnallite, chlorine gas collects in the porcelain hood which surrounds the anode.

g) The air in the electrolytic cell is replaced by hydrogen or coal gas to prevent the burning of Magnesium.

• **FROM MAGNESITE:**

a) Magnesite on calcination gives MgO and CO_2



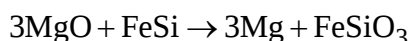
b) Magnesia is dissolved in fused mixture of MgF_2 , BaF_2 and NaF at $900-950^\circ\text{C}$. The fused mixture on electrolysis gives Magnesium.

c) In the electrolysis of Magnesia (MgO) cast iron rods act as cathode and carbon rods act as anode.

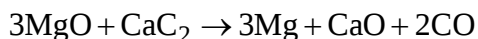
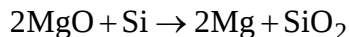
d) Mixture of MgO and coke on heating to 2000°C . Magnesium metal condenses to a powder. This method is known as **Hansging Method**.

(M.P of $\text{Mg} = 650^\circ\text{C}$ & $\text{B.P} = 1100^\circ\text{C}$)

e) In Pidgeon process Magnesium is obtained by the reduction of Magnesia or Magnesite with Ferro silicon.



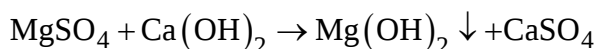
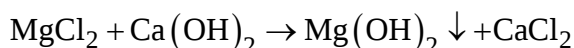
f) can be reduced to Magnesium by Silicon or Calcium carbide.



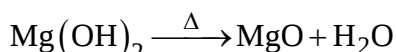
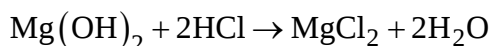
• **FROM SEA WATER:**

a) When slaked lime is added to sea water magnesium hydroxide is precipitated from

MgCl_2 and MgSO_4



b) $\text{Mg}(\text{OH})_2$ precipitated is converted into Magnesium chloride or Magnesium oxide.



c) Electrolysis of $MgCl_2$ or MgO gives Magnesium metal.

EXTRACTION OF SODIUM

- Sea water contains 2.0 to 2.9 % of NaCl.
- Sodium is a highly reactive metal occurring in combined state.
- Sir Humphry Davy obtained sodium for the first time by electrolysis of fused caustic soda.

MINERALS OF SODIUM

Rocket salt - $NaCl$

Chile salt petre or - $NaNO_3$

Caliche

Saji Mitti - Na_2CO_3

Mirabilite - Na_2SO_4

Borax - $Na_2B_4O_7 \cdot 10H_2O$

Tincal is crude borax. It contains nearly 55% of borax.

- Compounds of alkali metals are stable to thermal treatment.
- Chemical displacement methods are not useful as the alkali metals are highly reactive and placed at the top of electro chemical series.
- Alkali metals cannot be extracted by electrolysis of their aqueous solutions but are obtained by electrolytic reduction of fused compounds.
- Sodium metal is obtained by

1) Castner's method

2) Down's method

CASTNER'S METHOD:

1. Electrolyte - Fused NaOH

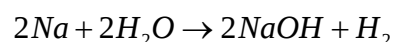
2. Cathode - Iron rod

3. Anode - Nickel

(Anode and Cathode are separated by wire gauze mesh)

- Cathode reaction - $Na^+ + e^- \rightarrow Na$

- Anode reaction



- The molten sodium metal formed in castner's process is taken out from time to time using perforated ladles.
- Castner method is not an economical method.

DOWN'S METHOD:

1. Electrolyte - Molten NaCl

2. Cathode - Iron ring

3. Anode - Graphite rod

(The Cathode and anode are separated by wire gauze mesh which prevents mixing up of products)

4. Cathode reaction - $Na^+ + e^- \rightarrow Na$

5. Anode reaction - $2Cl^- \rightarrow Cl_2 + 2e^-$

- The melting point of pure NaCl is .

This is decreased to $500 - 600^{\circ}\text{C}$ by adding a small quantity of anhydrous CaCl_2 or KCl .

- The advantages of adding CaCl_2 or KCl are:

1. The M.P. of NaCl is decreased, so the wastage of fuel is reduced.
2. The vapour pressure of sodium at the temperature of electrolysis is less. So possibility of burning of sodium is minimised.
3. At the temperature of electrolysis, the loss of sodium due to its dissolution in fused electrolyte is reduced.

नाइ