METALLURGY - (SUBTOPIC-I)

Genaral Principles of metallurgy:

- **Metallurgy:** The process of extraction of metals form their compound most economically is known as Metallurgy.
- Metals may exist in nature either in their native state (Uncombined state) or combined state.
- **Minerals:** Naturally occurring compounds of elements are called their minerals.
- **Ores:** The minerals from which metal can be conveniently and economically extracted are called ores
- All the ores are minerals but all the minerals are not ores.
- Cu, Ag, Au, Pt, Fe etc., are the metals that occur to some extent in native state
- **Gangue**: The impurities present in the mineral are called Gangue (or) Matrix.
- Al' is the most abundant metal and oxygen is the most abundant element in the earth's crust.

Principles of extraction:

- The term metallurgy includes a) Crushing and Grinding b) Concentration of the ore c) Working with concentrated ore d) Reduction of the ore e) Refining of impure metal

- The unwanted useless impurities are called
  Gangue or matrix

- The removal of these unwanted impurities from the ore is called as dressing or concentration of ores.
- The concentration of the ore can be done by
  i) Hand picking ii) Levigation (Gravity method or washing with water)
  iii) Magnetic separation IV) Froth floation v) Liquation

Froth floatation process:

- **Principle:** It is based upon the fact that the surface of sulphide ore is preferentially wetted by certain oils like pine oil while that of gangue is preferentially wetted by water.
- **Applicable to:** Commonly used for the concentration of sulphide ores as ZnS, PbS, $CuFeS_2$ etc.
- **Process:** The mixture (ore + frother + collector + activator or depressant) is agitated with air. A froth is formed which carries away along with it, the metallic particles due to the surface tension forces.

- **Collectors:** Which increase the non wettability of ore particles e.g. pine oil, xanthates and fatty acids.
- **Forth stabilitser** – Which stabilise the froth e.g: cresols and aniline
- **Depressants:** Depressants prevent the the formation of forth e.g: NaCN, when added to ore containing Zns and PbS form a complex with ZnS as $Na_2\left[Zn(CN)_4\right]$ and prevent it from forming froth. PbS is then easily separated from ZnS.

- **Liquations 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^{0}C and flows down leaving behind the gangue.

Reverberatory furnace

- The principle involved in in revrberatory furnace is indirect heating
- 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 Furance

- The principle involved in blast furnance is direct heating.

Extraction of crude Metal: (Reduction of the ores)

- The redction 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 form 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, Ca, Mg, Al etc.

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

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

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

$$Mo + O_3 + 3H_2 \xrightarrow{I.R} Mo + 3H_2O$$

$$WO_3 + 3H_2 + 3H_2 \xrightarrow{850^0 C} W + 3H_2O$$

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O$$

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

$$Cr_2O_3 + 2Al \xrightarrow{600^0 C} 2Cr + Al_2O_3$$

$$Fe_2O_3 + 2Al \xrightarrow{600^0 C} 2Fe + Al_2O_3$$

$$3Mn_3O_4 + 8Al \xrightarrow{600^0 C} 4Al_2O_3 + 9Mn$$

- The temperature of mixture in Alumino thermi process increases to 2500 – 3000^{0}C due to the exothermic nature of reaction. So the metal is obtained in molten state in the reaction.
- $TiCl_4$ on reduction with Mg gives titanium. UCl_4 On reduction with calcium gives uranium.

$$TiCl_4 + 2Mg \xrightarrow{750^0 C} Ti + 2MgCl_2$$

$$UCl_4 + 2Ca \rightarrow U + 2CaCl_2$$

- WC_6 on reduction with hydrogen gives tungsten

$$WCl_6 + 3H_2 \rightarrow W + 6HCl$$

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

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

- More electropositive metal can displace less electropositive metal form the aqueous solution of its salt. This is known as Hydro metallurgy.
- Silver (Gold also) can be obtained by adding zinc to aqueous sodium argento cyanide solution. This is an example for hydro metallurgy (Pyro meatallurgy)

$$2Na\left[Ag\left(CN_2\right)\right] + Zn \rightarrow Na_2\left[Zn\left(CN\right)_4\right] + 2Ag$$

$$2Na\left[Au(CN)_2\right]+Zn\rightarrow Na_2\left[Zn(CN)_4\right]+2Au$$

- **Roagtring:** The process of heating the ore either alone or mixed with other substances in air below its melting point is known as roasting.
- **Oxidizing roasting:** Sulphide ores on roasting gives metal oxide and sulpur dioxide.

$$\underset{Zinc\,hlende}{2ZnS}+3O_2\xrightarrow{high\,lemp}2ZnO+2SO_2$$

$$\underset{iron\ pyrues}{4FeS_2}+11O_2\rightarrow 2Fe_2O_2+8SO_2$$

$$2Cu_2S+3O_2\rightarrow 2Cu_2O+2SO_2$$

- **Sulphatizing roasting:** Sulphide ores on roasting gives metal sulphate.

$$\underset{Zinc\,blende}{ZnS}+\ 2O_2\xrightarrow{650^0 C}ZnSO_4$$

- **Chloridizing roasting:** Sulphide ores are mixed with a chloride salt and roasted. The sulphide ore changes to chloride ore.

$$\underset{Silver\,glance}{Ag_2S}+\ 2NaCl+2O_2\xrightarrow{600^0 C}2AgCl+Na_2SO_4$$

Calcination

- The process of heating an ore in the absence of air below its melting point as Calcination.
- Carbonate ores on calcinations decomposes giving metal oxide and CO_2

$$\underset{Limestone}{CaCO_3}\xrightarrow{\Delta}CaO+CO_2$$

$$\underset{Calamine}{ZnCO_3}\rightarrow ZnO+CO_2$$

Smelting

- 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 copper iron pyrites, coke and sand on heating in blast furnace gives **Matte.** The matte is molten Cu_2S containing a little FeS.

$$2CuFeS_2+O_2\rightarrow Cu_2S+2FeS+SO_2$$

- **FLUX:** The substance added to remove the impurities form the orer in the form of easily fusible mass is called a flux.

- Fluxes are of two types

  i) Acidic flux. Ex: Silica

  ii) Basic flux. Ex: Calcia, Magnesia.

- Acidic flux is used to remove gangue having basic nature.
- Basic flux is used to remove gangue having acidic nature.
- **SLAG:** The flux combines with the gangue (impurities) and form a easily fusible mass called slag.
- The slag can be very easily removed from the contents.

  Gangue + flux = slag

- Haematite ore contains silica as impurity. This impurity is removed by using lime stone as flux.

  $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$

  Flux Gangue Slag (Flue gas)

- In the extraction of copper from copper iron pyrites, FeO is gangue. This is removed by using silica as flux.

  $FeO + SiO_2 \rightarrow FeSiO_3$

  Gangue Flux Slag

- **Leaching:** Leaching is also used for the extraction of precious metals like silver, gold etc. by converting these metals or their ore into their soluble complexes.

  $4Ag + 8NaCN + O_2 + 2H_2O \rightarrow 4Na\left[Ag(CN)_2\right] + 4NaOH$

  $Ag_2S + 4NaCN \rightarrow 2Na\left[Ag(CN)_2\right] + Na_2S$

  $4Na_2S + 5O_2 \rightarrow 2Na_2SO_4 + 4NaOH + 2S$

- **Refining of Metals:** The process of removal of unwanted substances from impure metal (or) crude metal is known as refining.
- **Cupellation:** This method is based on different affinities of metals and impurity towards oxygen.
- Applicable to refining of the metals having easily oxidisable impurities. Ex.Ag.
- **Poling:** Applicable to refining of metals having metal oxide asan impurity. Ex. Cu,sn

  Electrolytic refining:

- The residue left below anode in the electro refining of metal is called **anode mud.**
- Method is used to refine metals like Cu, Ag, Au, Al.

Zone refining:

- This method is based on the difference in the solubilities of impurities in the molten state and solid state of metal.
- This method is applicable to refining of metals like Si, Ge, Ga etc.,
- **Example : Monds Process**
- In this process, Nickel is heated in a stream of carbon monoxide and their by forms a volatile complex, Nickel tetracarbonyl:

$$Ni + 4CO \xrightarrow{330-350K} Ni(CO)_4$$

The carbonyl is heated to get pure metal

$$Ni(CO)_4 \xrightarrow{450-470K} Ni + 4CO$$

Van arkel Method

- The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent. Volatilizes:

$$Zr + 2l_2 \rightarrow Zrl_4$$

METALLURGY (SUBTOPIC-II)

Extactio of copper, Zinc, Iron and Silver:

Extaction of copper

- Copper metal occurs in native state only to a small extent. The symbol "Cu'' comes from the word "cuprum"
- 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	$CuCO_3.Cu(OH)_2$

Azurite	$2CuCO_3.Cu(OH)_2$

- Copper is extracted from sulphide minerals (Copper iron pyrites).
- The $CuFeS_2$ ore is concentrated by froth flotation process.
- The concentrated ore roasted in a reverberatory furnace.
- The roasted ore contains Cu_2S ,FeS and small quantities Cu_2O and FeO

$$Cu_2S.Fe_2F_3 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$

- The roasted ore is mixed with a little coke and sand smelted blast furnace.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \rightarrow FeSiO_3$$

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

- The slag formed in the blast furnace contains Cu_2S and a little FeS .This mixture is called Copper matte.
- In Bessemer converter all iron is removed as $FeSiO_3$ slag.
- In Bessemer converter Cu_2S sundergoes self reduction giving **Blister** copper.
- Blister copper is 98% pure copper.
- Blister copper contains Cu_2O as impurity
- The copper metal obtained by electro refining is 100% pure.

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 is extracted from its ore by two methods

i) Reduction ii) Electrolysis

- **Reduction:** In this process the following steps are involved.

Concentration:

- i) Gravity process using Wifley's table ii) Froth floatation process.
- The zinc blende ore is subjected to electromagnetic separation to remove iron oxide impurity.

Roasting:

- Zinc blende ore on roasting in free supply or air gives ZnO, in rotary shelf burner.

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

$$ZnS + 2O_2 \rightarrow ZnSO_4$$

$$2ZnSO_4 \rightarrow 2ZnO + 2SO_2 + O_2$$

- The calamine ore on calcinations gives zinc oxide

Reduction:

- **Belgian process:** It is old process.
- The zinc oxide on reduction with carbon power gives zinc metal. This is known as Belgian process.

$$ZnO + C \xrightarrow{1100^0 C} Zn + CO$$

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

- The fule used in Blegian 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 I fused state is solidified in moulds. This zinc is called Spelter.
- The spelter is neary 98% pure zinc.
- The impurities present in spelter are Cd, Pb.
- Zinc metals are refined by electrolysis.
- Commerical zinc contains 1.3% of lead, 0.1% of Fe and trace of Cd and As.

Extraction of Iron:

The minerals of iron are

- **Oxides ores:** Haematite (reddish brown coloured) - Fe_2O_3

i) Magnetite (magnetic oxide) - Fe_3O_4

ii) Limonite (hydrated oxide) - $2Fe_2O_3.3H_2O$

iii) Haematite - Fe_2O_3

Carbonate ore: Siderite (or) Sepathic ore - $FeCO_3$

Sulphide ores: i) Iron pyrites - FeS_2 ii) Copper pyrites - $CuFeS_2$ (Chalcopyrites)

- Iron is extracted from its oxide ores especially from the magnetic, haematite and limonite ores.
- **Types of Iron:** i) cast iron (or) pig iron 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.
- 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^{0}C)

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

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

- In the blast furnace CO_2 is converted to CO in the zone of **heat absorption** (800-1000^{0}C)

$$CO_2 + C \rightarrow 2CO$$

$$CaCO_3 \rightarrow CaO + CO_2$$

- In the blast furnace slag is formed in the zone of heat absorption.

$$CaO + SiO_2 + CaSiO_3$$

- In the blast furnace coke is oxidised to CO_2 in the **zone of fusion** (1200-1300^{0}C)

$$C + O_2 \rightarrow CO_2$$

- The molten iron obtained from blast furnace is called pig iron.
- The salg formed in blast furnace is $CaSiO_3$

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.,
- Cast iron is heated in a reverboratory 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.

$$3C + Fe_2O_3 \rightarrow 2Fe + 3CO$$

$$3Si + 2Fe_2O_3 \rightarrow 3SiO_2 + 4Fe$$

$$3Mn + Fe_2O_3 \rightarrow 3MnO + 2Fe$$

$$MnO + SiO_2 \rightarrow \underset{(Slag)}{MnSiO_3}$$

$$6P + 5Fe_2O_3 \rightarrow 3P_2O_5 + 10Fe$$

$$P_5O_5 + Fe_2O_3 \rightarrow \underset{(Slag)}{2FePO_4}$$

- The CO formed escapes and burns with blue flames. The flames are known as Puddler's candles.
- 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.

Extraction of silver

- Silver occurs in native sate associated with Cu and Au in alluvial sands.
- The minerals of silver are

Argentire (or) Silver glance - Ag_2S

Horn silver (or) Chlorargyrite – AgCl

Pyrargyrite (or) Ruby silver - $Ag_3SbS_3\left(3Ag_2S.Sb_2S_3\right)$

- The silver is generallyextracted from its sulphide ores 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 cynide to get sodium argento cyanide.

$$Ag_2S + 4NaCN \rightarrow 2Na\left[Ag\left(CN\right)_2\right] + Na_2S$$

- Air is blown into the solution to oxides Na_2S to Na_2SO_4

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$$

$$Na_2S_2O_3 + 2O_2 + 2NaOH \rightarrow 2Na_2SO_4 + H_2O$$

- 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

  $AgCl + 2NaCN \rightarrow Na\left[Ag\left(CN\right)_2\right] + NaCl$

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

  $2Na\left[Ag\left(CN\right)_2\right] + Zn + \rightarrow Na_2\left[Zn\left(CN\right)_4\right] + 2Ag$

- Any metal which is more reactive or more electro positive than silver can be in place of zinc in this process.

METALLURGY (SUBTOPIC-III)

Extraction of aluminium, Magnesium and Sodium:

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 $\left(SiO_2\right)$ 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

- Pure Al_2O_3 is a bad conductor or 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:

  $4Al^{+3} + 12e^{-} \rightarrow 4Al$

- **Anode:** Bunch of graphite rods suspended in the electrolyte.

  a) Gas liberated – Fluorine b) Anode reaction:

  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 contant with carbon plate fixed at the bottom of the electrolytic cell.
- The aluminium metalobtained in Hoope's process is 99.98% pure.

  Extraction of magnesium

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

  Form Carnallite:

- a) Carnallite must be dehydrated to get anhydrous mlneral.

  b) The removal of first four water remaining two water molecules is difficult because they react chemically with $MgCl_2$ to form Magnesium oxide, which is an isulator.

  $$MgCl_2 + 2H_2O \rightarrow MgO + 2HCl + H_2O$$

  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 crytallsation.

- Presence of KCl and NaCl in anhydrous $MgCl_2$ prevents the hydrolysis giving Magnesium at

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

  at anode : $2Cl^- + Cl_2 + 2e^-$

  In the electrolysis of carnallite:

  Cathode – Iron tank

  Anode- Graphite rod coated with Lead.

  Extraction of sodium

- Sea water contains 2.0 to 2.9% of NaCl.
- Tincal is curde borax. It contains nearly 55% of borax.
- 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
- Ionization: $NaOH \rightarrow Na^+ + OH^-$
- Cathode reaction - $Na^+ + e^- \rightarrow Na$
- Anode reaction

  $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

  $2Na + 2H_2O \rightarrow 2NaOH + H_2$

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 precents mixing up of products)

  4. Cathode reaction - $Na^+ + e^- \rightarrow Na$
  5. Anode rection - $2Cl^- \rightarrow Cl_2 + 2e^-$

- The melting point of pure NaCl is 803^{0}C.
  This is decreased to 500-600^{0}C by adding a small queantity anhydrous $CaCl_2$ or KCI
- The advantages of adding $CaCl_2$ or KCI 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 electrolysis is less. So possibility of burning of sodium is minimized.
  3. At the temperature of electrolysis, the loss of sodium due to dissolution fused eletrolyts is reduced.

Thermodynamic Principles of metallurgy

- Gibbs energy concept of thermodynamics help us in understanding the theory of metallurgical transformations
- The change in Gibbs energy, ΔG for amy process at any specified temperature, is described by the equation

$\Delta G = \Delta H - T\Delta S$ ------(1)

ΔH = enthalpy change

ΔS = entropy change for the process.

- For any reaction, this change could also be explained through the equation.
  $\Delta G^0 = RT\ In\ K$ -------(2)

- Ellingham Diagram normally consists of plots of ΔG^0 Vs T for formation of oxides of Elements. i.e, for the reaction.
  $2xM_{(S)} + O_{2(g)} + 2M_xO_{(S)}$

Limitations of Ellingham diagram:

- The graph simply indicates whether a reaction is possible or not. It does not say about the kinetics of the reduction process.

Electrochemical principal of metallurgy

- Zinc is used for galvanizing iron, also used in batteries and in many alloys Brass (Copper 60% + Zinc 40) german silver (Copper 25-30% Zinc 25-30%, Ni 40-50%)
- Cast iron is used for casting stoves, railway sleeprs, gutter pipes, toys etc.