LECTURE NOTES

ON

ENGINEERING CHEMISTRY

I B. Tech I semester

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FRESHMAN ENGINEERING

INSTITUTE OF AEROSNAUTICAL ENGINEERING
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ENGINEERING CHEMISTRY
(Common for all Branches)

Semester: I								
Course Code	**IA16-A1805**	**Hours / Week**			**Credits**	**Maximum Marks**		
Category	**Foundation**	**L**	**T**	**P**	**C**	**CIE**	**SEE**	**Total**
		3	-	-	3	30	70	100
Contact Classes: 45	**Tutorial Classes: Nil**	**Practical Classes: Nil**				**Total Classes: 45**		

Goal: Inculcate basic principles of chemistry aspects in different disciplines of engineering.

Objectives:

The course should enable the students to:

I. Apply the electrochemical principles in batteries.
II. Understand the fundamentals of corrosion and development of different techniques in corrosion control.
III. Analysis of water for its various parameters and its significance in industrial applications.
IV. Improve the fundamental science and engineering principles relevant to materials.

UNIT-I ELECTROCHEMISTRY AND BATTERIES Hours: 10

Electrochemistry: Basic concepts of electrochemistry; Conductance: Specific, equivalent and molar conductance and effect of dilution on conductance; Electrochemical cells: Galvanic cell (daniel cell); Electrode potential; Electrochemical series and its applications; Nernst equation; Types of electrodes: Calomel electrode, quinhydrone electrode; Batteries: Classification of batteries, primary cells (dry cells) and secondary cells (lead-acid battery, Ni-Cd cell), applications of batteries, numerical problems.

UNIT-II CORROSION AND ITS CONTROL Hours: 08

Corrosion: Introduction, causes and effects of corrosion; Theories of corrosion: Chemical and electrochemical corrosion with mechanism; Factors affecting the rate of corrosion: Nature of the metal and nature of the environment; Types of corrosion: Waterline and crevice corrosion; Corrosion control methods: Cathodic protection- sacrificial anodic protection and impressed current cathodic protection; Surface coatings: Metallic coatings, methods of application of metallic coatings- hot dipping(galvanizing, tinning), electroplating(copper plating); Organic coatings: Paints, its constituents and their functions.

UNIT-III WATER TECHNOLOGY Hours: 09

Water: Sources and impurities of water, hardness of water, expression of hardness-units; Types of hardness: Temporary hardness, permanent hardness and numerical problems; Estimation of temporary and permanent hardness of water by EDTA method; Determination of dissolved oxygen by Winkler's method; Boiler troubles: Priming, foaming, scales, sludges and caustic embrittlement.

Treatment of water: Internal treatment of boiler feed water- carbonate, calgon and phosphate conditioning, softening of water by Zeolite process and Ion exchange process; Potable water-its specifications, steps involved in the treatment of potable water, Sterilization of potable water by chlorination and ozonization, purification of water by reverse osmosis process.

UNIT-IV MATERIALS CHEMISTRY Hours: 10

Materials chemistry: Polymers-classification with examples, polymerization-addition, condensation and co-polymerization; Plastics: Thermoplastics and thermosetting plastics; Compounding of plastics; Preparation, properties and applications of Polyvinylchloride, Teflon, Bakelite and Nylon-6, 6; Rubbers: Natural rubber its process and vulcanization; Elastomers: Buna-s and Thiokol rubber; Fibers: Characteristics of fibers, Preparation properties and applications of Dacron; Characteristics of fiber reinforced plastics; Cement: Composition of Portland cement, setting and hardening of Portland cement; Lubricants: Classification with examples, properties- viscosity, flash, fire, cloud and pour point; Refractories: Characteristics and classification with examples.

UNIT-V FUELS AND COMBUSTION Hours: 08

Fuel: Definition, classification of fuels and characteristics of a good fuels; Solid fuels: Coal, analysis of coal- proximate and ultimate analysis; Liquid fuels: Petroleum and its refining; Cracking: Fixed bed catalytic cracking; Knocking: Octane and cetane numbers; Gaseous fuels: Composition, characteristics and applications of Natural gas, LPG and CNG; Combustion: Calorific value-Gross calorific value(GCV) and Net calorific value(NCV), calculation of air quantity required for complete combustion of fuel, numerical problems.

Text Books:

1. P. C. Jain, Monica Jain, "Engineering Chemistry", Dhanpat Rai Publishing Company, 15th Edition, 2015.
2. Shasi Chawla, "Text Book of Engineering Chemistry", Dhantpat Rai Publishing Company, New Delhi, 1st Edition,

2011.

Reference Books:

1. B. Siva Shankar, “Engineering Chemistry”, Tata Mc Graw Hill Publishing Limited, 3rd Edition, 2015.
2. S. S. Dara, Mukkanti, “Text of Engineering Chemistry”, S. Chand & Co, New Delhi, 12th Edition, 2006.
3. C. V. Agarwal, C. P. Murthy, A. Naidu, “Chemistry of Engineering Materials”, Wiley India, 5th Edition, 2013.
4. R. P. Mani, K. N. Mishra, “Chemistry of Engineering Materials”, Cengage Learning, 3rd Edition, 2015.

Web References:

1. www.tndte.com
2. nptel.ac.in/downloads
3. www.scribd.com
4. cuiet.info
5. www.sbtebihar.gov.in
6. www.ritchennai.org

E-Text Books:

1. Corrosion.ksc.nasa.gov/electrochem_cells.htm
2. www.science.uwaterloo.ca/~cchieh/cact/applychem/watertreatment.html
3. www.acs.org/content/acs/en/careers/college-to-career/areas-of-chemistry/polymer-chemistry.html
4. www.darvill.clara.net/altenerg/fossil.htm
5. Library.njit.edu/research helpdesk/subject guides/chemistry.php

Unit - I

Electro Chemistry and Corrosion

Introduction:- Chemistry is the Study of matter, its properties and the changes it may undergo. All matter is electrical in nature. An atom is made up of sub atomic particles like electors, protons and neutrons etc.

Electro chemistry is a branch of chemistry which deals with the transformation of electrical energy into chemical energy or chemical into electrical energy.

1.1.1 Concept of electrochemistry:

Electrical Conduction: The substances are divided into 4 types depending upon their capability of flow of electrons.

i) Conductors: The Substances which allows electricity to pass through them are called conductors.

Ex :- Metals, metal sulphides, acids, alkalis, salt sol. and fused salts

The electrical conductors are of two types.

1. Metallic or Electronic conductors.

2. Electrolytic conductors

ii) Non-conductors: The substances which do not allow electricity are called non-conductors.

Ex: Pure water, dry wood, rubber, paper, non-metals etc.

iii) Semi conductors: The substances which partially conduct electricity are called semi-conductors. The conducting properties of semi-conducting properties are increased by the addition of certain impurities called “dopping”.

Ex: ‘si’ and addition of V group elements like ‘p’ ‘si’ produces n-type semi-conductor. On addition of iii group element like ‘B’, Al, ‘si’ produces p-type of semi-conductor.

Differences between Metallic Conductors and Electrolytic Conductors

Metallic conductors	Electrolytic conductors
1. Conductance is due to the flow of electrons. 2. It does not result any chemical change. 3. Metallic conduction decreases with increase in temperature. 4. It does not involve any transfer of matter**.**	1. Conductance is due to the movement of ions in a solution. 2. Chemical reactions take place at the electrodes. 3. Electrolytic conduction increases with increase in temperature. 4. It involves transfer of matter.

Electrical resistance – ohm's law.

The current strength flowing through a conductor at uniform temperature is directly proportional to the potential difference applied across to conductor.

$$V \alpha I$$

I → current strength

V → potential difference.

$$V=IR$$

R-Proportionality const which is called resistance

$$R=V/I$$

Units for Resistance is ohm

Specific resistance (or) Resistivity:

Ohm found that the solution of electrolyte also offers resistance to flow of current in the solution.

"The resistance (R) of a conductor is directly proportional to its length and inversely proportional to its cross sectional area (a)"

$$R \,\alpha\, l$$

$$R \,\alpha\, a$$

$$R \,\alpha\, l/a$$

$$R = \rho \rightarrow \boldsymbol{l/a}$$

ρ - Specific resistance.

If $l = 1$ cm and a= $1cm^2$ then R = ρ then the specific resistance is defined as

"The resistance offered by a material of unit length and unit area of cross section is called specific resistance"

$$\rho = R/\, l\, /a$$

$$= R \times a/\, l$$

Units: ohm × cm^2/cm = ohm cm

Conductance: The reciprocal of resistance is called Conductance

$$L = 1/R$$

Units: ohm $^{-1}$(or) mho (C.G.S)

Siemens (S) (M.K.S)

Specific Conductance (or) Conductivity:

Reciprocal of specific resistance is known as specific conductance.

$$1/R = 1/\rho \times 1/l/a$$

$$L = k.a/l$$

$$K = L/a/l \quad = L \times l/a$$

If l = 1cm, a =1 cm^2 then K = L, then the specific conductance is defined as.

"The conductance of a solution enclosed between two parallel electrodes of unit area of cross – section separated by unit distance".

Equivalent Conductance (or) Equivalent Conductivity:-

It is defined as the conductance of all ions produced by the dissociation of Igm equivalent of an electrolyte dissolved in certain volume 'V' of the solvent at const temperature

$$\wedge v = \frac{K\ X\ 1000}{N} = \frac{\mathbf{S.P\ Conductance\ X\ 1000}}{\mathbf{N}}$$

Units $= \frac{ohm-1\ cm-1\ cm3}{eq.} =$ Ohm^{-1} cm^{2} eq^{-1}

Molar Conductance (or) Molar Conductivity:-

It is defined as the conductance of all ions produced by the dissociation of 1gm mol. Wt. of electrolyte dissolved in certain volume 'V' of the solvent at const. Temperature.

$$\mu = \frac{kX1000}{M} = \frac{S.P\ Conductance\ X\ 1000}{M}$$

Units: $\frac{ohm-1}{moles/li} = \frac{ohm-1cm-1\ cm3}{mole}$

$=$ohm^{-1} cm^{2} mole^{-1}

Cell Constant: - It is a constant, characteristic of the cell in which the electrolyte is taken and its value depends on the distance between the electrodes and the area of cross – section of electrodes.

$$\text{Cell const} = \frac{\mathbf{Distance\ between\ the\ electrodes}}{\mathbf{A\ rea\ of\ cross-section\ of\ each\ electrode}}$$

$$= \frac{l}{a}$$

Specific conductance $K = Lx\ \frac{l}{a}$

$$K = \frac{1}{R} \times \frac{l}{a}$$

$$\frac{l}{a} = K \times R$$

cell const = specific conductance × resistance

Variation of Conductance with dilution:-

The conductance increases with increase in the concentration of the electrolyte to a certain maximum level and decreases on further increase in the concentration. This is because, on increase in the concentration, the population of free ions increases and these cons get closer and the electrostatic force of attractions and the viscosity of the electrolyte increases. These factors tend to reduce the conductance of the solution. But equivalent conductances are inversely proportional to the conc. Of electrolyte and hence increases with increase in dilution.

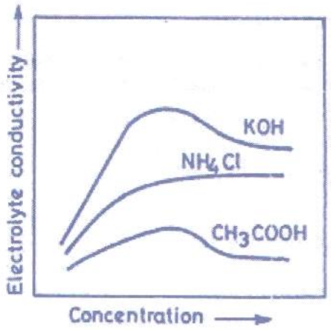
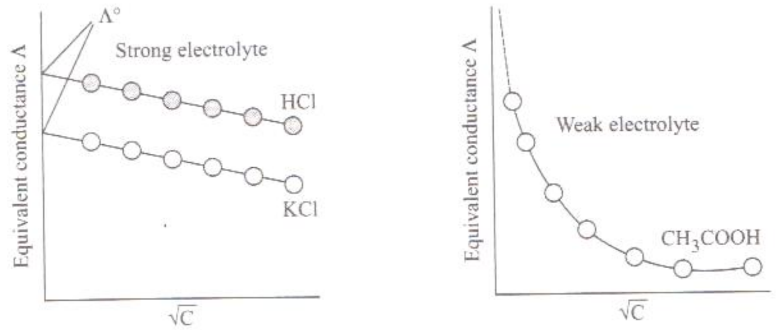


Fig:1.1 Variation of conductance with concentration of electrolyte

In case of strong electrolyte, a gradual and linear change in ^ (or) μ with square root of concentration is observed. But in case of weak electrolytes, there is a significant change of ^ (or) 'μ' with$\sqrt{c}$.

At higher concentrations, they show low ^ (or) μ and at higher dilutions (low cons). They show higher ^ (or) μ



(a) (b)

Fig1.2 Variation of ^ (or) 'μ' with$\sqrt{c}$ for strong and weak electrolytes

Measurement of Conductance of Electrolyte:

The measurement of Conductance (L) of an electrolyte solution involves the estimation of resistance (R) of the electrolytic solution. This is usually done by ‘wheat stone bridge circuit’ which involves a comparison of unknown resistance with standard resistance.

The whetstone bridge circuit is shown in fig.1.3

1. The electrolyte of known concentration is taken in a container called conductivity cell.
2. It consists of two platinum plates of area of cross section ‘a’ cm^2 and separated by a distance1cm.
3. These plates are generally canted with platinum black to decrease the polarization effect.
4. This forms one arm of the circuit.
5. The other arm of the circuit is fitted with a variable standard resistance.
6. These two arms are attached to both ends of a meter bridge.
7. A source of alternating current is also attached to both ends of Meter Bridge.
8 .The current balance detector D1 fixed between R_C and Rv.
9. Now the sliding contact jockey is moved over the meter bridge wire MN.
10 .The point of least current passing (X) is find out by detector (D).
11. According to wheat stone bridge principle, the ratio of resistances in the meter bridge arms i.e. Mx to Nx is equal to the ratio of LM to LN.

$$\frac{Mx}{Nx} = \frac{LM}{LM}$$

But LM $= R_c$
LN $= R_v$

$$\frac{Mx}{Nx} = \frac{Rc}{Rv}$$

Since Rv is known and M_x, N_x are determined through experiment, the resistance of the cell Rc can be calculated. The reciprocal of Rc gives the conductance of experimental solution.
To calculate the electrolytic specific conductance

We use $K = L \times \frac{l}{a}$.

For the experimental determination of equivalent conductance of 0.01 M$NaNO_3$solution
We can determine specific conductance by above method and we can calculate equivalent conductance by using.

$$\Lambda = \frac{Kx1000}{N}$$

Where Λ - equivalent conductance
K - Specific conductance
N - Normality of the solution.

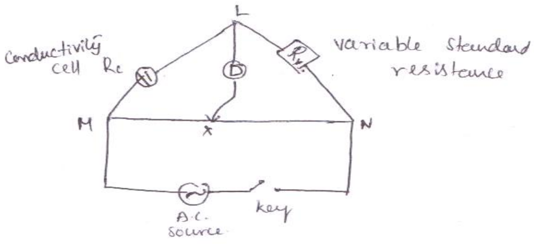


Fig1.3 Whetstone bridge circuit

1.1.3. Electro chemical cell (or) Galvanic cell:-

Galvanic cell is a device in which chemical energy is converted into electrical energy. These cells are called Electrochemical cells or voltaic cells. Daniel cell is an example for galvanic cell.

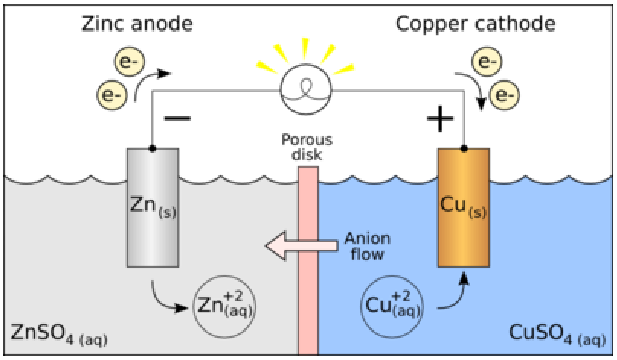


Fig1.9 Galvanic cell

This cell is made up of two half cells. One is oxidation or anodic half cell. The other is reduction or catholic half cell. The first half cell consists of ‘Zn’ electrode dipped in $ZnSO_4$solution and second half cell consists of ‘Cu” electrode dipped in $Cuso_4$ solution. Both the half cells are connected externally by metallic conductor. And internally by ‘salt bridge’ salt bridge is a U- tube containing concentrated solution of kCl or NH_4 NO_3 in agar-agar gel contained porous pot. It provides electrical contact between two solutions.

The following reactions take place in the cell.

At cathode:

$$Zn \quad \rightarrow \quad Zn^{+2} \quad +2e^{-}$$ (oxidation or de-elecronation)

At cathode:

$Cu^{+2} + 2e^{-} \rightarrow Cu$ (Reduction or electronatioin)

The movement of electrons from Zn to cu produces a current in the circuit.

The overall cell reaction is: $Zn + Cu^{+2} \longleftrightarrow Zn^{+2} + Cu$

The galvanic cell can be represented by

$$Zn / ZnSO_4 // CuSO_4 / Cu$$

The passage of electrons from one electrode to other causes the potential difference between them which is called E.M.F.

E.M.F:-

The difference of potential which causes flow of electrons from an electrode of higher potential to an electrode of lower potential is called Electro motive force (EMF) of the cell.

The E.M.F of galvanic cell is calculated by the reduction half – cell potentials using to following ex.

$$E_{cell} = E_{(right)} - E_{(left)}$$

$E_{cell} \rightarrow$ EMF of the cell.

$E_{right} \rightarrow$ reduction potential of right hand side electrode.

$E_{left} \rightarrow$ reduction potential of left hand side electrode.

Applications of EMF measurement:-

1. Potentiometric titrations can be carried out.
2. Transport number of ions can be determined.
3. P^H can be measured.
4. Hydrolysis const, can be determined.
5. Solubility of sparingly soluble salts can be found.

Differences between Galvanic cell and Electrolytic cell.

Galvanic cell / Electrochemical cell	Electrolytic cell
1. In this cell, chemical energy is converted into electrical energy. 2. In this cell anode is –ve electrode and cathode is +ve electrode. 3. Salt bridge is required. 4. This process is reversible and spontaneous. 5. EMF of the cell is +ve.	1. In this cell electrical energy is converted in to chemical energy. 2. In this cell anode is +ve electrode and cathode is –ve electrode. 3. Salt bridge is not required. 4. This process is irreversible and not spontaneous. 5. EMF of the cell is –ve.

Single electrode potential :-(E) When a metal rod dipped in it's salt solution, the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction). The process of oxidation or reduction depends on the nature of metal. In this process, there develops a potential between the metal atom and it's corresponding ion called the electrode potential. There is a dynamic equilibrium between the metal and metal ion and the potential diff. between the two is called electrode potential. It is measured in volts.

Standard electrode potential (E^0):-

The potential exhibited by single at unit concentration of its metal ion at $25^{0\ c}$ is called standard electrode potential (E^0)

Eg: E of cu^{+2} / cu = E^0 when concentration of cu^{+2} is IM. E^0 value of single electrode is determined experimentally by combining the single electrode with standard hydrogen electrode.

Electrochemical series:-

The electrode potentials of different electrodes can be finding using standard hydrogen electrode. The potential of hydrogen electrode is assumed as zero volts. So the measured Emf. Itself is the standard electrode potential of that electrode.

The arrangement of different electrode potential s of different electrodes from highest

-ve to highest +ve are called electrochemical series.

Electrode	**Half cell reaction**	**E^0volts (standard reduction potential**
Li^+/Li	$Li^+ + e^- \rightarrow Li$	-3.04
K^+/K	$K^+ + e^- \rightarrow K$	-2.9
Ca^{+2}/Ca	$Ca^{+2} + 2e^- \rightarrow Ca$	-2.8
Na^+/Na	$Na^+ + e- \rightarrow Na$	-2.7
Mg^{+2}/Mg	$Mg^{+2} + 2e^- \rightarrow Mg$	-2.3
Zn^{+2}/Zn	$Zn^{+2} + 2e^- \rightarrow Zn$	-0.76
Fe^{+2}/Fe	$Fe^{+2} + 2e^-$ Fe	-0.4
H^+/H_2,pf	$H^+ + e^- \rightarrow \frac{1}{2} H_2$	+ 0
Cu^{+2}/Cu	$Cu^{+2} + 2e^- \rightarrow Cu$	+0.15
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.7
Pt,Cl_2/Cl^-	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.3
Pt,F_2/F^-	$F_2 + 2e^- \rightarrow 2F^{--}$	+ 2.8

From the above series we can understand that the metals with higher –ve potentials are stronger reducing agents, and the metals with higher +ve potentials are stronger oxidizing agents. The metals with higher –ve potentials displaces a metals with lower –ve potentials.

1.1.4 Nernst Equation:

Nernst studied the theoretical relationship between electrode reaction and the corresponding cell e.m.f. This relationship generally Known as Nernst equation.

Consider a galvanic cell

$$aA + bB \rightarrow cC + dD.$$

Where a,b,c,d represents no. of moles respectively at equilibrium.

The Nernst eq' for the cell is written as

$$E_{cell} = E^0_{cell} - \frac{RT}{nf} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$= E^0_{cell} - \frac{2.303RT}{nf} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

R= 8.314 J/K. T= 298K. F=96, 500 columbs.

By substituting the values in the eq'

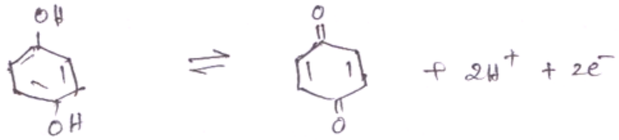
$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

1.1.5 Reference Electrodes:-

Because of the inconveniences in the usage of Hydrogen electrode like maintenance of accurate pressure, inconvenience in handling gas secondary electrodes were developed.

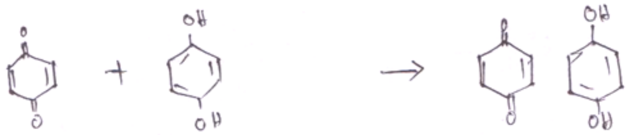
Quinehydrone Electrode:-

It is a type of redox electrode which can be used to measure H^+ concentration of a solution. Quine hydrone is an equimolar (1:1) mixture of quinine and hydroquinone. The electrode consists of pt electrode dipped in an acid or base test solution which is saturated with quine hydrone.The electrode reaction is.



Quinone (Q)   Hydroquinone (QH_2)

Each one of the substances can be easily get oxidized or reduced to other.



Quinone   Hydroquinone   Quinehydrone

The electrode reaction may be represented as

$$Q\,H_2 \leftrightarrow Q + 2H^+ + 2e^-$$

The electrode potential at 25^0c is

$$E_Q = E^0_Q - \frac{2.303RT}{2f} \log \frac{[Q]\,[\boldsymbol{H^+}]^{\boldsymbol{2}}}{[QH2]}$$

[Q] = [QH2], because the concentration of quinine and hydroquinone are equal

$$E_Q = E^0_Q - \frac{2.303RT}{2f} \log [H^+]^2$$

$$= E^0_Q - \frac{2.303RT}{F} \log [H^+]$$

By substituting the values of R, T, F,

$$E_Q = E^0_Q - 0.0591 \log [H^+]$$

$$= E^0_Q + 0.0591\ P^{H.}$$

This eq' is used to calculate the p^H is E_Q and E^0_Q values are known.

Advantages:-

1. This electrode is simple to set up and needs no removal of air.
2. We can measure p^H value quicker than hydrogen gas electrode

Limitations:-

1. This electrode cannot be used at P^H values greater than 8.
2. This electrode fails in presence of strong oxidizing and reducing agents.

Types of electrodes:

Standard calomel electrode (SCE):-

The calomel electrode consists of a glass tube having two side tubes. A small quantity of pure mercury is placed at the bottom of the vessel and is covered with a paste of Hg and $Hg_2\,Cl_2$. KCl solution of known concentration is filled through side tube, Shown on the right side of the vessel. The KCl sol. is filled in the left side tube which helps to make a connection through a salt bridge with the other electrode, which potential has to be determined.

A 'pt' wire is sealed into a glass tube as shown in the fig which is in contact with Hg.

When the cell is set up it is immersed in the given solution. The concentration of KCl. The electrode potentials of calomel electrode of different concentrations at 25^0c are

0.1 M KCl/ Hg_2cl_2 (s) / Hg,pt → 0.33v

1M KCl / Hg_2cl_2 (s) / Hg,pt → 0.28v

Saturated kcl /$Hg_2 cl_2$ (s) /Hg, pt → 0.24v

The corresponding electrode reaction is

$Hg_2 Cl_2 + 2e^- \rightarrow 2Hg + 2cl^-$

Nernst's expression is,

$$E_{Hg2\ cl2/\ cl-} = E^{o}_{Hg2\ Cl2\ /\ cl-} - \frac{2.303RT}{nf} \log \frac{[cl-]2}{[Hg]2}$$

$$= E^{0}_{Hg2\ cl2/cl-} - \frac{2.303RT}{F} \log a_{cl}^{-}$$

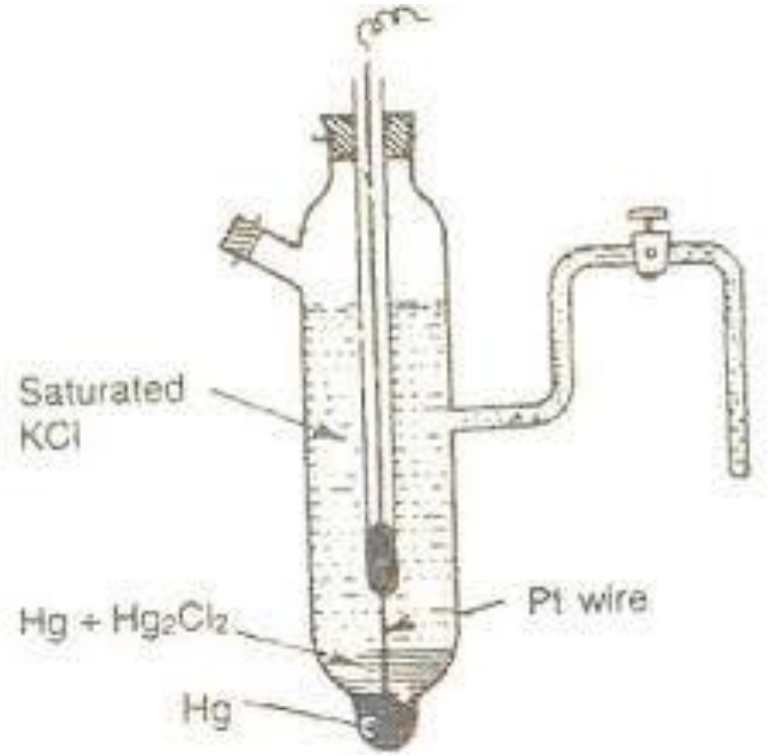


Fig1.11 Standard calomel electrode

1.1.8 Battery Chemistry:-

Batteries:

When two or more electrochemical cells are electrically interconnected, each of which containing two electrodes and an electrolyte is called a Battery.

Batteries are classified into a two categories depending on their recharging capabilities.

Primary Batteries: "These are non-rechargeable and are meant for single use and to be discarded after use".

These are non-reversed and are less expensive and are offer used in ordinary gadgets like torch lights, watches and toys.

Eg: Leclanche cell, Dry cell.

Secondary Batteries: - These are rechargble and are meant for multi cycle use. After every use the electrochemical reaction could be reversed by external application fades or lost due to leakage or internal short circuit. Eg: Lead-acid cell, Ni/cd cell

Differences between Primary and secondary batteries:

Primary cells	**Secondary cells**
1. These are non-rechargeable and meant for a single use and to be discarded after use. 2. Cell reaction is not reversible. 3. Cannot be rechargeable. 4. Less expensive. 5. Can be used as long as the materials are active in their composition. Eg: Leclanche cell, 'Li' Cells.	1. These are rechargeable and meant for multi cycle use. 2. Cell reaction can be reversed. 3. Can be rechargeable. 4. Expensive. 5. Can be used again and again by recharging the cell. Eg; Lead- acid cell, Ni-cd cells.

Primary Batteries:

Dry cell (Leclanche cell):

Anode: Zinc
Cathode: Graphite rod
Electrolyte: paste of NH_4Cl and $ZnCl_2$
Emf: 1.5V.

Dry cell consists of a cylindrical Zinc container which acts as an anode. A graphite rod displaced in the center. The graphite rod does not touch the base and it acts as a cathode. The graphite rod is surrounded by powdered MnO_2 and carbon. The remaining Space in between cathode and anode is filled with a paste of NH_4Cl and $ZnCl_2$.The graphite rod is fitted with a Metal cap and the cylinder is sealed at the top with a pitch.

The reactions takes place in the cell are:

At anode: $Zn \longrightarrow Zn^{+2} + 2e^{-}$

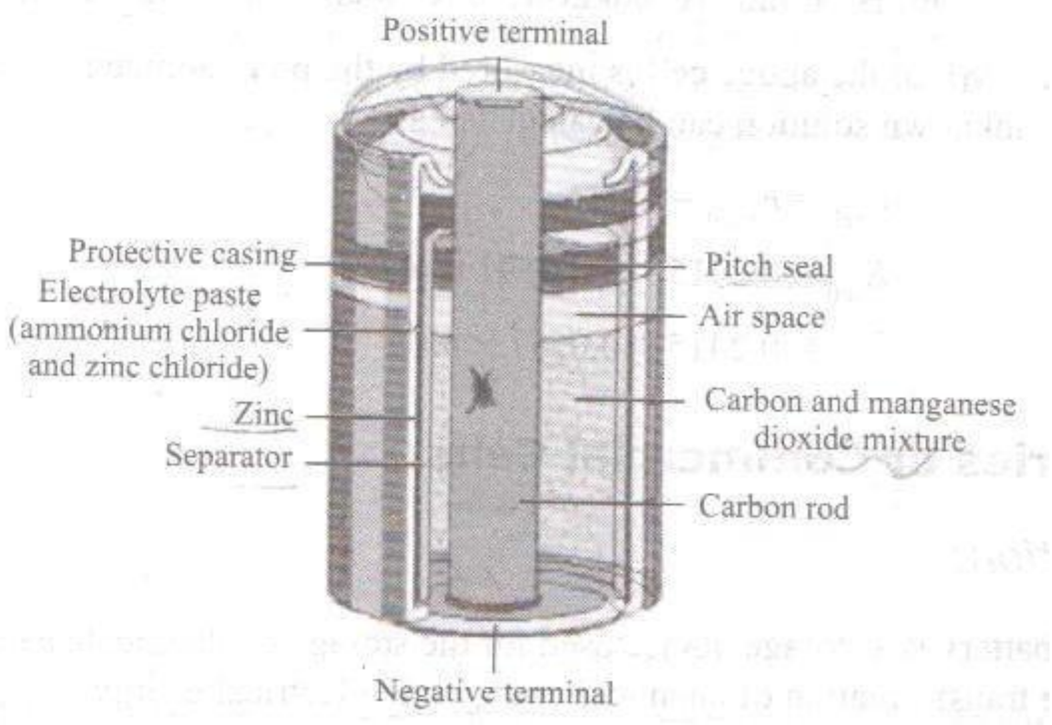
At cathode: $2MnO_2 + 2H_2O + 2e^{-} \longrightarrow 2Mn_2O_3 + 2OH^{-}$

Overall cell reactions: $Zn + 2MnO_2 + 2H_2O \longrightarrow Zn^{+2} + 2Mn_2O_3 + 2OH^{-}$

$2NH_4Cl + 2OH^{-} \longrightarrow 2NH_3 + 2Cl^{-}$

$+2H_2OZn^{+2}2NH_3+Cl^{-} \longrightarrow [Zn\ (NH_3)_2]\ Cl2$
Diaminedichlorozinc

The EMF of the cell is about 1.5volts.



Secondary Batteries:-

1) Lead – acid cell:

Anode: Sponge metallic lead

Cathode: Lead dioxide pbo$_2$

Electrolyte: Aqueous H_2SO_4.

Emf: 2V

Cell reactions:

$Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e^- + 0.356v$

$PbO_2 + SO_4^{-2} + \mathbf{2e^-} \rightarrow PbSO_4 + 2H_2o + 1.685v.$

The e.m.f. produced by the cell is 2v

Applications

1. Automobile and construction equipment.
2. Standby / backup system.
3. for engine batteries

Advantages:-

Low cost, long life cycle, Ability to withstand mistreatment, perform well in high and low temperature.

2) Nickel – Cadmium cells: (Ni-Cd Cell)

Anode: Cd

Cathode: Nickel oxy hydroxide Ni O OH

Electrolyte: Aqueous KOH

Emf: 1.4V

Cell reaction:

Anode: $Cd + 2\ 0H^- \rightarrow Cd\ (OH)_2 + 2\ e^-$

Cathode: $NiO\ OH + 2\ H_2O + 2\ e^- \rightarrow Ni\ (OH)_2\ H_2O + OH^-$

Applications:

Calculators, digital cameras, pagers, laptops, tape recorders, flash lights, medical devices, electrical vehicles, space applications.

Advantages: - Good performance in low temperature long life.

1.1.10 Numerical Problems

Q 1. The resistance of 0.1 N solution of an electrolyte is 40 ohms. If the distance between the electrodes is 1.2cm and the area of cross-section is 2.4cm. Calculate the equivalent conductivity.

A: Distance between electrodes l = 1.2cm

Area of cross-section a = 2.4cm^2

Cell const. $\frac{l}{a} = \frac{1.2}{2.4}$ = 0.5cm-1

Normality of given solution = 0.1 N.

Resistance R = 40 ohms.

Specific conductance K = $\frac{l/a}{R}$

$= \frac{0.5}{40} =$ 0.0125

Equivalent Conductivity = $\frac{K\,x\,1000}{N}$

$= \frac{0.0125\,x\,1000}{0.1}$

= 125 ohm^{-1}cm^2 eq^{-1}

2Q: Calculate the cell Constant of a cell having a solution of concentration N/30 gm eq/li of an electrolyte which showed the equivalent conductance of 120 Mhos cm^2 eq^{-1}, resistance 40 ohms.

A: Resistance R = 40 ohms.

Equivalent conductance of solution (A) = 120 mho cm^{2}eq^{-1}

Concentration of sol. N= $\frac{N}{30}$ gm eq/li

=0.033N.

Cell const =?

Equivalent conductance = $\frac{K\,x\,1000}{N}$

Specific cond. (K) = $\frac{eq\ conductance\ x\ N}{1000}$

$= \frac{120\,x\,0.033}{1000}$

$= 0.00396$

Cell constant = s p. conductance x Resistance

$= 0.00396 \times 40$

$= 0.1584\ cm^{-1}$

3Q: Calculate the emf for the cell,

Zn/Zn^{+} // Ag^{+}/Ag given $E^0_{Zn+/Zn}{}^{+2}$ / Zn = 0.762v and $E^0_{Ag+/Ag}$ = 0.8 v

A: Given cell is $zn/Zn^{+2}//Ag^{+}/Ag$.

$E^0_{Zn+2/Zn} = 0.762$ v

$E^0_{Ag+/Ag} = 0.8$ v

$E^0_{cell} = E^0_{right - E}{}^{0}_{left}$

$= 0.8 - (-0.762)$

$= 1.562$ v.

4Q: Calculate the $E^0 cu^{+2}/cu$, given $E^{-}{}_{cu}{}^{+2}{}_{/cu} = 0.296$ v and $[cu^{+2}] = 0.015M$.

A: cell reai is $cu \rightarrow cu^{+2} + Ze^{-}$

$$E = E^0 + \frac{0.0591}{n} \log [cu^{+2}]$$

$$0.296 = E^0 + \frac{0.0591}{2} \log [cu^{+2}]$$

$$E^0 = 0.296 - \frac{0.0591}{2} \log (0.015)$$

$= 0.296 - 0.2955\ (-\ 1.8239)$

$= 0.296 + 0.0538$

$= 0.3498$ v

5Q: Write the half cell and net cell reactions for the following cell,

Zn / $Znso_4$ (aq) // $cuso_4$ (aq) / cu.

Calculate the standard emf of the cell given,

$E^0_{Zn^{+2}/Zn} = 0.76$ v and $E^0_{cu+2/cu} = + 0.34$ v.

A: Half cell reactions

At anode: $Zn \rightarrow Zn^{+2} + Ze^-$

At cathode: $cu^{+2} + e^- \rightarrow cu$.

Net cell reaction = $Zn + cu^{+2} \rightarrow Zn^{+2} + cu$.

$$E^0_{cell} = E^0_{Cathode} - E^0_{Anode.}$$

$$= E^0_{cu^{+2}/cu} - E^0_{Zn^{+2}/Zn}$$

$$= 0.34 - (-0.76)$$

$$= 1.1 \text{ v.}$$

UNIT - II

Corrosion and Its Control

Corrosion

The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium.

The process of decay metal by environmental attack is known as corrosion.

Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc. E.g. Iron undergoes corrosion to form reddish brown colour rust [Fe2O3. 3H2O].

Copper undergoes corrosion to form a green film of basic carbonate [CuCO3 + Cu (OH) 2]

1.2.1 Causes of corrosion

1. The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.
2. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
3. Hence the isolated pure metals are regarded as excited states than their corresponding ores.

So metals have natural tendency to go back to their combined state (minerals/ores).

When metal is exposed to atmospheric gases, moisture, liquids etc., and the metal surface reacts and forms more thermodynamically stabled compounds.

Effects of corrosion

1. Wastage of metal in the form of its compounds.
2. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
3. Life span and efficiency of metallic parts of machinery and fabrications is reduced.

1.2.2 Theories of corrosion

Dry corrosion or Chemical corrosion

This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:

(1.) Oxidation corrosion

(2.) Corrosion due to other gases

(3.) Liquid metal corrosion

(1) Oxidation Corrosion: This is carried out by the direct action of oxygen low or high

Temperatures on metals in absence of moisture. Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, and Pt).

M -----→ M^{2+} + 2e- (Oxidation)

O_2 + 2e- ----→$2O_2$- (Reduction)

M + O_2 -----→M^{2+} + $2O^{2-}$ (Metal oxide)

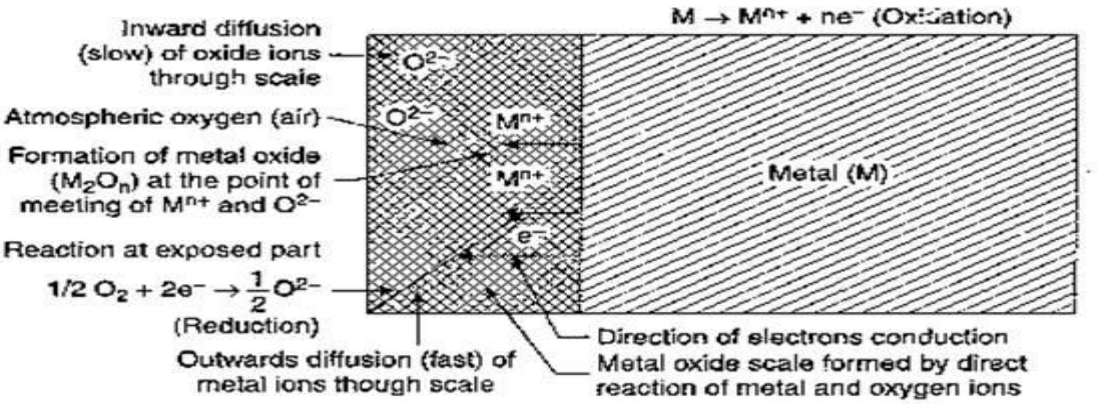


Fig.1.17 Oxidation corrosion

Mechanism: Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

(a) If the metal oxide is stable, it behaves has a protective layer which prevents further

Corrosion.

E.g., the oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

(b) If the metal oxide unstable, the oxide layer formed decomposes back into metal and oxygen. Oxidation corrosion is not possible.

E.g., Ag, Au and Pt do not undergo oxidation corrosion.

(c) If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO_3).

(d) If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed.

Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)

(2) Corrosion due to other gases: This type of corrosion is due to gases like SO_2, CO_2, Cl_2, H_2S, F_2 etc. In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent; non-porous does not allow the penetration of corrosive gases.

Ag + Cl2 ----→2AgCl (protective film)

(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms

Pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Ex. In petroleum industry, H_2S gas at high temperature reacts with steel forming a FeS scale. Fe (steel) + H_2S FeS (porous)

(3) Liquid metal corrosion: This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

Wet corrosion or electrochemical corrosion

- This type of Corrosion occurs where a conducting liquid is in contact with the metal. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
- At anodic area, oxidation reaction occurs there by destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

Mechanism*:* Electrochemical corrosion involves flow of electrons between anode and cathode.

The anodic reaction involves dissolution of metal liberating free electrons.

M-----→ M^{n+} + ne-

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

Evolution of hydrogen*:* This type of corrosion occurs in acidic medium.

E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with

Liberation of electrons.

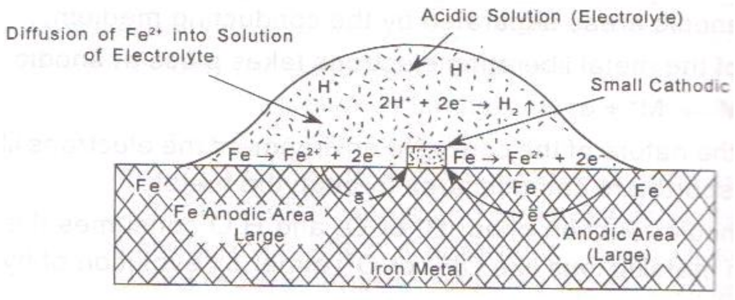


Fig.1.18 Hydrogen evolution corrosion

Anode: Fe----→ Fe2+ + 2e- (Oxidation)

The electrons released flow through the metal from anode to cathode, whereas H+ ions of acidic solution are eliminated as hydrogen gas.

Cathode: 2H+ + 2e- ----→H_2 (Reduction)

The overall reaction is: Fe + 2H+ -----→Fe2+ + H_2

This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H2 gas. The anodes are large areas, whereas cathodes are small areas.

Absorption of oxygen*:* For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large

Cathodes. The released electrons flow from anode to cathode through iron metal.

At anode: $Fe \text{ ----}\rightarrow Fe^{2+} + 2e^{-}$ (Oxidation)

At cathode: $\frac{1}{2} O_2 + H_2O + 2e^{-} \text{ ---}\rightarrow 2OH^{-}$ (Reduction)

Overall reaction: $Fe^{2+} + 2OH^{-} \text{ -----}\rightarrow Fe(OH)_2$

If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$

The product called yellow rust corresponds to Fe_2O_3. 3H2O.

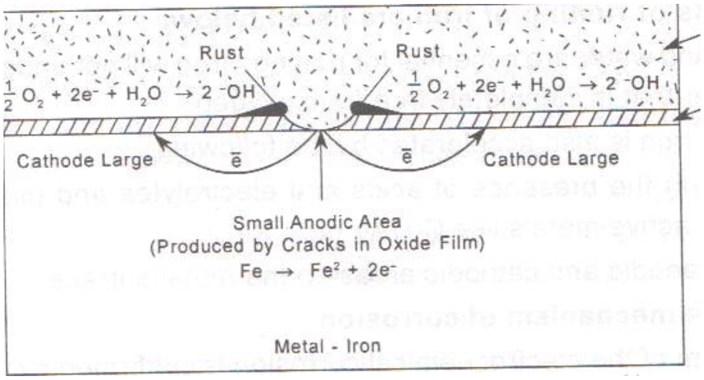


Fig.1.19 Oxygen absorption corrosion

1.2.3 Types of corrosion

1. Waterline corrosion or Concentration cell corrosion

This type of corrosion occurs due to electrochemical attack of the metal surface exposed to electrolyte of varying concentrations or varying aeration.

This type of corrosion is due to

(i) Difference in concentration of metal ions.

(ii) Difference in the exposure to air/oxygen (Differential aeration corrosion)

(iii) Difference in temperature.

- Differential aeration corrosion is the most common type of concentration cell corrosion. When a metal is exposed to different air concentrations, it has been found to be poorly oxygenated of the metal becomes anodic and well oxygenated part becomes cathodic.
- The potential difference is created which causes the flow of electrons from anode (metallic part immersed in NaCl solution) to cathode (exposed to atmosphere).

Eg. Zn rod immersed deep in NaCl solution: Anode

Zn rod above NaCl solution: Cathode

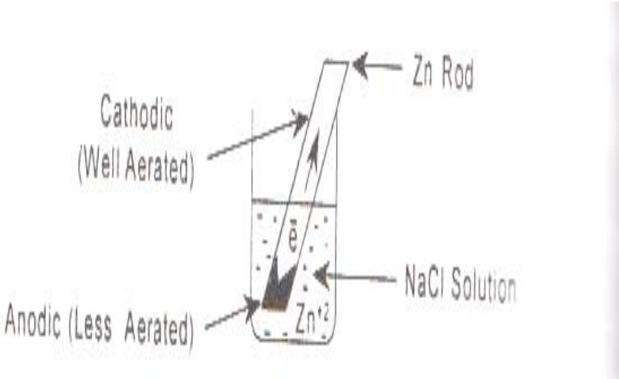


Fig.1.21Concen cell corrosion

Crevice corrosion

Crevice corrosion refers to corrosion occurring in confined spaces to which the access of the working fluid from the environment these spaces are generally called crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles.

Crevice corrosion usually occurs in gaps a few micrometers wide, and is not found in grooves or slots in which circulation of the corrodent is possible. Crevice corrosion is a very similar mechanism to corrosion. Crevice corrosion can be viewed as a less severe form of localized corrosion when compared with pitting. The depth of penetration and the rate of propagation in pitting corrosion are significantly greater than in crevice corrosion.

1.2.4 Factors effecting corrosion

The rate and extent of corrosion depends upon various factors due to nature of metal and nature of corroding environment.

Factors due to nature of metal

1. Purity of the metal*:* Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.

2. Electrode potentials*:* metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. Whereas the metals with lower reduction potentials readily undergo corrosion (eg. Zn, Mg, Al etc.).

3. Position of metal in galvanic series*:* Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.

4. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.

- When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.
- The rate of corrosion depends on the difference in their position in Galvanic series. Greater the difference more will be the extent of corrosion at anode.

Eg. The potential difference between Fe and Cu is 0.78V which is more than that between Fe and Sn (0.30V). Therefore, Fe corrodes faster when in contact with Cu than that with Sn. on this account, the use of dissimilar metals should be avoided wherever possible (Eg. Bolt & nuts, screw & washer).

4. **Relative areas of anodic and cathodic cells***:* the relative areas o of corrosion is influenced by cathodic to anodic cells.

5. If the metal has small anodic and large cathodic area, the rate of corrosion is very high. This is because the electrons are liberated at anode which is consumed at cathode. If the cathodic area is larger, the liberated electrons are rapidly consumed at cathode. This further enhances the anodic reaction leading to increase the rate of corrosion.

6. Hydrogen over voltage*:* when a cathode reaction is hydrogen evolution type, the metal with Lower hydrogen over voltage on its surface is more susceptible for corrosion, since the liberation of hydrogen gas is easy at this condition. Hence the cathodic reaction is very fast which in turn Makes anodic reaction fast. Hence the rate of corrosion increases. Higher the over voltage, lesser is the corrosion.

7. Physical state of metal: Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.

8. Nature of surface film: If the corrosion product formed is more stable, insoluble and nonporous, it acts as protective layer and prevents further corrosion (Eg. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

Factors due to nature corrosive environment

1. Temperature*:* the rate of corrosion reactions increases with increase in temperature.

2. Humidity in air*:* the moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.

3. Presence of impurities*:* Atmosphere is contaminated with gases like CO_2, SO_2, H_2S; fumes of H_2SO_4, HCl etc. and other suspended particles in the vicinity of industrial areas. They are Responsible for electrical conductivity, thereby increasing corrosion.

4. P^H value*:* pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.

5. Amount of oxygen in atmosphere: As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

1.2.5 Corrosion control methods

I. Cathodic protection

The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.

There are two types of cathodic protection

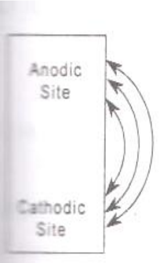
(a) Sacrificial anode method
(b) Impressed current method.

a. Sacrificial anode method

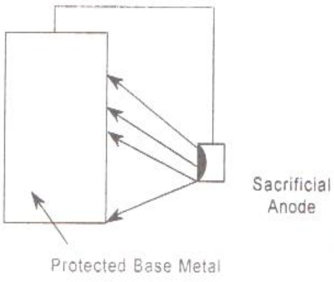
- In this protection method, the metallic structure to be protected (base metal) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.
- Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

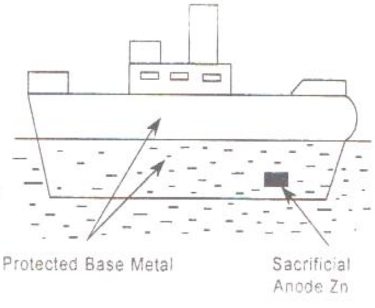
Eg. The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



Unprotected metal being corroded



(b) Sacrificial anodic protection



(c) Protection of ship-hull below water line by

Fig.1.25 Sacrificial anode method: ship hull and underground water pipeline

b. Impressed current method

- In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.
- The impressed current is slightly higher than thecorrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current is taken from a battery or rectified on A.C. line. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.

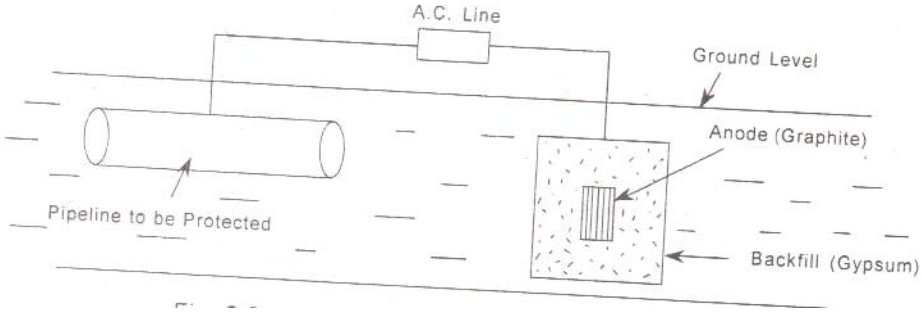


Fig.1.26 Impressed current method

1.2.6 Metallic coatings

The surface of the base metal is coated with another metal (coating metal). Metallic coatings are broadly classified into anodic and cathodic coatings.

1. Anodic coating*:* the metal used for the surface coating is more anodic than the base metal which is to be protected.

- For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially.
- The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.

2. Cathodic coating:

- Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature.
- Cathodic coating protects the base metal only when the coating is uniform and free from pores.
- The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

Methods of application of metallic coatings

1. Hot dipping

- Hot dipping process is applicable to the metals having higher melting point than the coating metal.
- It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer.
- The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Eg. Coating of Zn, Pb, Al on iron and steel surfaces.

The most widely used hot dipping processes are galvanizing and tinning.

a. Galvanizing

- Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.
- It is the anodic protection offered by the zinc. In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution at a temperature range of 60-90oC for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present and then washed well in a water bath and dried.
- Then after dipped in the bath containing molten zinc which is at 425-450oC. To prevent it from oxide formation, the surface of bath is covered with a ammonium chloride flux**.** When the iron sheet is taken out it is coated with a thin layer of zinc.

- To remove excess zinc, it is passed through a pair of hot rollers and then it is annealed at a temperature of 450^{o}C followed by cooling.

- Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.

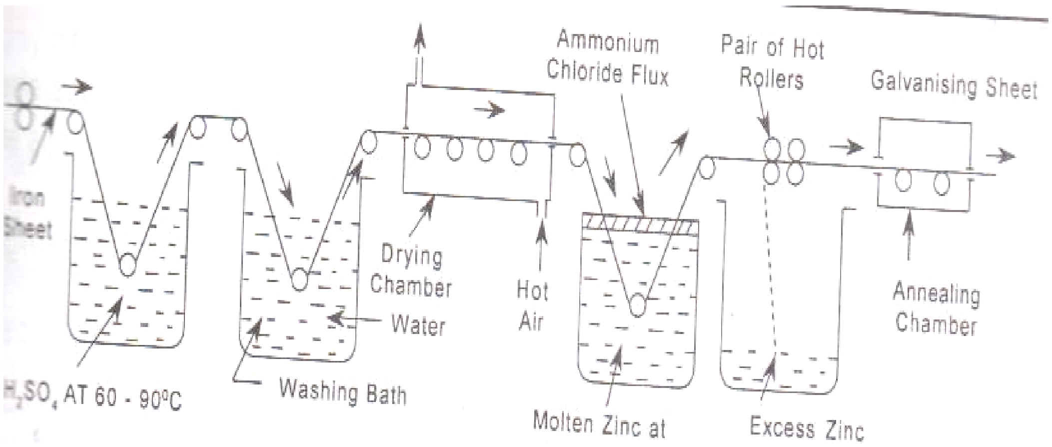


Fig.1.27 Galvanising

b. Tinning

- The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.

- Tin is a noble metal and therefore it possess more resistance to chemical attack. It is the cathodic protection offered by the tin. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.

- A cleaned iron sheet is passed through a bath $ZnCl_2$ molten flux followed by molten tin and finally through a suitable vegetable oil. The $ZnCl_2$ flux helps the molten metal to adhere to the base metallic surface.

- . Palm oil protects the tin coated surface against oxidation. Tinning of mild steel plates is done mostly for the requirements of the food stuff industry.

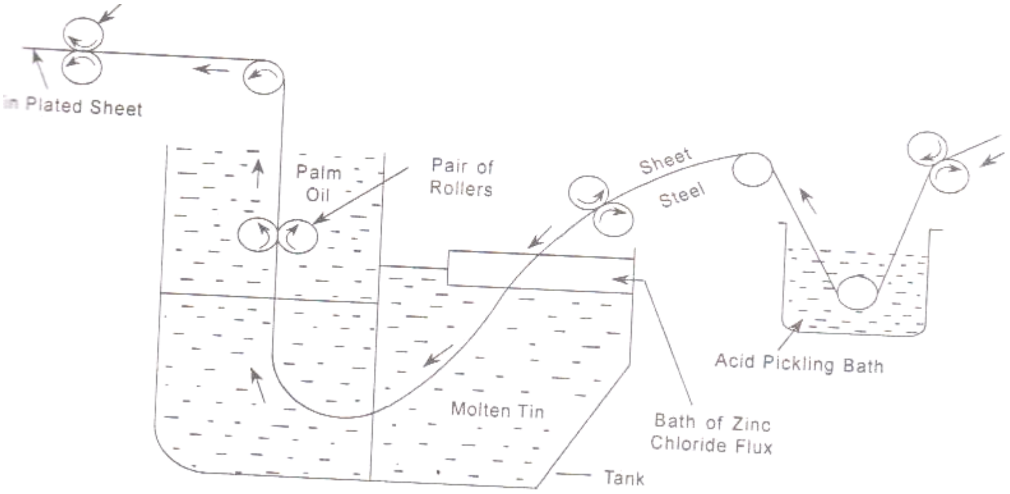


Fig.1.28 Tinning

3. Electroplating

Electroplating is the process of coating metals and protects them from corrosion, wear and chemical attack.

- Electroplating is the method of electro-deposition of metal by means electrolysis over surface of metals and alloys.
- The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.
- The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.
- When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.
- Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.

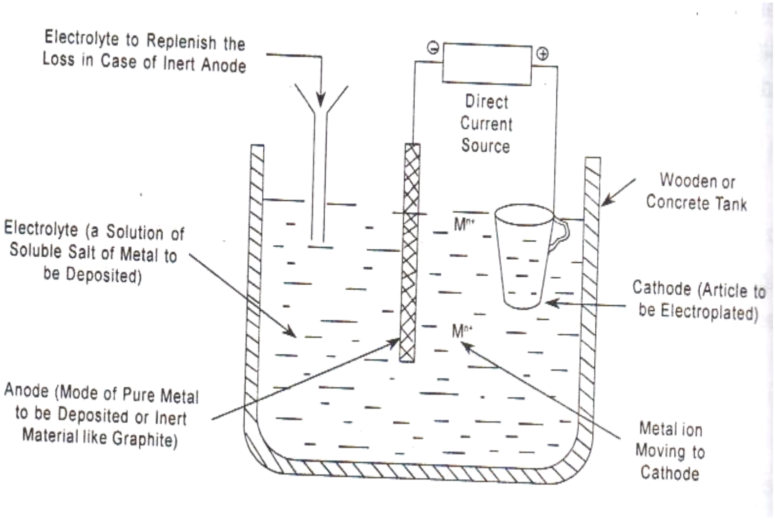


Fig1.30 Electroplating

1.2.7 Surface coatings

The application of surface coating is the common method to protect the surface of the metal from the corroding environment. These surface coatings exhibit chemical inertness to corrosive environment, adhesive properties and impermeable.

a. Organic surface coatings

- Organic surface coatings are applied over the metallic surfaces to prevent from the corrosion.
- Properties of Organic surface coatings.
- Chemical inertness to the corrosive environment
- Good surface adhesion
- Impermeability to water, gases and salts
  Eg. Paints
- Paint is a mechanical dispersion mixture of several constituents in a vehicle oil or drying oil.
- The following are the constituents of paints and their functions.

Constituent Functions Examples

1. Pigment

- It is a major constituent of the paint.
- Provides desired colour to the paint
- It protects the paint by reflecting harmful U.V radiation.
- Gives strength and increases weather resistance of the film.

- White- white lead, ZnO
- Red- Red lead,
- Ferric oxide

2. Vehicle oil/ Drying oil

- It forms the film forming constituent of the paint.
- It acts as medium for the dispersion of various constituents.
- It gives durability, adhesion and water proofness to the paint.
- Sunflower oil, Mustard oil, Soya bean oil.

3. Thinners

- Reduces the viscosity and increases the elasticity of the
- Paint film.
- Enhances the dissolving the additives in vehicle medium. Turpentine, Kerosene, Naphtha.

4. Driers

- Driers are oxygen carrying catalysts.
- They accelerate the drying of the paint film through oxidation, polymerization and condensation. Tunstates and nahthalates of Pb, Zn and Co.

5. Extenders/ Fillers

- Low refractive indices materials.
- They reduce the cost and cracking nature of the paint film.
- $BaSO_4$, gypsum,

6. Plasticizers

- They provide elasticity to the film and minimize cracking.
- Tributylphosphate,
- triphenylphosphate

7. Anti skinning agents

- They prevent the gelling nature the paint film.
- Polyhydroxy phenols

Unit - III

Water and It's Treatment

Introduction

The pure water is composed of two parts of hydrogen and one part of oxygen by volume and dissolves many substances. These dissolved salts are the impurities in water. Water is a very good solvent. So it is called as universal solvent.

3.1 Hardness of water: -

The water which does not give lather with soap is called Hard water. The Hard water contains dissolved calcium & magnesium salts.

Soft water: - The water which can give lather with soap easily is called as soft water.

$\text{Na-stearate} + H_2O \longrightarrow NaOH + \text{stearic acid}$

Soap (soft water)

$\text{Stearic acid} + \text{Na- stearate} \longrightarrow \text{formation of lather}$

$2\ \text{Na – stearate} + ca^{2+} \longrightarrow \text{ca-stearate} \downarrow + 2\ Na^{+}$

(Soluble salt)

Hard water

Types of Hardness:- Hardness in water is of two types.

(1) Temporary hardness and (2) permanent hardness

Temporary hardness:- The hardness that can be removed simply by boiling is called the temporary hardness. It is due to the presence of boiling. On boiling $Ca(Hco_3)_2$, $Mg(Hco_3)_2$ are precipitated as insoluble salts. Which can remove through filtration?

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2\ CO_2 \uparrow$$

Permanent Hardness:- Permanent hardness cannot be removed by boiling . It is due to $CaCl_2$, CaSO4, MgCl2, $MgSO_4$ and nitrates in H_2O. These salts cannot remove this hardness. Fe^{3+}, Al^{3+} & Mn^{2+} also cause hardness in water.

Units of Hardness:-

(1) Parts per million (ppm):- It is the number of parts of equivalents of $CaCO_3$ hardness causing salt present in one million parts(10^6 parts) of water.

(2).Miligram per litre(mg/l):-It is the number of milligrams of equivalentof $CaCO_3$ per litre

of hard water. E.g.:- 1mg/li means 1 mg of equivalent $caco_3$ present in litre of hardwater.

(3)Degree Clarke (o cl):-It is the number of gains of equivalent $CaCO_3$ equivalents of hardness causing salt in 70,000 parts of water.

(4)Degree French (o Fr):- It is a French unit. The number of parts of $caco_3$ equivalent hardness causing substance in 10^5 parts of water.

Inter conversion: - 1ppm=1mg/l == $0.07\ ^{o}$ cl = 0.1^{0} Fr

$1^{o\ cl}=1.43^{o\ Fr}$ = 14.3 ppm=14.3 mg/l

Determination of Hardness of Water: - Two different methods are there

(1)EDTA method:- In EDTA methods, the known water sample is titrated against standard EDTA solution using EBT as indicator in the presence of basic buffer solution(PH=10). At the end point the wine red color changes to blue.

Principle:- The ca^{2+} &Mg^{2+} ions present in water are responsible for hardness. These icons form selectable complexes with the indicator (EBT) and these metal icons forms stable complexes with EDTA. This fact is used to estimate the hardness of water sample.

The metal ions ca^{2+} & Mg^{2+} react with the EBT indicator and forms a stable complex at PH-10.

$$M^{2+} \quad + \quad EBT \xrightarrow{PH\ 9\text{-}10} M^{2+} \text{—} EBT \text{ (or) } M\text{- } In$$

Ca^{2+} or Mg^{2+} Indicator less stable wine red color

Hard water complex

Whenever we are adding EDTA solution to the wine- red color (M-In) solution, the metal ions form more stable complex with EDTA. When all the metal ions in the sample complexed with EDTA, further addition of EDTA liberates the free indicator solution at PH-10 which in blue color indicates the end point of the titration

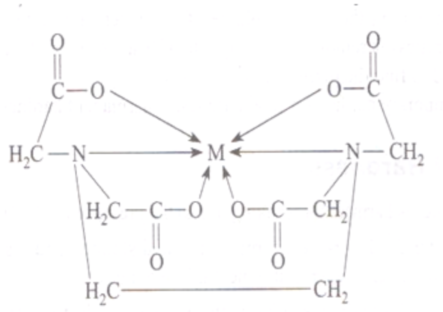


Fig3.1 Metal ion-EDTA complex

Experimental procedure:- A known volume of Hardware sample is titrated with about 3 ml of buffer solution and 4- 5 drops of EBT indicator. This solution is treated against a standard EDTA solution. The end point is the color change from wine –red to blue.

Let the titer value = v1 ml (End point)

1ml of EDTA (0.01m) = 1 mg of CaCO3

V_1 ml of EDTA (0.01m) =v_1 mg of CaCO3

So v_1 mg of equivalent $CaCO_3$ hardness is presented in v ml of hard water

The total hardness of sample = $\frac{v_{1\times}1000}{v}$ ppm

A known volume of water sample is taken in a beaker and boiled for half an hour, after cooling it is filtered and the filtrate titrated against EDTA by adding EBT indicator & PH-10 buffer solution. Here the volume of EDTA consumed $v_2$ml gives us the permanent hardness of water.

Permanent hardness of water = $\frac{v_{2\times}1000}{v}$ ppm

The total hardness of water= (Temporary hardness + permanent hardness)

Temporary hardness= (Total hardness-permanent hardness)

Determination of Hardness of Water by Winkler's method:

The determination of dissolved oxygen is to bring about the oxidization of potassium iodide with the dissolved oxygen present in the water sample after adding MnSO4, KOH and KI. The basic manganic oxide formed acts as an oxygen carrier to enable the dissolved oxygen in the molecular form to take part in the reaction. The liberated iodine is titrated against standard hypo Solution using starch indicator.

$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$

$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2$

Basic manganic oxide (Brown precipitate)

$MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + [O]$

$2KI + H_2SO_4 + [O] \rightarrow K_2SO_4 + H_2O + I_2$

$I_2 + Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

Starch + $I_2 \rightarrow$ blue colored complex.

Experimental Procedure:

Take the standard flask with 200 ml of water to that add 2ml of $MnSO_4$ and 2ml of KI + KOH (alkali potassium iodide).Light brown precipitate forms, to this add 2ml of conc.H_2SO_4 precipitation dissolved into brown colour. Take 100 ml of solution which is in the standard flask and pour it into conical flask. To the conical flask add 1–2ml of starch needed immediately colour changed to blue. Then titrate the solution with hypo solution until the solution becomes colourless. Note down the readings and repeat it. Amount of dissolved oxygen content is obtained in mg/ lit (or) ppm.

FORMULAE:

$$\boxed{\text{D.O} = \frac{\text{Normality of Hypo} \times V \times 8 \times 1000}{\text{Volume of the sample}}}$$

Effects of hardness: - (1) Hard water is harmful for drinking due to the presence of excess of

Ca^{+2} and Mg^{+2} ions

(2)Hard water used in boilers forms scales & sludge and results in corrosion, priming caustic embrittlement of the boilers.

(3)Hard water used does not give lather with soap, so it sticks to clothes and body.

(4)Hardness in water causes blockage in holes.

(5)Hard water is not suitable for laboratory analysis, because hardness producing icons interfere in various reactions.

3.2 Boiler Troubles: - Continues use of hard water in boilers causes boiler troubles that are

1. Priming: - The carrying out of water droplets with steam in called "priming" Because of rapid and high velocities of steam, the water droplets moves out with steam from the boiler. This process of wet steam generation is caused by (i) The presence of large amount of dissolved solids.(ii)High stream velocities (iii) sudden boiling (iv) improper designing of boilers (v) sudden increase in stream production rate and (vi) The high levels of water in boilers.

Prevention of priming: - The priming is avoided by

(i)Fitting mechanical steam purifiers

(ii)Avoiding rapid change in steaming rate

(iii) Maintaining low water levels in boilers and

(iv)Efficient softening and filtration of boiler feed water.

2. Foaming: - Formation of stable bubbles at the surface of water in the boiler is calling foaming. More foaming will cause more priming. It results with the formation of wet steam that harms the boiler cylinder and turbine blades. Foaming is due to the presence of oil drops, grease and some suspended solids.

Prevention of Foaming:- Foaming can be avoided by

(1)Adding antifoaming chemicals like castor oil. The excess of castor oil addition can cause foaming.

(2) Oil can be removed by adding sodium aluminates or alum.

(3) Replacing the water concentrated with impurities with fresh water.

3. Scale &sludge formation:- The water in boiler is continuously heated causes the increase in the concentration of dissolved and suspended solids. These are precipitated and slowly precipitate on the inner walls of the boiler plate. This precipitation takes place in two ways.

(1)The precipitation in the form of soft loose and slimy deposits (sludge)

(2)The precipitation in the form of hard deposits, which are sticky on the walls of boilers (scale)

Sludge: The muddy solid at the bottom of the boiler (or) the loose, slimy and soft deposits in the boiler are called sludge.

Causes of the sludge:- The sludge is caused by $MgCO_3$, $MgCl_2$,$CaCl_2$ which have more solubility in hot water.

Disadvantages of sludges: - 1. sludges are bad conductors of heat and results in wastage of heat and fuel.

2. Sludges entrapped in the scale get deposited as scale causes more loss of efficiency of boiler.

3. Excessive sludge formation leads to setting of sludge in slow circulation. Areas such as pipe connections leading to chocking (or) blockage of the pipes.

Prevention of sludge formation: - (1) By using soft water which is free from dissolved salts like , $MgCO_3$, $MgCl_2$, $CaCl_2$&$MtgSO_4$.

(2)Blow down operation can prevent sludge formation

Scale: - Scales are hard sticky deposits on the inner walls of boiler. The scales are very difficult to remove.

Reason of Scale:- (1) Due to the decomposition of $Ca(HCO_3)_2$ at high temperature & pressure present in boiler, It forms $caco_3$ insoluble salt settles as ppt in the boiler.

$$(H\,CO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + CO_2 \uparrow + H2O$$

(2) $CaSO_4$ present in water in highly solute in cold water and less soluble in hot water. So the $CaSO_4$ in boiler water is precipitates out as hard scale, whenever the temp of boiler increases.

(3) Hydrolysis of $MgCl_2$:- The dissolved $mgcl_2$ present in water is precipitates as $Mg(OH)_2$ at high temperature, deposits as scale.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 \downarrow + 2HCl$$

(4)Sio_2 present in water deposits as calcium silicate or magnesium Silicate. The deposits are very hard.

Disadvantages of Scale: - (1) As the scale is hardly sticky on the walls of the boiler and it is very bad conductor of heat. So there is loss of heat and fuel.

2. Due to the scale formation we have to heat the boiler to high temperatures this causes the weakening of boiler material.

3) Due to scale deposits the chocking of boiler is observed.

4) Due to uneven heat there may be developing of cracks in Scale. Whenever the water passes through this crack comes to contact with boiler plate and generates sudden steam and high pressure results explosion of boiler.

Removal of Scales:-

(1) If the scale is soft. If can be removed by scrapper.

(2) By giving thermal shocks done by heating to higher temperature and suddenly cooling.

(3)The $CaCO_3$ scale is removed by the washing with 5-10% HCl Solution and $CaSO_4$ scale in removed washing with EDTA solution.

(4)Blow down operation also removes Scale

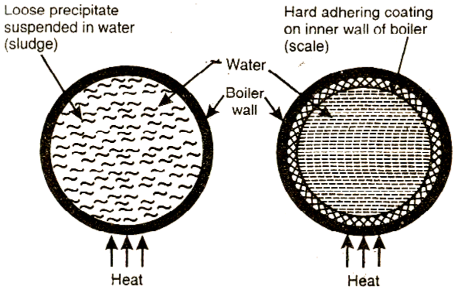


Fig3.2 Sludge Scale

4. Caustic embrittlement:- The Na_2 CO3 present in water hydrolysed to NaOH at high pressures in boilers.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2 \uparrow$$

The NaOH formed concentrates after long use. It causes inter-granular cracks on the boiler walls, especially at the stress points. The concentrated alkali is dissolved iron as sodium ferrote in cracks and cause brittlement of boiler.

The formation of cracks in boilers due to NaOH is called caustic embrittlement. The created concentration cell is explained

Iron at bends	concentrated	Diluted	Iron at plane surface
(Anode)	NaoH	NaoH	(cathode)

The iron is dissolved at anode i.e undergoing corrosion

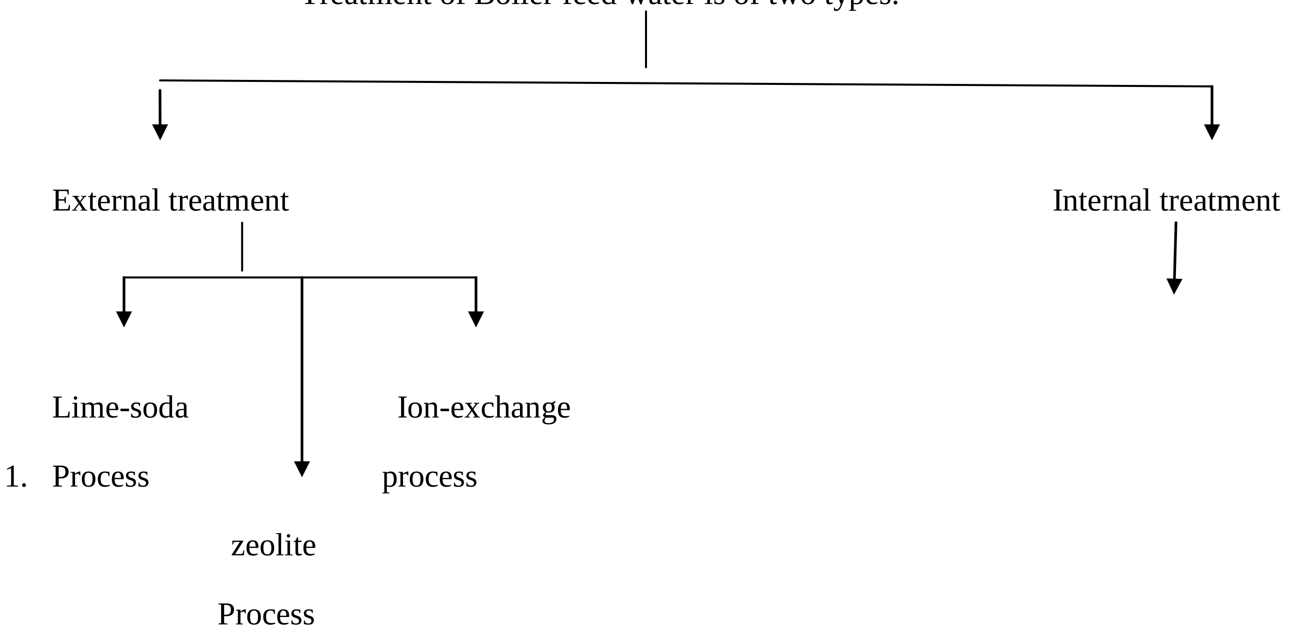
Prevention of caustic embrittlement :- 1) by using sodiumphosphate as softening agent instead of Na_2CO_3.

2) By adding tannin or lignin to boiler water which block the hair cracks and pits in boiler.

3) By adding sodium sulphate to soften the water and this also blocks the hair cracks present on the surface of the boiler plate.

3.3Treatment of boiler feed water (Softening of water):-

Treatment of Boiler feed water is of two types.



(1)Zeolite (or) permutit process:- Zeolite is a three-dimensional silicate. The chemical formula of zeolite is hydrated sodium aluminum silicate represented as $Na_2OAl_2O_3.xH_2O\ yH_2O$ (x=2 to 10 &y=z-6). Zeolites are capable exchanging ions with sodium ions. So it is capable of exchanging hardness producing icons present in water. This process also called as permutit process. Zeolite can be written as Na_2Ze The two Na^+ icons is replaced by one Ca^{2+} or Mg^{2+} ions.

$Na_2Ze + Ca^{2+} \longrightarrow CaZe + 2 Na^+$

Naturally occurring Zeolite is Natolite –$Na_2O.Al_2O_3.SiO_2.2H_2O$.The Synthetic Zeolites are also prepared with the help of feldspar &China clay on heating.

Process:-The apparatus is made of cylindrical metallic vessel several beds are made inside it where zeolite salt is kept. Raw water is poured inside the apparatus through inlet that passes through beds and thus chemical ion exchange reactions are takes place. After the use of this process for a certain time, Zeolite is exhausted .i.e all Na^+ ions are replaced by ca^{2+}/mg^{2+} and therefore this will not be used for soften the water.

$Na_2Ze + CaCl_2$ (or) $CaSO_4$ (or) $Ca(HCO_3)_2 \longrightarrow CaZe+2NaCl(or)Na_2SO_4$ or $2NaHCO_3$
Exhausted zeolite can be regenerated or reactivated by heating it with brine solution(10% NaCl solution)

$(Ca^{2+}/Mg^{2+}) Ze + NaCl \longrightarrow Na_2Ze + CaCl2(or)MgCl_2$

Exhausted Zeolite on washing with cold water, CaC_2 & $MgCl_2$ can be removed and regenerated zeolite is this ready to be reused.

Zeolite softener

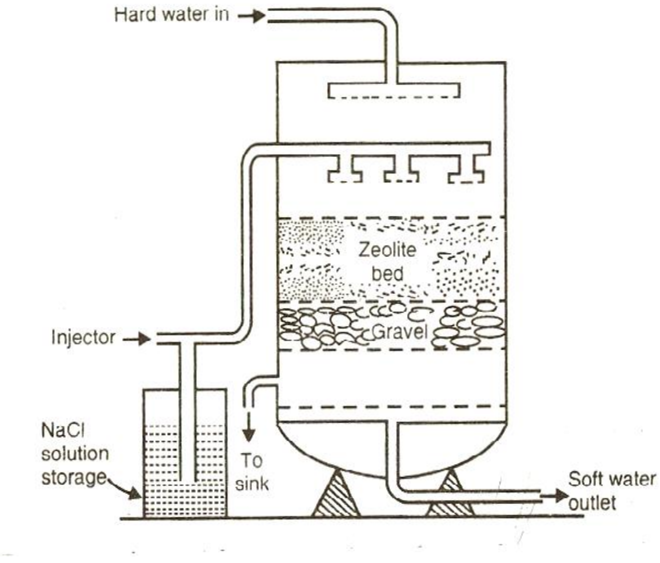


Fig 3.4 Zeolite softener

Advantages:- Hardness of water is removed and it is about 10ppm in the soft water obtained by this process. It is easy to operate (3) It occupies less space (4) sludge or Scale in not formed (5)

The process can be made automatic & continuous. (6) This process is very cheap since regenerated permutit is used again.

Disadvantages:-1) In zeolite process $2Na^+$ ions replaces by ca^{2+}/mg^{2+} icons. The soft water obtained by this process has excess of Na^+ ions.
2) If the hard water containing acid destroys the zeolite bed.
3) The turbidity (or) suspended particles present in water will block the pores of zeolite.
4) Bicarbonate & carbonate ions present in water are converted as sodium salts resulting the alkalinity of water.
(5) The coloured ions like Mn^{2+} &Fe^{2+} cannot be removed by this process.

(2) Ion exchange process (or) deionization or demineralization:-

Ion exchanges are of two types. Anionic & Cationic. These are co-polymers of styrene & divinyl benzene.i.e. Long chain organic polymers with a micro porous structure.

cation exchange resins:- The resins containing acidic functional groups such as -COOH,-SO_3H etc. are capable of exchanging their H^+ ions with other cations are cation exchange resins , represented as RH^+

Anion exchange resins:- The resins containing amino or quaternary ammonium or quaternary phosphonium(or) Tertiary sulphonium groups, treated with "NaoH solution becomes capable of exchanging their oH^- ions with other anions. These are called as Anion exchanging resins represented as $R\ OH^-$

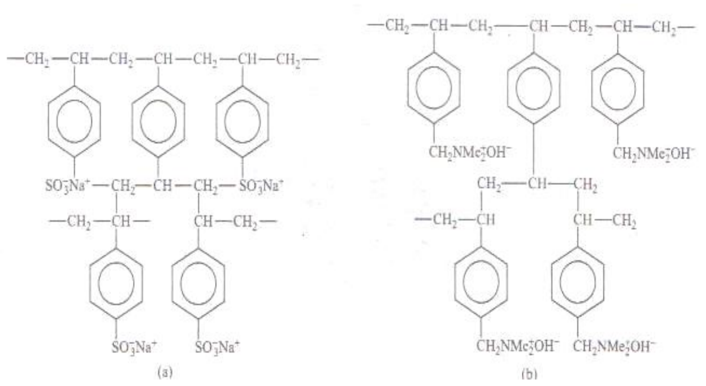


Fig 3.5 Cation exchange resin Anion exchange resin

Process: The hard water is passed first through cation exchange column. It removes all the cation (ca^{2+} & $Mg^{2+)}$ and equivalent amount of H^+ icons are released from this column.

$$2RH^+ \quad + Ca2^+ \quad \text{(or)}\ Mg^{2+} \longrightarrow R_2Ca^{2+} \quad +2H^+$$

(Or)

R_2Mg^{2+}

After this the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-},Cl^-,CO_3^{2-} etc and release equal amount of OH^- from this column.

$$R^1OH + Cl^- \longrightarrow R^1Cl + OH^-$$

$$2R^1OH + SO_4^{2-} \longrightarrow R_2{}^1SO_4 + 2OH^-$$

The output water is also called as de -ionised water after this the ion exchanges get exhausted. The cation exchanges are activated by mineral acid (HCl) and anion exchanges are activated by dil NaOH solution.

$$R_2Ca + 2H^+ \longrightarrow 2RH + Ca^+$$

$$R_2{}^1SO_4 + 2OH^- \longrightarrow 2R^1OH + SO_4^{2-}$$

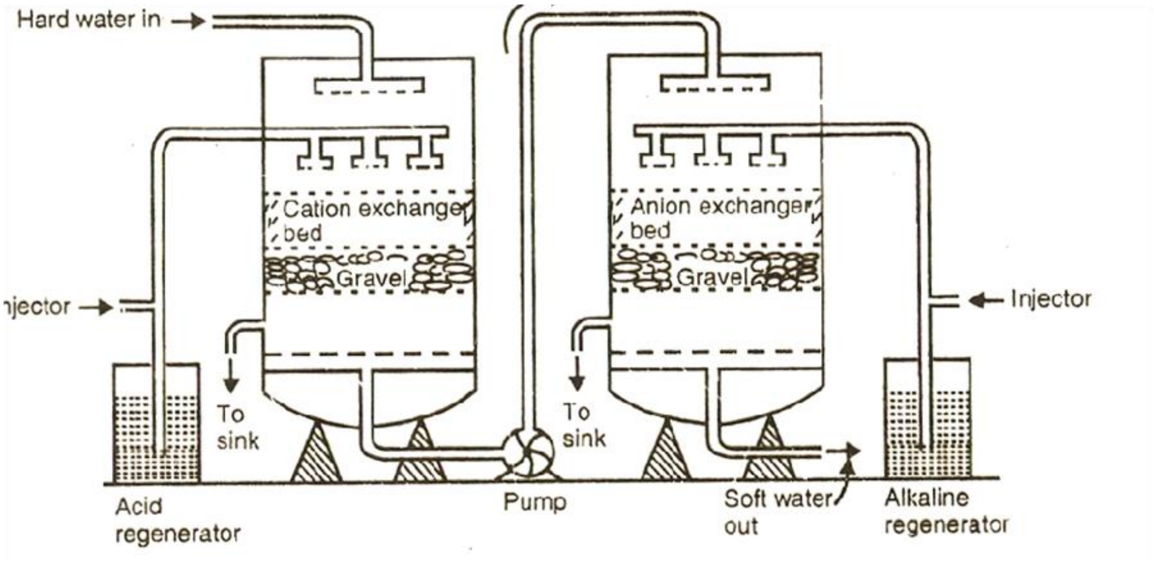


Fig3.6 Ion exchanger

Advantages:-The process can be used to soften highly acidic or alkaline wate. (2) It produces water of very low hardness. So it is very good for treating for use in high pressure boilers.

Disadvantages:- The equipment is costly and common expensive chemicals required. (2) It water contains turbidity, and then output of this process is reduced. The turbidity must be below 10 ppm.

Internal treatment: - In this method raw water in treated inside the boiler. This is a process of adding suitable chemical to residue scale &sludge formation. It is mainly based on solubility. This is a corrective method. This method is also called conditioning method.

Conditioning of water:-

1) Carbonate conditioning:- In low pressure boilers scale formation can be avoided by treating the boiler water with $Naco_3$. Where $CaSO_4$ is converted into $CaCO_3$.

$CaSO_4$ is precipitated as loose sludge in the boiler which can be scrapped off.

2) Calgon conditioning: - calgon means calcium gone i.e the removal of ca^{2+}. Sodium hexa-meta phosphate is called calgon. It reacts with calcium ion and forms a water solute compound.

Converted to scale which on drying converted to scale reduces the efficiency of the boiler.

$$Na_2 \left[Na_4 [PO_3]_6 \right] + 2\, Ca^{2+} \longrightarrow Na_2 \left(Ca_2 [PO_3]_6 \right)$$

At higher temperature $NaPO_3$ is converted to $Na_2P_2O_4$ that also reacts Ca^{2+} to foam loose sludge of Cap_2O_7.removed by blowing air.

3) Phosphate conditioning: - It is applied to high pressure boilers. When sodium phosphate is added to boiler water, It reacts with Ca & Mg salt forming soft sludges.

$$3\, CaCl_2 + 2\, Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 \downarrow + 6NaCl$$

$$3\, MgCl_2 + 2\, Na_3PO_4 \longrightarrow Mg_3(pO_4)_2 \downarrow + Na_2SO_4$$

Trisodium phosphate is used when the alkalinity of boiler water is 9.5 to 10.5 at that PH Ca gets precipitated.

If alkalinity is too high NaH_2pO_4 (acidic) is used and Na_2HPO_4 is used if sufficiently of alkaline.

(4). Treatment with Sodium Aluminate: - when boiler water heated with Sodium aluminate it gets hydrolyses to give NaOH and gelatinous precipitate of $Al(OH)_3$.

$$NaAlO_2 + 2\, H_2O \longrightarrow NaOH + Al(OH) \downarrow$$

The NaOH formed react with $MgCl_2$ to form $Mg(OH)_2$. These two precipitates entrap colloidal impurities like oil drops, sand and make them settle down.

Disadvantages of hard water in domestic and Industrially In Domestic use:-

Washing:-

Hard water, when used for washing purposes, does not producing lather freely with soap.
As a result cleaning quality of soap is decreased and a lot of it is wasted.
Hard water reacts with soap it produces sticky precitates of calcium & Mg soaps. These are insoluble formations.

(a) **Bathing:-**
Hard water does not produce lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleaning quality of soap is depressed and a lot of it is wasted.

(b) **Cooking:-**
The boiling point of water is increased because of presence of salts. Hence more fuel and time are required for cooking.

(c) **Drinking:-**
Hard water causes bad effects on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

Industrial use:-

(a) **Textile industry:-** Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
(b) **Sugar Industry:-** Water containing sulphates, nitrates, alkali carbonates etc. if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so produced may be de-liquiscent.
(c) **Dyeing industry:-** The dissolved salts in hard water may reacts with costly dyes forming precipitates.
(d) **Paper Industry:-** Calcium, magnesium, iron salts in water may affect the quality of paper.
(e) **Pharmaceutical Industry:-**Hard water may cause some undesirable products while preparation of pharmaceutical products.
(f) **Concrete making:-** water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.
(g) **Laundry:-** Hard water, if used in laundry, causes much of the soap used in washing to go as waste iron salts may even causes coloration of the cloths.

Why is hard water harmfull to boilers?

Steam generation purpose boilers are used in Industries. If the hard water is fed directly to the boilers, there arise many troubles such as:

(a) **Scale & Sludge formation**:- The hardness of water fed to the many causes scale & sludge formation.
(b) **Corrosion:-** Hard water may cause caustic embrittlement which is a type of boiler corrosion.

(c) Priming & Foaming:- Hard water used in boiler cause priming and foaming which results in the formation of wet steam

(d) Caustic embrittlement

Hardness- Numerical problems:-

(1) One litre of water from an underground reservoir in tirupathi town in Andhra Pradesh showed the following analysis for its contents. Mg $(HCO_3)_2$= 42 Mg, $Ca(HCO_3)_2$= 146 Mg, $CaCl_2$= 71 Mg, NaOH= 40 Mg, $MgSO_4$=48 Mg,organic impurities=100 Mg, Calculate temporary, permanent and total hardness?

Hardness causing salt (H.C.S)	**Quantity (H.C.S)**	**Mol.Wt.of (H.C.S)**	**Equivalent of $CaCO_3$**
$CaCl_2$	71	111	$\frac{71*100}{111}$=64
$MgSO_4$	48	120	$\frac{48*100}{120}$=40
$Ca(HCO_3)_2$	146	162	$\frac{146*100}{162}$=90.1
$Mg(HCO_3)_2$	42	146	$\frac{42*100}{146}$=28.7
NaOH	40	-	-

Temporary Hardness= $Mg(HCO_3)_2$+$Ca(HCO_3)_2$

= 28.7+90.1=118.8ppm

Permanent Hardness=$CaCl_2$+$MgSO_4$

= 64+40 = 104ppm

Total Hardness=Temporary Hardness + Permanent Hardness

= 118.8+104=222.8ppm

(2) One liter of water from khammam Dist in A.P showed the following analysis. $Mg(HCO_3)_2$=0.0256 gms, $Ca(HCO_3)_2$=0.0156 gms, NaCl=0.0167gms, $CaSO_4$=0.0065gms, and $MgSO_4$=0.0054gms. Calculate temporary, Permanent & total hardness.

S. No	**Constituent**	**Amount Mg/l**	**Mol. Wt. of salt**	**Equivalent of CaCO3 mg/l**
1	$CaSO_4$	6.5	136	$\frac{6.5*100}{136}$=4.77
2	$MgSO_4$	5.4	120	$\frac{5.4*100}{120}$=4.5
3	$Ca(HCO_3)_2$	15.6	162	$\frac{15.6*100}{162}$=9.6
4	$Mg(HCO_3)_2$	25.6	146	$\frac{25.6*100}{146}$=17.5
5	NaCl	16.7	_	_

Temporary hardness=$Mg(HC_3)_2$+$Ca(HCO_3)_2$

= 17.5+9.6=27.1 ppm

Permanent hardness=$CaSO_4$+$MgSO_4$

=4.77+4.5=9.27 ppm

Total hardness=Temporary hardness +Permanent hardness

= 27.1+9.27=36.37 ppm

(3) Calculate the temporary & permanent hardness of 100 litre of water containing the following impurities per litre $MgCl_2$=19 mg, $MgSO_4$=60 mg, NaCl=36.5 mg, $CaCl_2$=11.1 mg, $Ca(HCO_3)_2$=32.4 mg & $Mg(HCO_3)_2$=7.3 mg

S No	**Constituent**	**Amount Mg/l**	**Mol.wt. of salt**	**Equivqlent of $CaCO_3$(Mg/l)**
1	$CaCl_2$	11.1	111	$\frac{11.1*100}{111}$=10
2	$MgCl_2$	19	95	$\frac{19*100}{95}$=20
3	$MgSO_4$	60	120	$\frac{66*100}{120}$=50
4	$Ca(HCO_3)_2$	32.4	162	$\frac{32.4*100}{162}$=20
5	$Mg(HCO_3)_2$	7.3	146	$\frac{7.3*100}{146}$=5
6	NaCl	36.5	_	_

Temporary hardness=Mg $(HCO_3)_2$+Ca $(HCO_3)_2$

=5+20=25

Temporary hardness for 100ml = 25×100=2500 Mg/l

Permanent hardness= $CaCl_2$+$MgCl_2$+$MgSO_4$

= 10+20+50=80 Mg/l

Permanent hardness for 100l= 80*100=8000 Mg/l

Total hardness= Temporary hardness + Permanent hardness

=25+80=105Mg/l

Total hardness for 100 litre = 105×100=10,500 Mg/l

(4) A sample of hard water contains the following dissolved salts per liter CO_2=44Mg, Ca $(HCO_3)_2$=16.4Mg, Mg $(HCO_3)_2$=14.6 Mg

$CaCl_2$=111 Mg, MgSO4=12 Mg, &$CaSO_4$=13.6 Mg. Calculate the temporary &

Permanent hardness of water in °Fr &° Cl. (2013)

S.No	**Constituent**	**Amount Mg/l**	**Mol.wt. of salt**	**Equivqlent of CaCO3(Mg/l)**
1	CO_2	44	44	$\frac{44*100}{44}$=100
2	$Ca(HCO_3)_2$	16.4	162	$\frac{16.4*100}{162}$=10
3	$Mg(HCO_3)_2$	14.6	146	$\frac{14.6*100}{146}$=10
4	$CaCl_2$	111	111	$\frac{111*100}{111}$=100
5	$MgSO_4$	12	120	$\frac{12*100}{120}$=10
6	$CaSO_4$	13.6	136	$\frac{13.6*100}{136}$=10

Temporary hardness of water= CO2+$Ca(HCO_3)_2$+$Mg(HCO_3)_2$

=100+10+10=120 mg/l

Permanent hardness of water=$CaCl_2$+$MgSO_4$+$CaSO_4$

=100+10+10=120 mg/l

Conversion of hardness:-

1ppm = 1 mg/l = 0.07 °cl = 0.1 °fr

Temporary hardness = 120 mg/l, 120 ppm, 120*0.07 = 8.4 °cl

= 120*0.1 = 12° French

Permanent hardness = 120 mg/l, 120 ppm, 120*0.07 = 8.4°cl

= 120*0.1= 12°french.

(5) Calculate the lime and soda needed for softening 50,000 litres of water containing the following salts: $CaSO_4$ = 136 mg/l, $MgCl_2$=95mg/l, $Mg(HCO_3)_2$ = 73 mg/l, $Ca(HCO_3)_2$= 162 mg/l. given that molar mass of $Ca(HCO_3)_2$ is 162 and that of $MgCl_2$ is 95.

S No	**Constituent**	**Amount mg/l**	**Mol.wt**	**CaCO3 equivalent**
1	$CaSO_4$	136	136	$\frac{136*100}{136}$=100
2	$MgCl_2$	95	95	$\frac{95*100}{95}$=95
3	$Mg(HCO_3)_2$	73	146	$\frac{73*100}{146}$=50
4	$Ca(HCO_3)_2$	162	162	$\frac{162*100}{162}$=100

Lime required= ($Ca(HCO_3)_2$ + $2Mg(HCO_3)_2$+$MgCl_2$)

$=\frac{74}{100}(100+2*50+100+100)$

$=\frac{74}{100}*\frac{400}{1}$=296 mg/l

For 50,000 lit of water= 50,000*296=148kg of lime required

Soda required=$\frac{106}{100}$($CaSO_4$+$MgCl_2$)

$= \frac{106}{100}*\frac{200}{1}$=212mg/l

For 50,000 lit of water: 50,000*212=10.6kg of soda required.

3.4 Disinfection:- The process of destroying/killing the disease producing bacteria, micro organisms, etc, from the water and making it safe are, is called Disinfection.

Disinfectants:- The chemicals or substances which are added to eater for killing the bacteria. The disinfection of water can be carried out by following methods

(a) Boiling:- Water for 10 -15 min.boiled,all the disease producing bacteria are killed and water become safe for use.

(b) Bleaching powder:-

It is used to purity the drinking water from micro organisms. The purification process is achieved by dissolving 1 kg of bleaching powder in 1000 kilo litres of water. This dissolved water solution is left undisturbed for many hours when bleaching powder is mixed with water, the result of chemical reaction produces a powerful Germicide called Hypochlorous acid. The presence of chlorine in the bleaching powder produces disinfection action, kills germs and purifies the drinking water effectively.

$CaOCl_2+H_2O \rightarrow Ca(OH)_2+Cl_2$

$H_2O+Cl_2 \rightarrow HCl+HOCl$

HOCl+ germs → germs are killed → water purified.

(c) Chlorination:-

Chlorination is the process of purifying the drinking water by producing a powerful Germicide like hypochlorous acid. When this chlorine is mixed with water it produces Hypochlorous acid which kills the Germs present in water.

$$H_2O+Cl_2 \rightarrow HOCl+HCl$$

Chlorine is basic (means PH value is more than 7) disinfectant and is much effective over the germs. Hence chlorine is widely used all over the world as a powerful disinfectant. Chlorinator is an apparatus, which is used to purity the water by chlorination process.

(d) Ozonisation:-

Ozone is powerful disinfectant and is readily dissolved in water. Ozone being unstable decomposes by giving nascent oxygen which is capable of destroying the Bacteria.This nascent oxygen removes the colour and taste of water and oxidizes the organic matter present in water.

$O_3 \rightarrow O_2+ [O]$

Break- Point Chlorination:-

Break Point Chlorination is a controlled process. In this process suitable amount of chlorine is added to water. In order to kill all the bacteria present in water, to oxidize the entire organic matter and to react with free ammonia the chlorine required should be appropriate.

Break point determines whether chlorine is further added or not. By chlorination, organic matter and disease producing bacteria are completely eliminated which are responsible for bad taste and bad odour in water. When certain amount of chlorine is added to the water, it leads to the formation of chloro-organic compounds and chloramines.

The point at which free residual chlorine begins to appear is terms as “Break-Point”.

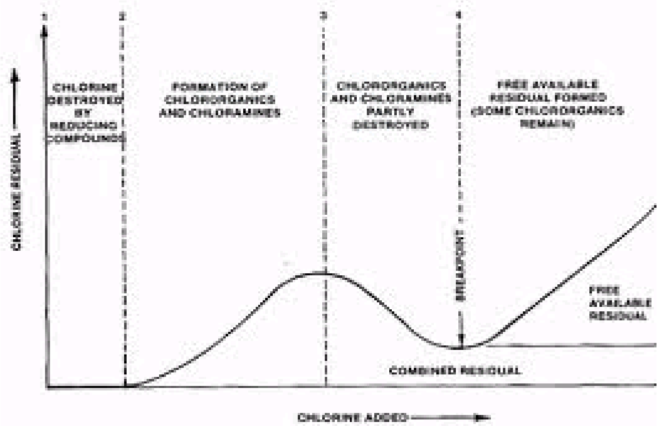


Fig3.9 Breakpoint chiorination

3.5 Desalination

The removal of dissolve solids (NaCl) from water is known as desalination process. It can be carried out by

(1) Reverse osmosis and (2) electro dialysis.

Reverse osmosis process:-

The membrane process used in the water purification system has been of much use now a days. Electro dialysis and reverse osmosis are part of the membrane process.

In osmosis, if a semi-permeable membrane separates two solutions, solvent from the lower concentration passes to the higher concentration to equalize the concentration of both. But in the reverse osmosis, pressure higher than osmotic pressure is applied from the higher concentration side so that the path of the solvent is reversed, i.e. from higher concentration to lower concentration.

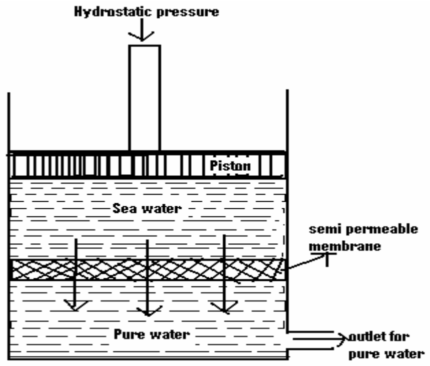


Fig 3.10 Reverse Osmosis

This method is applicable mainly for the desalination of sea water. Sea water and pure water are separated by a semi-permeable membrane made up of cellulose a cetate fitted on both sides of a perforated tube. Inventions are in progress to search for better membrane. Polymethylmethacrylate and polyamides have been proved to be better membranes.

The process is very easy. It is used to make pure water. It removes the ionic and non ionic substances in the water. It also can remove suspended colloidal particles. The life of a membrane is nearly 2 years and it should be replaced after this period. By this process, sea water is made to fit for drinking water obtained after being treated by this process is used in boilers.

UNIT-IV

MATERIAL CHEMISTRY

2.1 Polymers

Introduction:

Polymers form very important components in our daily life. The polymers are highly useful in domestic industrial & medical fields. The following are the reasons for the extensive use of polymers.

1) Most of the polymers are non-toxic & safe to use
2) They have low densities (light in weight) so transportation polymers will be easy.
3) They posses good mechanical strength.
4) These are resistant to corrosion and will not absorb moisture when exposed to the atmosphere.
5) These can function as good thermal & electrical insulators.
6) These can be moulded and fabricate easily.
7) They posses esthetic colors

But the limitations for the use of polymers are

1. Some polymers are combustible.
2. The properties of polymers are time dependent
3. Some of them canot with stand high temperature.

It is also interesting to note that many carbohydrates, Proteins & enzymes, DNA & RNA are natural polymers. Polymers can be defined as the large molecules (macro molecular) formed by the linkage of small molecules called monomers. (In Greek language poly means many & mer means units)

E.g.:- poly ethylene

$$nCH_2 = CH_2 \xrightarrow{\text{polymerization}} -(CH_2 - CH_2)_n-$$

Thus the repeated unit of polymer is called monomer. The number of repeating units in a polymer chain is called degree of polymerization. For e.g.:- if 100 molecules of ethylene polymerize to give the polymer chain, the degree of polymerization is 100.

Important terms:-

Homopolymer:-

Polymer made up of only one type of monomer. e.g.:- polyethylene

$(\text{-M-M-M-M-})_{n}$

Copolymer:-

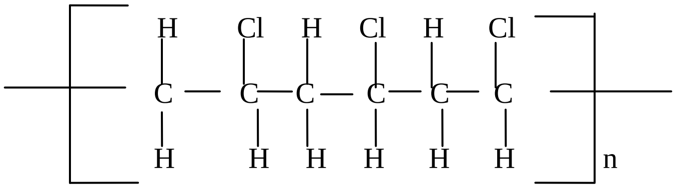
Polymer formed by the reaction between different monomers

eg: buna-s $-\!\!\left(M_{1}\text{-}\ M_{2} - M_{1}\ \text{-}\ M_{2}\right)_{n}\!\!-$

Tacticity:-

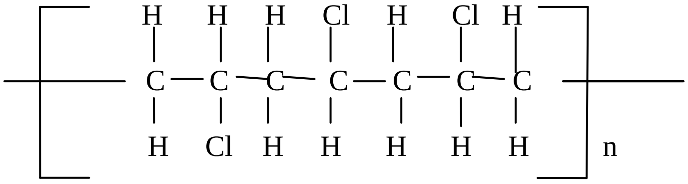
The arrangement of functional groups on carbon backbone of the polymer is called Tacticiy. It is manly divided into 3 types.

1) **Isotactic polymers:** Those polymers in which the functional groups are arranged on the same side are called Isotactic polymers. E.g.:- PVC



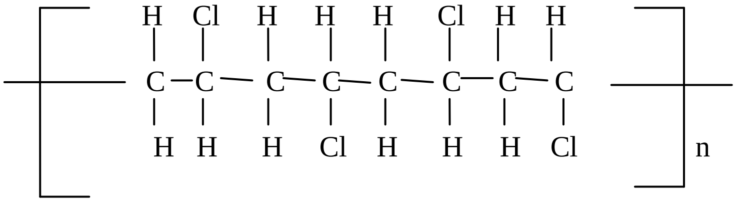
$$-\!\!\left[\begin{array}{cccccc} H & Cl & H & Cl & H & Cl \\ | & | & | & | & | & | \\ C - & C - & C - & C - & C - & C \\ | & | & | & | & | & | \\ H & H & H & H & H & H \end{array}\right]_{n}\!\!-$$

2) **Atactic polymers**: When there is no regular arrangement of functional groups on the back bone of the polymer chain these polymers are called atactic polymers.
E.g.: PVC (Poly Vinyl chloride)



$$-\!\!\left[\begin{array}{ccccccc} H & H & H & Cl & H & Cl & H \\ | & | & | & | & | & | & | \\ C - & C - & C - & C - & C - & C - & C \\ | & | & | & | & | & | & | \\ H & Cl & H & H & H & H & H \end{array}\right]_{n}\!\!-$$

3) **Syndiotactic Polymers:** The polymers with alternate arrangement of functional groups are called syndiotactic polymers for e.g.:- PVC



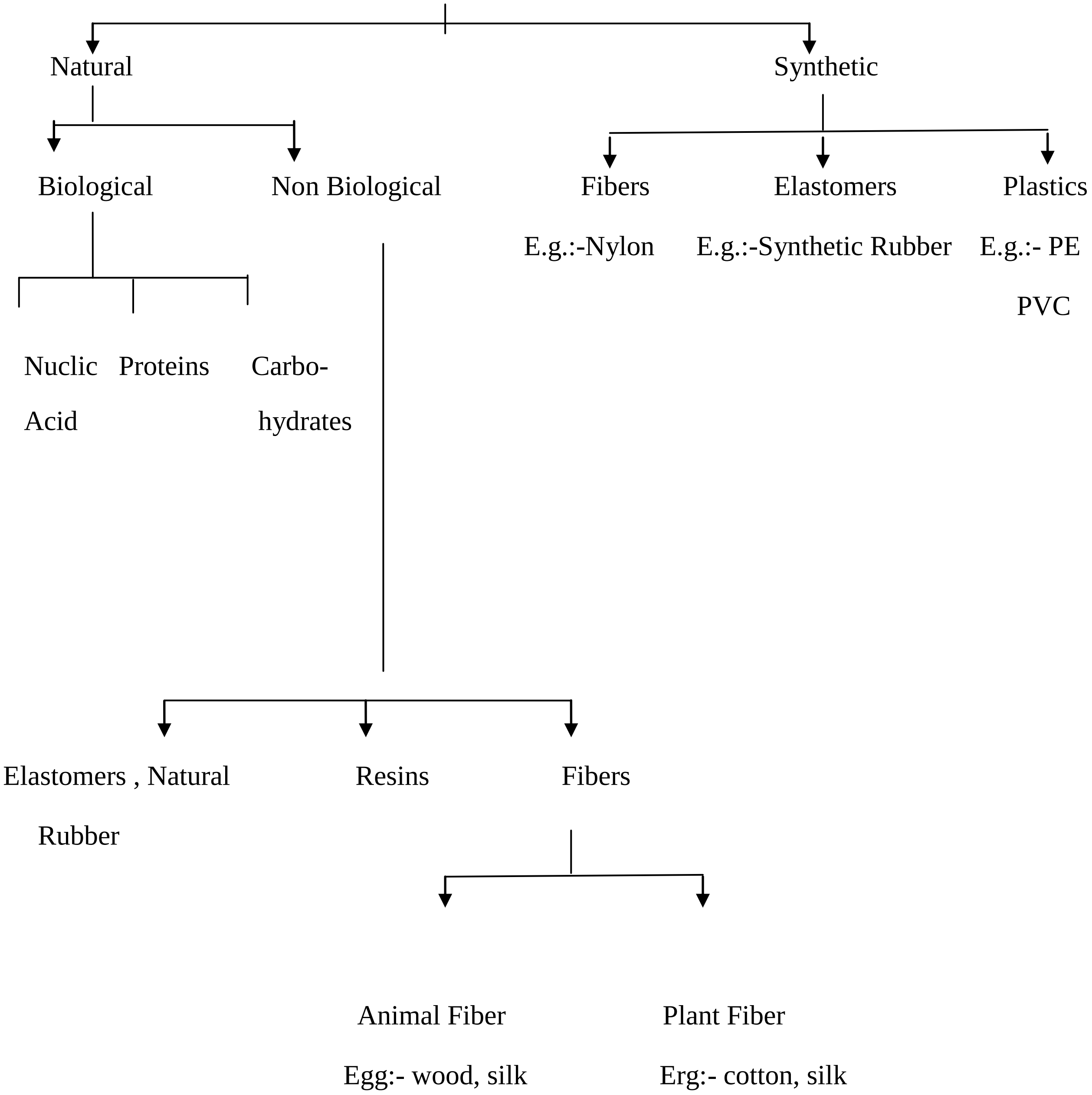
$$\left[-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}- \right]_n$$

Synthetic high polymers classification:-

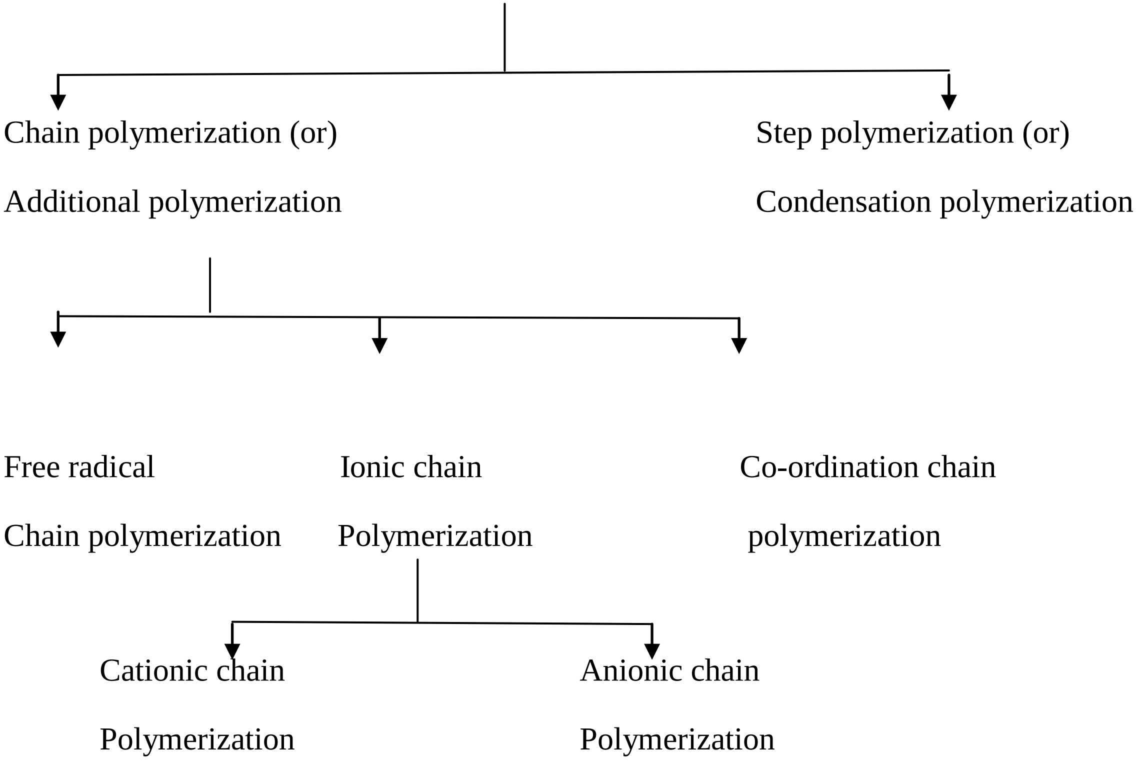
S. No	Type	Division		
1.	Structure/shape	Linear	Branched	Cross linked
2.	Tacticity	Isotactic	Syndiotactic	Atactic
3.	Physical state	Amorphous	Crystalline	
4.	Heat	Thermoplastic	Thermosetting	
5.	Conductance	Insulators	Conductors	
6.	Origin	Natural	Synthetic	
7.	Environment	Biodegradable	Durable	
8.	Monomer	Polar	Non-polar	
9.	Number of monomers	Homo-polymer	Co-polymer	
10.	Polymer chain	Homo – chain	Hetero – chain	
11.	Polymerization	Addition	Condensation	

Classification of polymers:-

Polymers are classified in to



Mechanism of polymerization (Types of polymerization)



2.1.1Types of Polymerisation:-

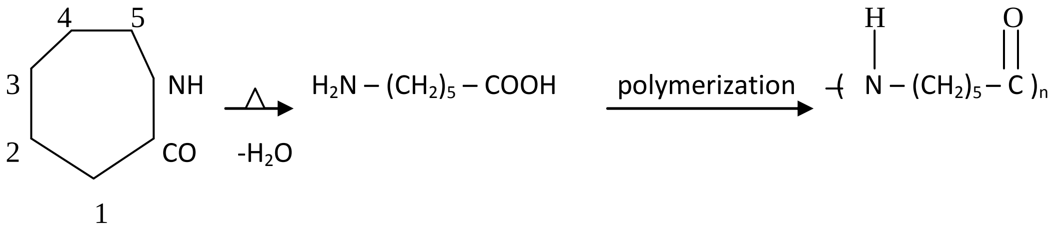
There are two types of polymerization. They are

(1) **Condensation polymerization:-**_Condensation polymers are those in which two like or unlike monomers join each other by the elimination of small molecules such as H_2O, HCl, etc.

When the same kind of monomers joins, the polymer is called homopolymer.

E.g.:- Nylon -6

It is prepared by the self condensation of w-amino caproic acid which is produced from caprolactum.



Caprolactum ω -amino caproic acid Nylon-6

Two or more different monomers join to form copolymer

Eg: - (1) Polyamide (Nylon 6,6)

n $H_2N - (CH_2)_6 - NH_2$ + n $HOOC - (CH_2)_4 - COOH$

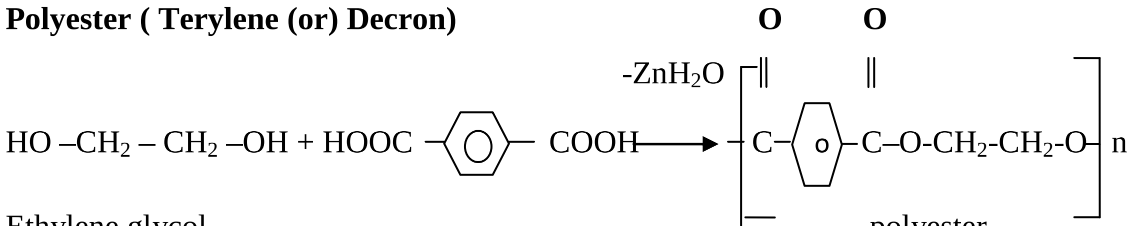
Hexa methylene di amine Adipic acid

↓

$-[NH-(CH_2)6- NH - CO - (CH_2)_4 - CO]_n-$ + ZnH_2O

Nylon 6, 6

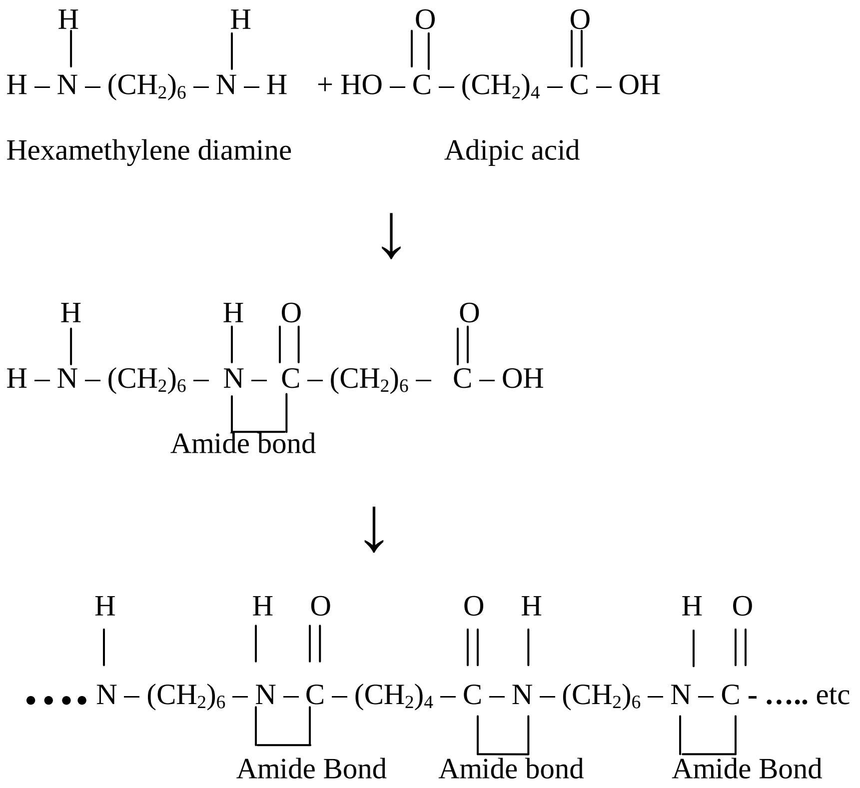
(2) Polyester (Terylene (or) Decron)



Ethylene glycol polyester

Mechanism:-

A general mechanism for condensation polymerization involves a simultaneous combination of any two monomers to give dimers. Which in turn combine to give tetramers and soon and finally grow into a polymer in a step wise manner.



$$\underset{\text{Hexamethylene diamine}}{H-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-H} + \underset{\text{Adipic acid}}{HO-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}-OH}$$

$$\downarrow$$

$$H-\overset{H}{\overset{|}{N}}-(CH_2)_6-\underbrace{\overset{H}{\overset{|}{N}}-\overset{O}{\overset{||}{C}}}_{\text{Amide bond}}-(CH_2)_6-\overset{O}{\overset{||}{C}}-OH$$

$$\downarrow$$

$$\bullet\bullet\bullet\bullet\ \overset{H}{\overset{|}{N}}-(CH_2)_6-\underbrace{\overset{H}{\overset{|}{N}}-\overset{O}{\overset{||}{C}}}_{\text{Amide Bond}}-(CH_2)_4-\underbrace{\overset{O}{\overset{||}{C}}-\overset{H}{\overset{|}{N}}}_{\text{Amide bond}}-(CH_2)_6-\underbrace{\overset{H}{\overset{|}{N}}-\overset{O}{\overset{||}{C}}}_{\text{Amide Bond}}-\ \ldots\ldots \text{ etc}$$

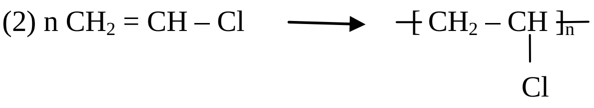
Poly (hexa methylene adipamide) or Nylon – 6, 6.

(2) Chain Polymerization:- (Addition Polymerization)

Addition polymers are formed by adding monomer units without any loss of atoms or groups.

E.g.:- (1) n CH_2 = CH2 $\longrightarrow$ $-[CH2 - CH_2]-_n$

Ethene polythene



$$(2)\ n\,CH_2 = CH - Cl \longrightarrow -[\,CH_2 - \underset{\underset{Cl}{|}}{CH}\,]_n-$$

Vinyl Chloride Polyvinyl chloride

Difference between condensation of additional polymerisation:-

Condensation polymerisation	Additional polymerisation
(1) It is also known as step growth polymerisation	(1) It is also known as chain growth polymerization
(2) It takes place in monomers having reactive functional groups	(2) It takes place only in monomers having multiple bonds.
(3) It takes place with elimination of simple molecule like H_2O,NH_3,HCl etc.,	(3) It takes place without elimination of simple molecule.
(4) Repeat units of monomers are different	(4) Repeat units & monomers are same.
(5) The polymer is formed in gradual steps	(5) Reaction is fast and polymer is formed at once.
(6) The molecular mass of polymer increases throughout the reaction	(6) There is very little change in the molecular mass throughout the reaction
(7) Product obtained may be thermosetting/thermoplastic	(7) Product obtained are thermoplastic
(8) E.g.:- Bakelite, polyester ,polyamides etc.,	(8) E.g:-Polyethylene, PVC, poly styrene.

2.1.3 Plastics:- Plastic is a substance that can be easily formed or moulded into a desired shape.

Plastic can be formed in a desired shape by the effect of mechanical force & heat.

In the manufacture of plastic raw materials like coal, petroleum, cellulose, salt, sulphur, limestone, air, water etc are used.

Plastics as engineering materials:-

Advantages of plastics over other engineering materials.

(1) Low fabrication cost, low thermal & electrical conductivities, high resistance to corrosion & solvents.

(2) The stress – strain relationship of plastics is similar to that of the metals.

(3) Plastics reduce noise & vibration in machines

(4) Plastics are bad conductors of heat are useful for making handles used for hot objects, most plastics are inflammable.

(5) Plastics are electrical insulators & find large scale use in the electrical industry.

(6) Plastics are resistance to chemicals.

(7) Plastics are clear & transparent so they can be given beautiful colours.

Types of Plastic: - (1) Thermoplastics

(2)Thermosetting plastics.

Difference between thermoplastic & thermosetting resins:-

Thermoplastic resins (or) Polymers	**Thermosetting resins**
(1) These are produced by additional polymerization	(1) These are produced by condensation polymerization.
(2) The resins are made of long chains attached by weak Vander Waal’s force of attraction	(2) The resins have three dimensional network structure connected bonds.
(3) On heating they soften and on cooling become stiff chemical nature won’t change	(3) On heating they become stiff & hard. No change on cooling. Chemical nature changes.

(4) They can be remoulded	(4) They cannot be remoulded because once set means they are permanently set
(5) Scrap (waste product) can be used	(5) Scrap cannot be used
(6) The resins are soft, weak and less brittle	(6) The resins are usually hard, strong tough & more brittle
(7) These are easily soluble in some organic substances E.g.:- PVC, polyethylene etc.,	(7) Resins are not soluble in organic solvents E.g.:- Nylon, Bakelite etc.,
(8) Contain long chain polymer with no cross linkage.	(8) They have 3D network structure.

2.1.4 Compounding of plastics:-

Compounding of plastics:- Compounding of plastics may be defined as the mixing of different materials like plasticizers, fillers of extenders, lubricants, pigments to the thermoplastic & thermosetting resins to increase their useful properties like strength, toughness, etc.

Resins have plasticity or binding property, but need other ingredients to be mixed with them for fabrication into useful shapes.

Ingredients used in compounding o plastics are

(1)Resins (2) Plasticizers (3) fillers (4) pigments (5) Stabilizers.

(1) Resins:- The product of polymerization is called resins and this forms the major portion of the body of plastics. It is the binder, which holds the different constituents together. Thermosetting resins are usually, supplied as linear – polymers of comparatively low molecular weight, because at this stage they are fusible and hence, mouldable. The conversion of this fusible form into cross-linked infusible form takes place, during moulding itself, in presence of catalysts etc.

(2) Plasticizers: - Plasticizers are substances added to enhance the plasticity of the material and to reduce the cracking on the surface.

Plasticizers are added to the plastics to increase the flexibility & toughness. Plasticizers also increase the flow property of the plastics.

e.g.:- Tricresyl phosphate, Dibutyle oxalate, castor oil

(3) **Fillers (or) extenders:-** Fillers are generally added to thermosetting plastics to increase elasticity and crack resistance.

Fillers improve thermal stability, strength, non combustibility, water resistance, electrical insulation properties & external appearance.

E.g.:- Mica, cotton, carbon black, graphite, $BaSO_4$ etc.

(4) **Dyes and pigments:-** These are added to impart the desired colour to the plastics and give decorative effect.

e.g.:- Lead chromate (yellow), ferro cyanide (blue)

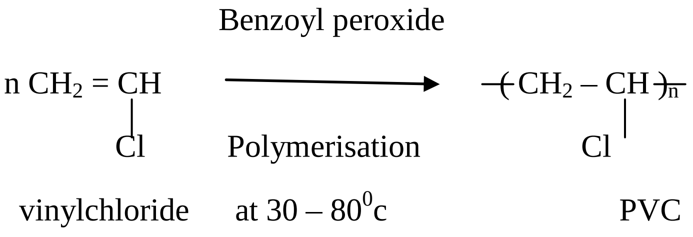
(5) **Stabilizers:-** Stabilizers are used to improve the thermal stability of plastics, e.g.:- PVC. At moulding temperature, PVC undergoes decomposition & decolourisation. So during their moulding, stabilizers are used. E.g.:- white lead, head chromate.

2.1.5 Chemistry of some important thermoplastic & thermoset Resins:-

(1) **Polyvinyl chloride (PVC):-** The monomer used for the manufacture of PVC is vinyl chloride.Vinyl chloride is prepared by treating acetylene with HCl at 60-80^{0}c and in presence of a metal oxide catalyst

$$\underset{\text{Acetylene}}{CH \equiv CH + HCl} \xrightarrow[60-80^0c]{\text{Metal oxide}} \underset{\text{Vinyl chloride}}{CH_2 = CHCl}$$

Poly vinyl chloride is produced by heating vinyl chloride in presence of benzyl peroxide or H_2O_2.



$$\underset{\text{vinylchloride}}{n\,CH_2 = \underset{|}{\overset{}{CH}}\!-\!Cl} \xrightarrow[\text{Polymerisation at } 30-80^0c]{\text{Benzoyl peroxide}} \underset{\text{PVC}}{-\!\left(CH_2 - \underset{Cl}{\underset{|}{CH}}\right)_n\!-}$$

There are two kinds of PVC plastics

(a) **Rigid PVC: -** (Unplasticized PVC):- It is chemically inert & non-inflammable powder having a high softening point of 148^0c.

This PVC is used for making safety helmets, refrigerator components, tyres, cycle & motor cycle mud guards.

(b) **Plasticizers PVC: -** It is produced by mixing plasticizers like disbutyl phthalate with PVC resin uniformly. It is used for making rain coats, table-cloths, handbags curtains & electrical insulators, radio, T.V components. All PVC – shoes for beach wear.

(2) **Teflon (poly tetra fluoro ethylene):-** Teflon is obtained by polymerization of water-emulsion tetrafluoroethylene under pressure in presence of benzoyl peroxide as catalyst

$$n\ F_2C = CF_2 \xrightarrow[\text{benzoyl peroxide / } H_2O]{\text{Polymerisation}} \underset{\text{Teflon}}{-\!\left(F_2c - CF_2 \right)_n\!-}$$

Properties:-

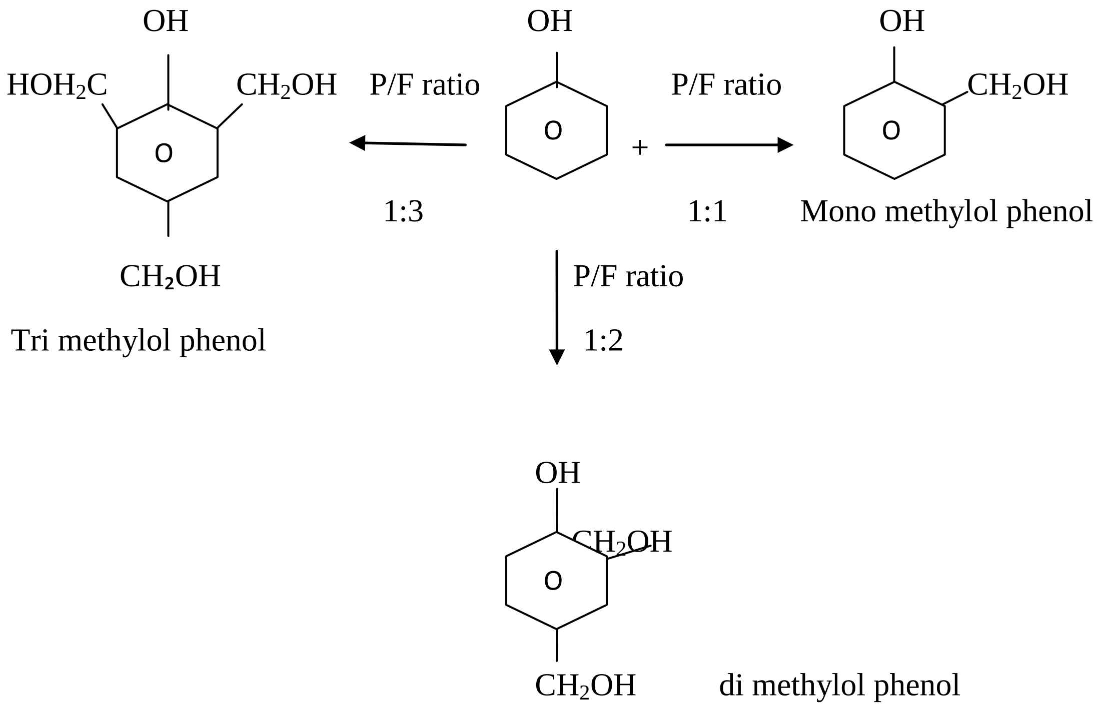
Teflon is also known as Fluon. Due to the presence of highly electronegative fluorine atoms. There are strong attractive force is responsible for high toughness & high chemical resistance towards all chemicals except hot alkali metal & hot fluorine.

Uses:-It is used in making seals & gaskets, which have to withstand high temperature. It is also used for insulation of electrical items and for making non-sticky surface coating, particularly for cooking utensils. Teflon used as insulating material for motors, transformers, cables, wires, fitting etc.

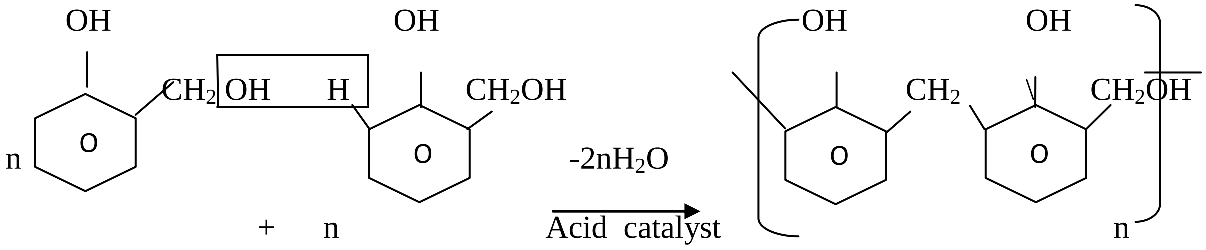
Some examples for Thermosetting Resins:-

Bakelite (or) phenol formaldehyde Resin:- The condensation reaction of phenol & formaldehyde in the presence of acid or alkali catalyst and at proper temperature produces the phenol formaldehyde resin or Bakelite resin.

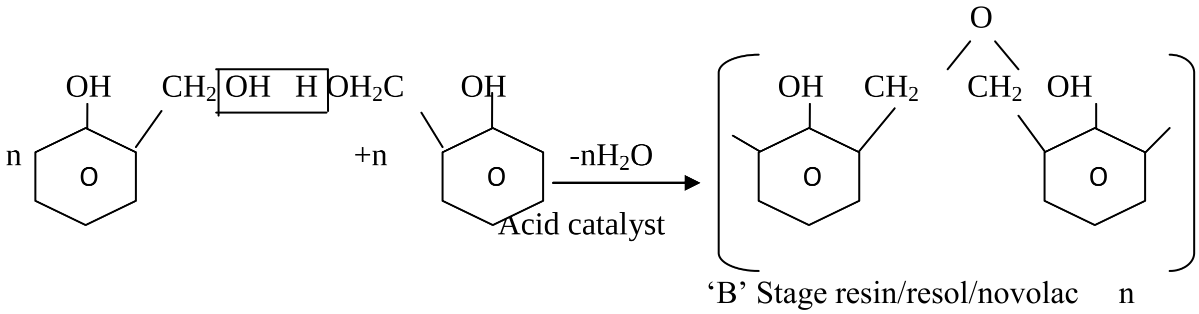
I Stage:- The initial reactions of phenol & formaldehyde in presence of acid or alkali produces mono, cli, tri methylol phenols depending on the phenol formaldehyde ratio (P/F ratio)



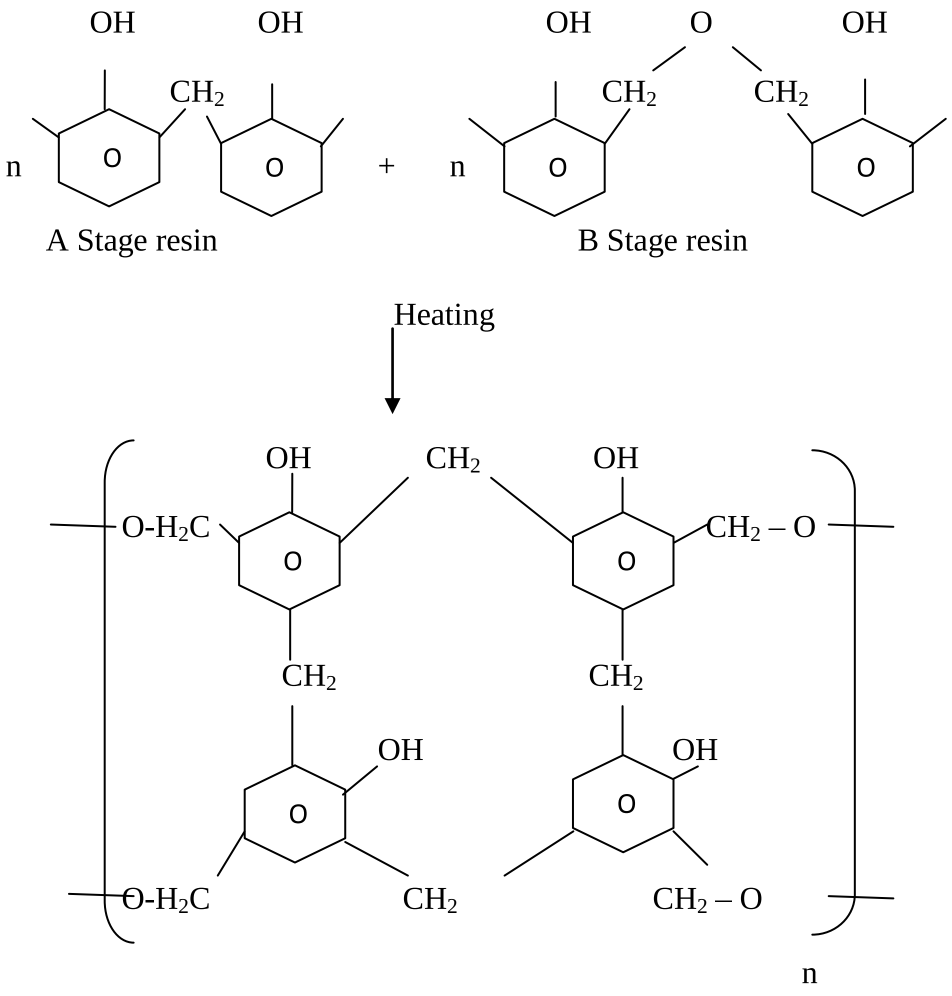
II Stage:- The mono, di, tri methyl phenols are heated to produce two types of straight chain resin by condensation of methylol group with hydrogen atom of benzene ring or another methylol group.



A Stage resin/resol/novolac



III stage:-This stage of preparation includes heating of 'A' stage resin and 'B' stage resin together, which develops cross linkings and Bakelite plastic resin is produced.



Bakelite

Properties:-

1. Phenol resins are hard, rigid and strong materials
2. They have excellent heat and moisture resistance.
3. They have good chemical resistance
4. They have good abrasion resistance
5. They have electrical insulation characteristics
6. They are usually dark coloured
7. Lower molecular weight grades have excellent bonding strength and adhesive properties.

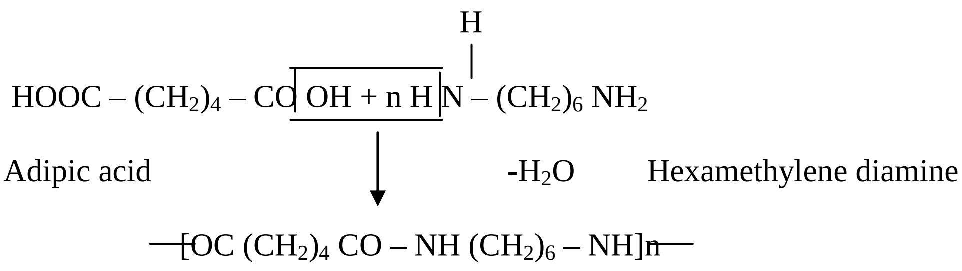
Applications:-

1. It is used for making electric insulator parts like switches, plugs, switch boards etc.
2. For making moulded articles like telephone parts cabinet of radio and television
3. As an anion exchanger in water purification by ion exchange method in boilers
4. As an adhesive (binder) for grinding wheels etc.,
5. In paints and varnishes
6. For making bearings used in propeller shafts, paper industry and rolling mills

Nylon (Poly amide resin):-

Nylon is a polyamide resin containing recurring amide groups (-NH CO-) in its structure produced by copolymerization of diamine with acid. Depending on the number of C atoms in diamine & dioxide there are different types of nylons like nylon 6, 6, nylon 6, 10 etc., where the first number indicates number of carbon atoms in diamine & the second number indicates the number of ‘c’ atoms in diacid.

Nylon 6, 6:- It is prepared by condensation polymerization of adipic acid and hexamethylene diamine in the absence of air.



$$HOOC-(CH_2)_4-CO\boxed{OH + n\,H}\overset{\overset{H}{|}}{N}-(CH_2)_6\,NH_2$$

Adipic acid $\quad\downarrow -H_2O\quad$ Hexamethylene diamine

$$-[OC\,(CH_2)_4\,CO-NH\,(CH_2)_6-NH]_n-$$

Nylon 6, 6

Properties:-

The structures of nylons are linear that permits side by side alignment. Moreover, the molecular chains are held together by hydrogen bonds. Thus, nylons have high crystalline which imparts high strength, high melting point, elasticity, toughness, abrasion resistance and retention of good mechanical properties up to 125^0C. They are polar polymers, they have good hydrocarbon resistance.

Applications:-

(1) The major application is in textile industry.

(2) Because of its high thermal & abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there.

(3) Flexible tubing's for conveying petrol etc are made from nylons

(4) Nylons are used as electrical insulators.

(5) Nylon 6 is used for making tire cords.

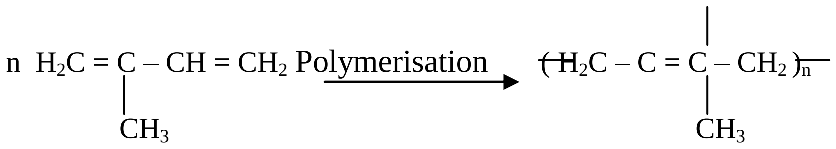
(6) Nylons are used in automobile industry and telecommunication industry for making radiator parts and coil formers respectively.

Rubbers

Rubbers also known as elastomers, they are high polymers, which have elastic properties in excess of 300%.

2.1.8 Natural Rubber:-

Natural Rubber is a high molecular weight hydrocarbon polymer represented by the formula $(C_5H_8)_x$. it is obtained from a milk emulsion called latex by tapping the bark of the tree. “Hevea brasiliensis”. It is a polymer of isoprene units.



$$n\ H_2C = \underset{\substack{|\\ CH_3}}{C} - CH = CH_2 \xrightarrow{\text{Polymerisation}} \left(H_2C - C = \underset{\substack{|\\ CH_3}}{\overset{|}{C}} - CH_2 \right)_n$$

Isoprene Natural Rubber

The polymer chain of natural rubber is made of 2000 to 3000 monomer units.

Processing of Natural Rubber:-

By cutting the bark of rubber tree the milky colloidal rubber milk is obtained. The main constituent of rubber latex is 25-45% of rubber and the remaining are water, protein & resinous materials. The rubber latex is coagulated by using 5% acetic acid and made in to sheets. The rubber sheets are cured under mild heat and then subjected to further processing.

Crepe rubber:-

To the rubber latex a small amount of sodium bisulphate is added to bleach the colour and feed in to roller which produce 1mm or more thickness sheets which are dried in air at about 40-50^{0}C. the dried thin sheet of rubber are known as “smoked crepe rubber”.

Mastication:-

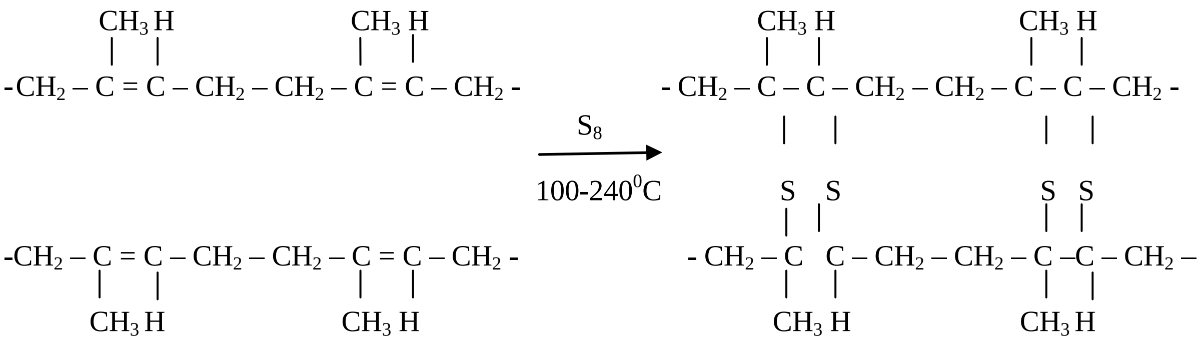
Rubber becomes soft and gummy mass when subjected to severe mechanical agitation. This process is known as mastication. Mastication followed by the addition of certain chemical (compounding) which is carried out on roll mills or internal mixers. After mastication is complete, the rubber mix is prepared for vulcanization.

Vulcanization:-

Vulcanization process discovered by Charles good year in 1839.It consists of heating the raw rubber at 100-140^{0}C with sulphur.The combine chemically at the double bonds of different rubber spring and provides cross-linking between the chains. This cross linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs.

The amount of sulphur added determines the extent of stiffness of vulcanized rubber.

For eg, ordinary rubber (say for battery case) may certain as much as 30% sulphur.



$$\begin{array}{c} -CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2- \\ -CH_2-\underset{CH_3}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_2- \end{array} \xrightarrow[100\text{-}240^0C]{S_8} \begin{array}{c} -CH_2-\overset{CH_3}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-CH_2- \\ \quad | \quad\; | \qquad\qquad\qquad | \quad\; | \\ \quad S \quad\; S \qquad\qquad\qquad S \quad\; S \\ \quad | \quad\; | \qquad\qquad\qquad | \quad\; | \\ -CH_2-\underset{CH_3}{\underset{|}{C}}\;\;\underset{H}{\underset{|}{C}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}-CH_2- \end{array}$$

Un vulcanized Rubber Vulcanized Rubber

Advantages of vulcanization:-

(i) The tensile strength increase

(ii) Vulcanized rubber has excellent resilience
It has better resistance to moisture, oxidation & abrasion

(iii) It is resistance to organic solvents like CCl_4, Benzene petrol etc.

(iv) It has only slight thickness

(v) It has low elasticity

Applications

(i) The major application of natural rubber is in the manufacture of tyres.

(ii) In heavy duty tyres, the major portion of the rubber used is natural rubber.

(iii) The tank linings in chemical plants where corrosive chemicals are stored are prepared from rubber.

(iv) To reduce machine vibrations, rubber is used for sandwiching between two metal surfaces.

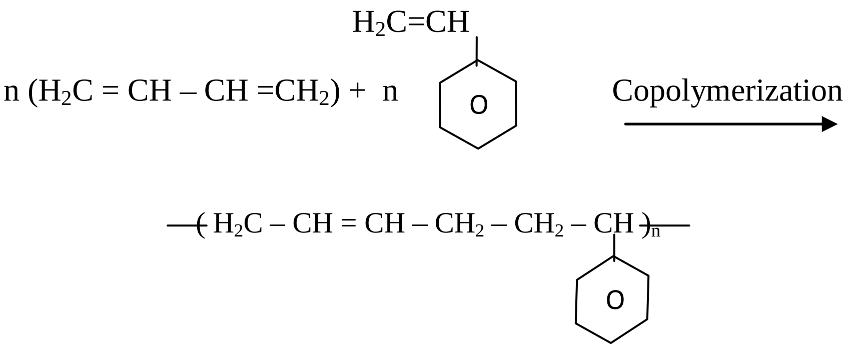
(v) Foam rubber is used for making cushions’, matrices, padding etc. toys and sports items are manufactured from natural rubber.

(vi) Gutta percha is used for making submarine cables, golf ball covers, tissue or adhesive etc.

2.1.9 Synthetic Rubber:-

(1) Styrene rubber or Buna-s-Rubber:-

It is a copolymer of butadiene (75%) and styrene (24%). In the early days of its synthesis sodium was used as the catalyst. Hence the name bu (butadiene), na (symbol Nafor sodium) and S (for styrene). It is also called GRS (government rubber styrene) or SBR (styrene butacliene Rubber). The Buna-S-Rubber is the first synthetic rubber developed during the second time of world war by US in order to overcome the scarcity of natural rubber. It is prepared by the copolymerization of butadiene & styrene.



BUNA -S

Properties:-

(1) It is a strong & tough polymer.
(2) The rubber can be vulcanized similar to natural rubber using either sulphur ot sulphur mono chloride.
(3) It is a good electrical insulator.
(4) It possess excellent abrasion resistance
(5) It is resistance to chemicals but swell in oils and attacked by even traces of ozone present in the atmosphere
(6) It possess high load bearing capacity and resilience

Applications:-

(1) Major application of styrene rubber is in manufacture of tyres.
(2) It is used in foot wear industry for making shoe soles and footwear components
(3) It is also used for making wires and cable, insulators.
(4) It is also used for the production of floor files, tank linings in chemical industries.

(1) Thiokol rubber (or) poly sulphide rubber (or) GR-P:-

Thiokol is prepared by the condensation polymerization of sodium poly sulphide (Na_2S_x) and ethylene dichloride ($Cl\ CH_2\ CH_2\ Cl$).

In these elastomers, sulphur forms a part of the polymer chain.

$Cl - CH_2 - CH_2 - Cl$ + $Na - S - S - Na$ + $Cl - CH_2 - CH_2 - Cl$

1, 2 dichloroethane sodium poly sulphide 1,2 dichloro ethane

$$\Big\downarrow \text{Polymerization}$$

$-\!\!(CH2 - CH_2 - S - S - CH_2 - CH_2\,)_n\!\!-$ + NaCl

Thikol (ethylene poly sulphide polymer) Sodium Chloride

Properties:-

(1) These rubbers possess strength and impermeability to gases.
(2) This rubber cannot be vulcanized because its structure is not similar to natural rubber and it cannot form hard rubber.
(3) It possesses extremely good resistance to mineral oils, fuels, oxygen, solvents ozone & sunlight.

Applications:-

(1) Fabrics coated with Thiokol are used for barrage balloons
(2) It is mainly used as solid propellant fuel for rocket
(3) It is also used for making gaskets, hoses, cable linings, tank linings etc.
(4) It is also used for printing rolls
(5) Containers for transporting solvents
(6) Diaphragms and seats in contact with solvents.

2.1.10 Fibers:-

Fibers are a class of materials that are continuous filaments or discrete elongated pieces.

They are crystalline, present in both plants & animals.

They are used for making textiles, ropes, utilities, strings etc.

These are of two types \

(1) Natural Fibers
(2) Synthetic fibers

1. **Natural fibers: -** Produced by plants, animals & geological materials.

(a) **Vegetable fibers:-** Cellulosic material
Eg:- cotton, jute etc. used for making textiles, ropes, mats, paper, bags etc. Dietary fiber important component of food, deficiency causes cancer.

(b) **Wood fiber:-** The strength of a plant is due to presence of wood fiber. Wood pulp is used in making paper and wood fibers like jute are used for making bags.

(c) **Animal fibers:-** They are largely made of protein pure silk, wool, hair are animal fibers. Spider silk is used for making special bullet proof jackets.

(d) **Mineral fibers:-** Asbestors is a typical example of mineral fiber. Mica & other minerals are used as fibers.

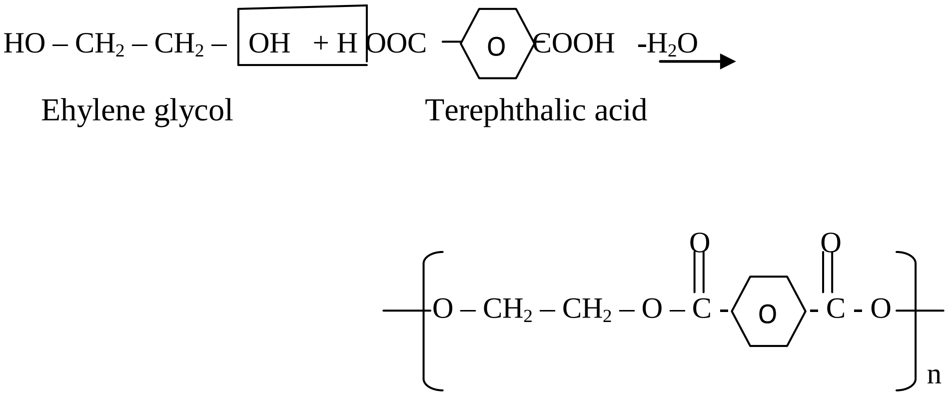
2. **Synthetic fibers:-** This type fibers can be produced in large quantities and are cheaper than some of the natural fibers like pure silk. Poly amide nylons, poly esters, PVC, phenol-formaldehyde resin, poly ethylene are often used for making textiles.

Dacron or Polyester (or) Terylene (or) Polyethylene Phthalate:-

These categories of polymers have ester linkages in the main chain. It takes 18% of market share of synthetic polymers.

Preparation:-

Terylene is a polyestar fiber made from ethylene glycol and terephthalic acid. Terephthalic acid required for the manufacture of terylene is produced by the catalytic atmospheric oxidation of P-xylene.



Terelene (polyester)

Properties:-

This occurs as a colourless rigid substance.

This is highly resistant to mineral & organic acids but is less resistant to alkalies. This is hydrophobic in nature. This has high melting point due to presence of aromatic ring.

Uses:-

It is mostly used for making synthetic fiber.

It can be blended with wool, cotton for better use and wrinkle resistance.

Other application of poly ethylene terephthalate film is in electrical insulation.

2.1.11 Fiber Reinforced Plastics (FRP):-

Combination of plastic material & solid fillers give hard plastic with mechanical strength & impact resistant is known as reinforced plastic.

The fiber polymers with solid/fillers to impart mechanical strength & hardness without losing plasticity are known as fiber reinforced plastics (FRP).

Fillers like carborandum, quartz & mica – impart hardness & strength.

Barium salt impervious to x-rays.

Asbestos provide heat & corrosion resistant for FRP.

Nature of polymers used for FRP:-

Composition of FRP – 50% of the mould able mixture contain fillers.

- Addition of carbon black to natural rubber increase the 40% strength of rubber & used in the manufacture of tyres.
- China clay improves the insulation property of PVC, Teflon.
- When $CaCO_3$ is added to PVC, then they are used for insulation of tubing, sear covers, wires & cables.
- Asbestos filled FRP → for electrical appliances'.
- FRP has good shock & thermal resistances, mould ability, dimensional stability & reparability.

Applications:-

Fiber reinforced plastics find extensive use in space crafts, aeroplanes, boat nulls, acid storage tanks, motor cars and building materials.

Melamine FRP is used for insulation & making baskets.

Advantages of FRP:-

(a) Low efficient of thermal expansion
(b) High dimensional stability
(c) Low cost of production
(d) Good tensile strength
(e) Low dielectric constant
(f) Non inflammable & non-corrode and chemical resistance

2.2.1 Cement:

Cement is a construction materials which posses adhesive and cohesive properties and used for binding the building blocks, bricks, stones etc.

Chemical Composition of Portland cement:

Cement contains silica, lime and alumina. The proportion this continence in cements should be maintained to get good quality cement.

$$\frac{\%SiO_2}{\%Al_2O_3} = 2.5 \text{ to } 4$$

$$\%CaO\text{-}\%SO_3 \Big/ \%SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3 = 1.9 \text{ to } 2$$

Setting and Hardening Of Portland Cement:

Cement is mixed with water to produce a plastic paste. The past is subjected to hydration and gelation and finally crystalline products are formed.

a) Initial setting of cement involves hydration of tricalcium aluminate.
$3CaO.Al_2O_3+6H_2O \rightarrow 3CaO.Al_2O_3.\ 6H_2O+880$ kj/kg

b) Second step of the reaction involves gelatin in which tobermonite gel is formed. It also produces calcium hydroxide and hydrated tricalcium aluminate.
$2(2CaO.SiO_2)+4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 +250$ kj/kg

c) Crystallisation of tricalcium aluminate takes place. even though initial reaction involve the formation of tetracalcium aluminate. Hardening of tricalcium aluminate takes place finally through crystallization.
$4CaO.Al_2O_3.Fe_2O_3+7H_2O \rightarrow Ca_3Al_2O_6.6H_2O+CaO.Fe_2O_3.H_2O+420$kj/kg

2.2.2 Lubricants:

Definition: Any substance introduced between the two moving and sliding surfaces with a view to reduce frictional resistance to know as lubricant.

Lubrication Mechanisms:

Three mechanisms have been proposed to explain the action of lubricants they are

a) Thin film (or) Boundary Lubrication:

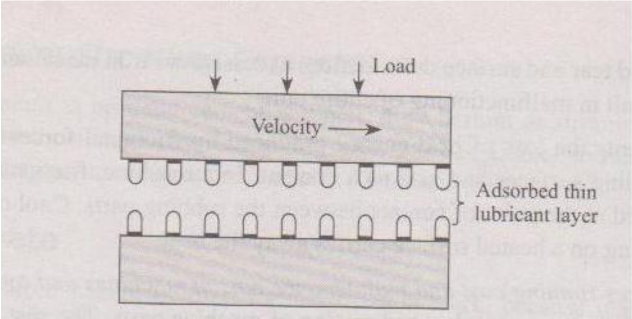


Fig 2.7Boundary film lumbrication

In this type of lubrication a thin film of lubricant is absorbed on the surface and held by vandarwaals forces. When the lubricant is not viscous enough to generate a film of sufficient thickness for the separation of surfaces under heavy loads, friction is reduced by thin film lubrication. Thin film lubrication is applied when the speed is very low, the loading heavy, the oil has low viscosity.

Some peaks may have higher thickness than the film of lubricant which results in wearing and tearing. Hence the chemical or physical forces on some metal surfaces would avoid the direct contact of metals and absorb a thin layer of lubricating oil. The co-efficient of friction is reduced due to oiling.

b) Fluid Film (or) Hydrodynamic Lubrication:

This type of lubrication is also known as thick film lubrication. It is carried out with the help of liquid lubricants. In fluid film lubrication the two sliding surfaces are separated by a thick film of about 1000A° which is applied to prevent direct surface to surface contact. Wearing and tearing of metals is minimized.

In a ball bearing the irregularities of the shaft and bearing surfaces are covered by a thick film of lubricants and don’t not allow. The content of metallic surfaces with each other as shown in the figure. The resistance to moment is only due to resistance of the lubricant. Fluid film lubrication is useful in delicate and light machines like watches, clocks, guns, scientific equipments.

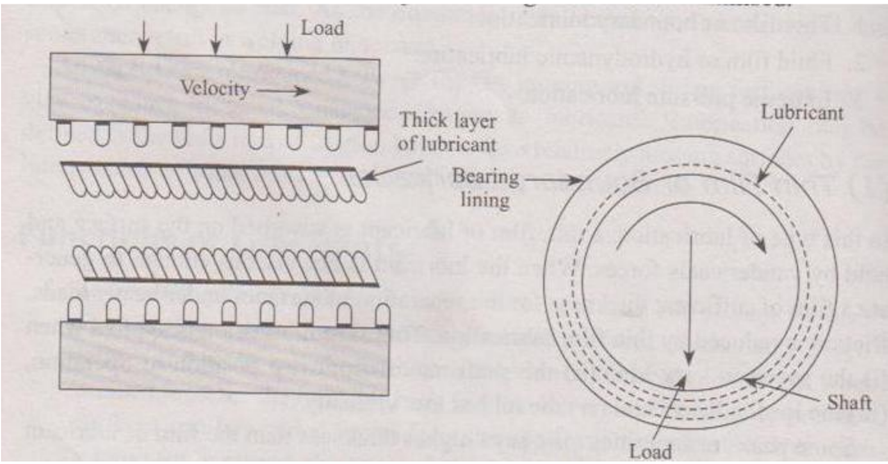


Fig 2.8 Fluid film lubrication

Extreme Pressure Lubrication:

It involves chemical action on the part of lubricant. Under heavy load and high speed conditions, high local temperature is generated. The liquid film may not stick, it may decompose and vaporizes. Hence special additives called extreme pressure additive are blended with lubricating oil to form more durable film to with stand high temperature and pressure. Chlorinated esters, sulpharised oils and tricrysyl phosphates are used as extreme pressure additives. These additives combined with the metallic surfaces with high temperature to form metallic chlorides.

Properties of Lubricants:

Cloud and Pour Points:

Cloud Point: The temperature at which the impurities being to separate from the solution and lubricating oil becomes cloudy or hazy in appearance is called cloud point.

Pour Point: The temperature at which the oil ceases to flow and pour is called pour point.

Flash point: The flash point of a volatile material is the lowest temperature at which vapors of the material will ignite, given an ignition source.

Fire point: The fire point of a fuel is the lowest temperature at which the vapour of that fuel will continue to burn for at least 5 seconds after ignition by an open flame.

Viscosity:

Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flow ability of lubricating oil. The lower viscosity greater the flow ability. If temperature increases viscosity of the lubricating oil decreases and pressure increases viscosity of lubricating oil increases.

Viscosity Index:

The rate at which the viscosity of oil changes with temperature is measured by an empirical number known as the viscosity index. A relatively small change in viscosity with temperature is indicated by high viscosity index. Where as a low viscosity index shows a relatively large change in viscosity with temperature.

2.2.3 Refractories:

Refractories are the inorganic materials which can with stand very high temperature without softening or suffering deformation. Therefore they are used for the construction of kilns, ovens, crucibles, furnaces etc. The main function of refractories varies depending on the purpose to which they are subjected like confining heat with in the furnace, transmitting or storing heat in refrigerators.

Characteristics of Refractories:

1). High temperature resistance under working conditions.
2). Good abrasions resistance by dusty gases and melt on metals.
3). Low ability to contain heat.
4). High mechanical strength.
5). Thermal strength to with stand thermal shock due to rapid and repeated temperature fluctuations.

Classifications of Refractories:

Refractories are broadly classified into three categories on the basis of their chemical nature

1. **Acidic refractories:** They are made from acidic materials such as aluminium & silica they are resistant to acid slags but attacked by basic materials.
   E.g.:- silica, alumina and fireclay refractories.
2. **Basic Refractories:-** Basic refractories are those which consist of basic materials, but attacked by acidic materials. They find extensive use in steel-making open-hearth furnaces.
3. **Neutral Refractories:-** They are not completely neutral in chemical sense. They consist of weakly basic/acidic materials like carbon, zirconia (ZrO_2), chromites ($FeOCrO_2$), graphite, and silicon carbide.

Unit - V

Fuels & Combustion

Introduction:-

Fuels are the main energy sources for industry and domestic purposes.

"A fuel is a substance containing carbon as the major substituent which provides energy on combustion for industry and domestic purposes".

The combustion is the process of oxidation that provides heat energy. Every combustion is an oxidation but every oxidation is not combustion.

Ex: - Combustion of wood, Petrol and kerosene gives heat energy.

4.2 Classification of Fuels:-

Classification of fuels is based on two factors.

1. Occurrence (and preparation)
2. The state of aggregation

On the basis of occurrence, the fuels are further divided into two types.

A. natural or primary fuels: - These are found in nature such as Wood, peat, coal, petroleum, natural gas etc.

B. artificial or secondary fuels: - These are prepared artificially from the primary fuels.

Ex: - charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast Furnace gas etc.

4.3 Characteristics of a good fuel:-

1. The fuel should be easily available.
2. It should be dry and should have less moisture content. Dry fuel increases its calorific value.
3. It should be cheap, easily transportable and has high calorific value.
4. It must have moderate ignition temperature and should leave less ash after combustion.
5. The combustion speed of a good fuel should be moderate.
6. It should not burn spontaneously to avoid fire hazards.
7. Its handling should be easy and should not give poisonous gases after combustion.
8. The combustion of a good fuel should not be explosive.

The second classification is based upon their state of aggregation like:

a) Solid fuels;

b) Liquid fuels and

c) Gaseous fuels.

Type of fuel	Natural or primary fuel	Artificial or secondary fuel
Solid	Wood, peat, lignite, dung, bituminous coal and anthracite coal	Charcoal, coke etc.
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum

Gaseous	Natural gas	Coal gas, oil gas, bio gas, water gas etc.

Characteristic properties of solid, liquid and gaseous fuels:

S.NO	Characteristic property of a fuel	Solid fuels	Liquid fuels	Gaseous fuels
1	example	Coal	Crude oil	Coal gas
2	Cost	Cheap	Costlier than solid fuels	Costly
3	Storage	Easy to store	Closed containers should be used for storing	Storage space required is huge and should be leak proof.
4	Risk towards fire hazards	Less	More	Very high, since these fuels are highly inflammable
5	Combustion rate	It is a slow process	Fast process	Very rapid and efficient
6	Combustion control	Cannot be controlled	Cannot be controlled or stopped when necessary	Controlled by Regulating the supply of air

7	Handling cost	High since labour is required in their storage & transport.	Low, since the fuel can be transported through pipes	Low, similar to liquid fuels, these can be transported through pipes
8	Ash	Ash is produced and its disposal also possess problems	No problem of ash	No problem of ash
9	Smoke	Produce smoke invariably	Clean, but liquids associated with high carbon and aromatic fuels produce smoke	Smoke is not produced
10	Calorific value	Least	High	Highest
11	Heat efficiency	Least	High	Highest efficiency

4.4 Solid Fuels:-

The main solid fuels are wood, peat, lignite, coal and charcoal.

Coal: - Coal is a fossil fuel which occurs in layers in the earths crust. It is formed by the partial decay of plant materials accumulated millions of years of ago and further altered by action of heat and pressure. The process of conversion of wood into coal can be represented as

Wood → Peat → Lignite→ Bituminous Coal → Anthracite

1) Peat:- Peat is brown-fibrous jelly like mass.
2) Lignite:- these are soft, brown coloured, lowest rank coals

3) Bituminous coals:- These are pitch black to dark grey coal
4) Anthracite:- It is a class of highest rank coal

Fuel	Percentage of carbon	Calorific value (k.cal/kg)	Applications
Wood	50	4000-4500	Domestic fuel
Peat	50-60	4125-5400	Used if deficiency of high rank coal is prevailing
Lignite	60-70	6500-7100	For steam generation in thermal power plants
Bituminous	80-90	8000-8500	In making coal gas and Metallurgical coke
Anthracite	90-98	8650-8700	In households and for steam raising

4.5 Analysis of Coal:-

The analysis of coal is helpful in its ranking.

The assessment of the quality of coal is carried out by these two types of analyses.

A) Proximate analysis
B) Ultimate analysis

A. Proximate analysis: In this analysis, the percentage of carbon is indirectly determined. It is a quantitative analysis of the following parameters.

1. Moisture content
2. Volatile matter
3. Ash
4. Fixed carbon

1. **Moisture Content:** About 1 gram of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105 to 110 ^{0}C for one hour. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in desiccators and weighed. Loss in weight is reported as moisture.

$$\text{Percentage of Moisture} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \text{ X } 100$$

2. **Volatile Matter:** The dried sample taken in a crucible in and then covered with a lid and placed in an electric furnace or muffle furnace, maintained at 925 + 20C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside desiccators and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \text{ X } 100$$

3. **Ash:** The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700 + 50 C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

   Thus,

$$\text{Percentage of ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \text{ X } 100$$

4. Fixed carbon:

Percentage of fixed carbon = 100 - % of (Moisture + Volatile matter + ash)

Significance of proximate analysis: Proximate analysis provides following valuable information's in assessing the quality of coal.

1. Moisture: Moisture is coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover over, it quenches the fire in the furnace, hence, lesser, the moisture content, better the quality of coal as a fuel. However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of “fly-ash”.

2. Volatile matter: a high volatile matter content means that a high proportion of fuel will distil over as gas or vapour, a large proportion of which escapes un-burnt, So, higher volatile content in coal s undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

3. Ash: Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes trouble during firing by forming clinkers, which block the interspaces of the grate, on which coal is being burnt. This in-turn causes obstruction to air supply; thereby the burning of coal becomes irregular. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

4. Fixed carbon: Higher the percentage of fixed carbon, greater is it’s calorific and betters the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of fixed carbon is desirable. The percentage of fixed carbon helps in designing the furnace and the shape of the fire-box, because it is the fixed carbon that burns in the solid state.

B. Ultimate analysis: This is the elemental analysis and often called as qualitative analysis of coal. This analysis involves the determination of carbon and hydrogen, nitrogen, suphur and oxygen.

1. Carbon and Hydrogen: About 1 to 2 gram of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weights. The increase in weights of these are then determined.

$$C + O_2 \rightarrow CO_2$$

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

$$CaCl_2 + 7 H_2O \rightarrow CaCl_2.7H_2O$$

$$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube X 12 X 100}}{\text{Weight of Coal sample taken X 44}}$$

$$\text{Percentage of H} = \frac{\text{Increase in weight of } CaCl_2 \text{ tube X 2 X 100}}{\text{Weight of Coal sample taken X 18}}$$

2. Nitrogen: About 1 gram of accurately weighed powdered coal is heated with concentrated H_2SO_4 along with K_2SO_4 (catalyst) in a long-necked Kjeldahl's flask. After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

$$\text{Percentage of N} = \frac{\text{Volume acid X Normality of acid X 1.4}}{\text{Weight of coal taken}}$$

3. Sulphur: Sulphur is determined from the washings obtained from the known mass of coal, used in bomb calorimeter for determination of a calorific value. During this determination, S is converted in to Sulphate. The washings are treated with Barium chloride solution, when Barium-sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\text{Percentage of Sulphur} = \frac{\text{Weight of } BaSO_4 \text{ obtained X 32 X 100}}{\text{Weight of coal sample taken in bomb X 233}}$$

4. Ash: The residual coal taken in the crucible and then heated without lid in a muffle furnace at 700 + 50^0c for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

Thus,

$$\text{Percentage of ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \text{ X 100}$$

5. Oxygen: It is determined indirectly by deducting the combined percentage of carbon, hydrogen, nitrogen, sulphur and ash from 100.

Percentage of Oxygen = 100 – percentage of (C + H + S + N + Ash)

Significance of ultimate analysis:

Carbon and Hydrogen: Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile mater and hence, it affects the use to which the coal is put.

Nitrogen: Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus, a good quality coal should have very little Nitrogen content.

Sulphur: Sulphur, although contributes to the heating value of coal, yet on combustion produces acids like SO_2, SO_3, which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 0.3% and derived from ores like iron, pyrites, gypsum, etc., mines along with the coal. Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry. Since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur pollute the atmosphere and leads to corrosion.

Ash: Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

Oxygen: Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is a combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

4.6 Liquid Fuels

Liquid fuels are the important commercial and domestic fuels used these days. Most of these fuels are obtained from the naturally occurring petroleum or crude oil.

Primary Petroleum:-

Petroleum or crude oil is a dark greenish brown, viscous oil found deep in the earth crust. Crude oil is a source of many liquid fuels that are in current use. The composition of crude petroleum approximately is C = 80-85%, H= 10-14%

S= 0.1-3.5% and N=0.1-0.5%.

Refining of Petroleum:-

Crude oil obtained from the mine is not fit to be marked. It contains a lot of soluble and insoluble impurities which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining. Refining can be defined as the process by which petroleum is made free of impurities, division of petroleum into different fractions having different boiling points and their further treatment to impart specific properties.

Refining of petroleum is done in different stages:

a. Removal of solid impurities: The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernant liquid is then centrifuged where in the solids get removed.

b. Removal of water (Cottrell's process): The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.

c. Removal of harmful impurities: In order to remove sulphur compounds in the crude oil. It is treated with copper oxide. The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration. Substances like NaCl and $MgCl_2$ it present will corrode the refining equipment and result in scale formation. These can be removed by techniques like electrical desalting and dehydration.

d. Fractional distillation: Heating of crude oil around 400^0C in an iron retort, produces hot vapor which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapors go up they get cooled gradually and fractional condensation takes place. Higher boiling fraction condenses first later the lower boiling fractions.

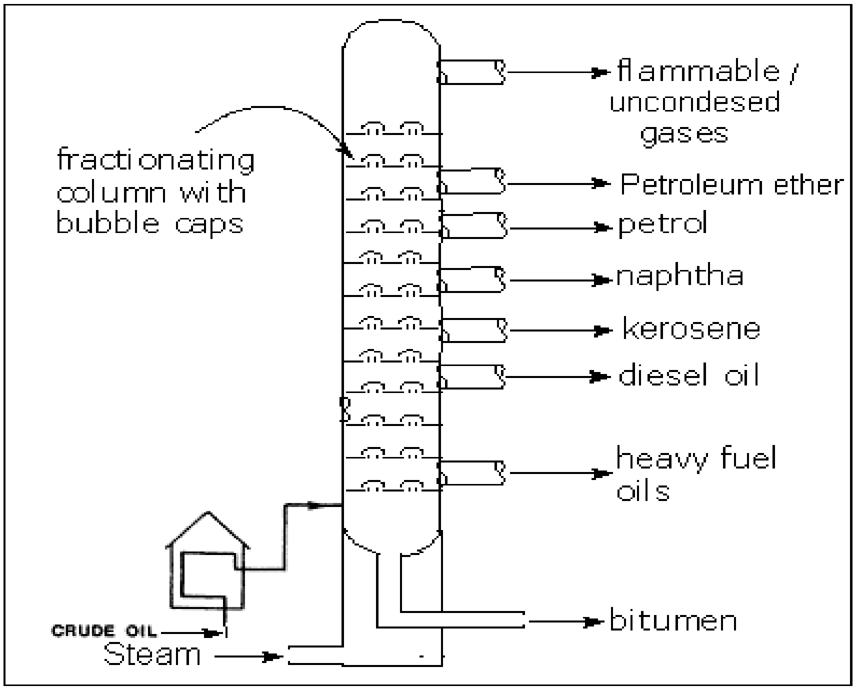


Fig. 4.1 Refining of Petroleum

4.7 Cracking:-

Decomposition of larger hydrocarbon molecules to smaller molecules is cracking.

Cracking

Ex. $C_{10}H_{12} \rightarrow C_5H_{12} + C_5H_{10}$

(Decane) (Pentane) (Pentene)

Cracking is mainly two types:

A. Thermal Cracking
B. Catalytic Cracking

A. **Thermal cracking:** If the cracking takes place at high temperature then it is thermal cracking. It may take place by two ways. They are i) Liquid-phase Thermal cracking

ii) Vapour-phase Thermal cracking

The liquid phase cracking takes place at 475^0C to 530^0C at a pressure $100kg/cm^2$. While the vapor phase cracking occurs at 600 to 650^0C at a low pressure of 10 to 20 kg/cm^2

B. **Catalytic cracking**: If the cracking takes place due to the presence of catalyst than it is named as catalytic cracking. Catalytic cracking may be fixed bed type or moving bed type.

i) Fixed bed catalytic cracking: The oil vapors are heated in a pre-heater to cracking temperatures (420 – 450 ^{0}C) and then forced through a catalytic chamber maintained at 425 – 450 ^{0}C and 1.5 kg/cm^2 pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2 – 4% carbon is formed. The latter adsorbed on the catalyst bed. The vapour produced is then passed through a fractionating column, where heavy oil fractions condense. The vapors are then led through a cooler, where some of the gases are condensed along – with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a ‘stabilizer’, where the dissolved gases are removed and pure gasoline is obtained.

The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activated interval, the vapors are diverted through another catalyst chamber.

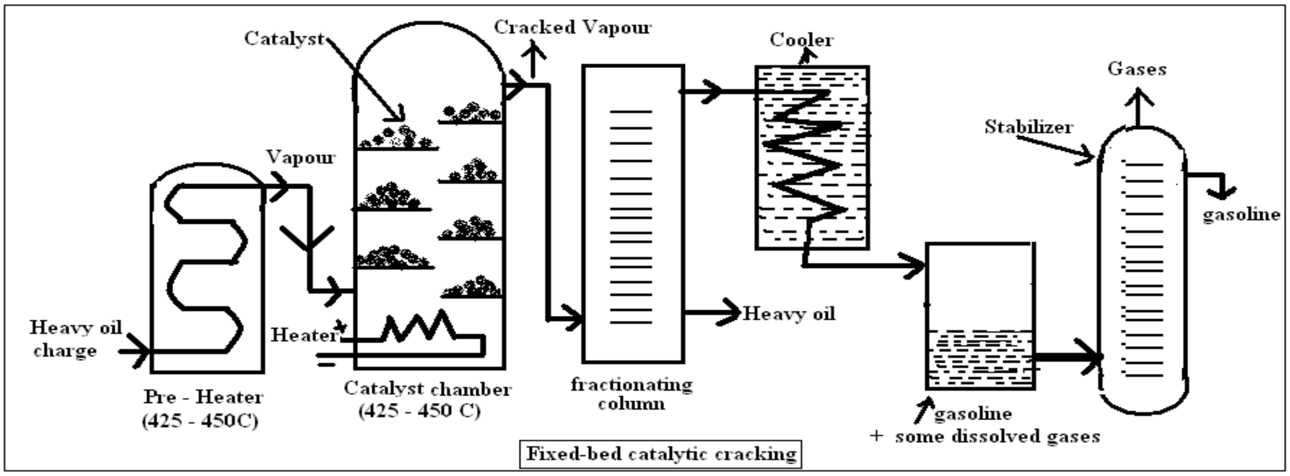


Fig. 4.2 Fixed-Bed Catalytic Cracking

4.8 Knocking

Premature and instantaneous ignition of petrol – air (fuel-air) mixture in a petrol engine, leading to production of an explosive violence is known as knocking.

In an internal combustion engine, a mixture of gasoline vapor and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder.

The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression ratio. The efficiency of an internal combustion engine increases with the compression ratio, which is dependent on the nature of the constituents present in the gasoline used. In certain circumstances (due to the presence of some constituents in the gasoline used), the rate of oxidation becomes so great that the last portion of the fuel air mixture gets ignited instantaneously, producing an explosive violence, known as knocking. The knocking results in loss of efficiency.

Some of the effects of knocking or detonation are:

a. Carbon deposits on liners and combustion chamber
b. Mechanical damage
c. increase in heat transfer
d. Noise and roughness
e. decrease in power output and efficiency
f. preignition

The knocking can be controlled or even stopped by the following methods:

i. increasing engine r.p.m
ii. reducing pressure in the inlet manifold by throttling
iii. Retarding spark
iv. Making the ratio too lean or rich, preferably latter.
v. Water injection increases the delay period as well as reduces the flame temperature.
vi. Use of high octane fuel can eliminates detonation. High octane fuels are obtained by adding additives known as dopes like tetraethyl lead, benzol, xylene to petrol

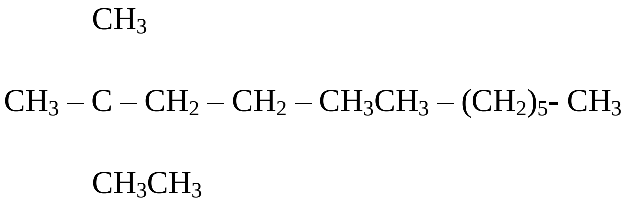
Chemical structure and knocking: The tendency of fuel constituents to knock in the following order.

Straight-chain paraffins > Branched-chain paraffins (i.e., iso paraffins) > Olefins > Cyclo paraffins (i.e., naphthalenes) > aromatics.

Thus, olefins of the same carbon chain length possess better anti knock properties than the corresponding paraffin and so on.

Octane number:-

The knocking characteristic of a fuel can be easily expressed by octane number. The anti-knocking value of n-heptane is taken as 0 (zero) because n-heptane knocks very badly. Whereas the anti-knock value of iso-octane is approximately taken as 100 because iso-octane knocks very little. Actually the octane number is the percentage of iso-octane in a mixture of n-heptane in order to matches the knocking characteristics of the fuel. In this way, an “80-octane” fuel is one which has the same combustion characteristics as an 80:20 mixture in iso-octane and n-heptanes. Gasoline with octane rating as high as 135 are used for aviation purposes. The octane number of poor fuels can be raised by the addition of extremely poisonous materials as tetra ethylene lead $(C_2H_4)_4Pb$ and diethyl-telluride $(C_2H_4)_2Te$



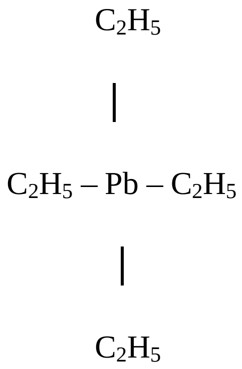
$$CH_3 - \overset{CH_3}{\underset{CH_3CH_3}{C}} - CH_2 - CH_2 - CH_3CH_3 - (CH_2)_5\text{-}\ CH_3$$

2, 2, 4- trimethyl pentane n-heptane

(Isooctane) octane number 100 (good fuel)

Octane number zero (bad fuel)

Lead petrol: The variety of petrol in which tetra ethyl lead is added, it is leaded petrol.



$$C_2H_5 - \overset{\overset{C_2H_5}{|}}{\underset{\underset{C_2H_5}{|}}{Pb}} - C_2H_5$$

Tetra ethyl lead (TEL)

Octane rating: It has been found that n-heptane, Knocks very badly and hence, its anti-knock value has arbitrarily been given zero. On the other hand, isooctane (2: 2: 4 – trimethyl pentane). It gives very little knocking, so its anti-knock value has been given as ‘100’. Thus, octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of isooctane in a mixture of isooctane and n-heptane, which matches the fuel under test in knocking characteristics. In this way, an “80-octane” fuel is one which has the same combustion characteristics as an 80:20 mixture of isooctane and n-heptane.

Advantages: Usually petrol with low octane number is not good quality petrol. It often knocks (i.e., produces huge noise due to improper combustion). As a result of knocking, petrol is wasted; the energy produced cannot be used in a proper way.

When tetra ethyl lead is added, it prevents knocking, there by saves money and energy. Usually 1 to 1.5 ml of TEL is added per 1lit of petrol.

The mechanism of action is as follows:

First TEL will be transformed into finely divided particles of PbO which looks like a cloud. This takes place in the cylinder. Then the PbO particles react with hydrocarbon peroxide molecules formed, thus slowing down the oxidation process and prevent early detonation. Thus either knocking may be stopped or greatly reduced.

Disadvantages: Deposits of PbO are harmful to engine. So PbO must be eliminated from the engine. For this purpose, little amount of ethylene dibromide is added to petrol. It converts the harmful PbO to volatile $PbBr_2$ and eliminated through exhaust. Presence of any sulphur compounds reduces the efficiency of TEL.

Cetane Number:-

Cetane number is defined as the percentage of hexadecane (n-cetane) present in a mixture of hexadecane and 2-methyl naphthalene, which has the same ignition characteristic of diesel fuel in test. Generally diesel fuels with cetane numbers of 70-80 are used.

The knocking tendency of diesel fuel is expressed in terms of cetane number. Diesel engines works on the principle of compression ignition. Cetane (n-cetane) or hexadecane [CH3 – $(CH_2)_{14}$-CH_3] is a saturated hydrocarbon, its cetane number is arbitrarily fixed as 100. A methyl naphthalene is an aromatic hydrocarbon, its cetane number is arbitrarily fixed as zero.

4.10 Gaseous Fuels:-

The gaseous fuels are most preferred because of their ease of storage, transport, handling and ignition. These are classified into two types.

a) Primary fuels Ex:- Natural gas
b) Secondary fuels ex: - Coal gas, producer gas, water gas.

Natural Gas:-

The natural gas is obtained from the wells dug in the earth during mining of petroleum. It is mainly composed of methane and small quantities of ethane along with other hydrocarbons.

If the lower hydrocarbons are present, the gas is called dry gas or lean gas but if the hydrocarbons having the higher molecules are present, the gas is known as rich or wet gas.

The average composition of natural gas is as follows.

Methane – 88.5%, Ethane – 5.5%, Propane – 3.7%

Butane – 1.8%,

Pentane, hydrogen and higher hydrocarbons – 0.5%

The calorific value of natural gas varies from 8000-14000 K.cal/m^3.

Applications:-

- It is an excellent domestic fuel and industrial fuel.
- It is also used as raw material for the manufacture of carbon-black, methanol, formaldehyde etc.
- Methane on microbiological fermentation gives synthetic proteins which are used as animal feed.

LPG (Liquefied Petroleum Gas)

The gas is obtained from natural gas or as a byproduct in refineries during cracking of heavy petroleum products. Nowadays LPG has been a common fuel for domestic work and also in most of the industries. The main components of LPG are n-butane, isobutane, butylenes and propane (traces of propene and ethane). The hydrocarbons are in gaseous state at room temperature and 1 atmospheric pressure but can be liquefied under higher pressure.

LPG is kept in metallic cylinder attached with burner through pipe. It has two stoppers, one at the cylinder and other at burner. LPG has special odour due to the presence of organic sulphides which are added specially for safety measure.

Characteristics of LPG:-

1. It has high calorific value (27,800 kcal/m^3)
2. It gives less CO and least unburnt hydrocarbons. So it causes least pollution.
3. It gives moderate heat which is very good for cooking
4. Its storage is simple. It is colourless
5. It has tendency to mix with air easily
6. Its burning gives no toxic gases though it is highly toxic
7. It neither gives smoke nor ash content
8. It is cheaper than gasoline and used as fuel in auto vehicles also
9. It is dangerous when leakage is there

Applications

1. In Food industry: LPG is widely used in the food industry like hotels, restaurants, bakeries, Canteens etc. Low sulphur content and controllable temperature makes LPG the most Preferred fuel in the food industry.

2. In Glass & Ceramic: The use of a clean fuel like LPG enhances the product quality thereby reducing technical problems related to the manufacturing activity of glass and ceramic products.

3. In Building Industry: LPG being a premium gaseous fuel makes it ideal for usage in the Cement manufacturing process.

4. In Automotive Industry: The main advantage of using automotive LPG is, it is free of lead, Very low in sulphur, other metals, aromatics and other contaminants.

5. In Farming industry: LPG in the farming industry can be used for the following:
    - Drying of crops
    - Cereal drying
    - Curing of tobacco and rubber
    - Soil conditioning
    - Horticulture etc

6. LPG is used in metal industry, aerosol industry, textile industry and it can also be used in Steam rising.

CNG (Compressed Natural Gas)

Natural gas contains mainly CH_4. When natural gas is compressed at high pressure (1000atm) or cooled to -160^oC, it is converted to CNG. It is stored in cylinder made of steel. It is now replacing gasoline as it releases less pollutant during its combustion. In some of the metro cities, CNG vehicles are used to reduce pollution.

Characteristics of CNG:-

1. Natural Gas being lead/sulphur free, its use substantially reduces harmful engine emissions.

2. Natural gas being lighter than air, will rise above ground level and disperse in the atmosphere, in the case of a leakage.

3. Natural Gas in the gaseous state, and is colourless.

4. Predominantly Methane is available in the lean gas, hence CNG contains mostly methane

Applications:-

1. It was used to generate electricity, heat buildings, fuel vehicles, power industrial furnaces and Air conditioners.

2. Natural gas is also consumed in homes for space heating and for water heating

3. It is used in stoves, ovens, clothes dryers and other appliances.

4. In some of the metro cities, CNG vehicles are used to reduce pollution.

4.12 Combustion

Combustion may be defined as the exothermic chemical reaction, which is accompanied by heat and light. It is the union of an element or a compound with oxygen.
Example: $\mathbf{C(s) + O_2\,(g) \rightarrow CO_2\,(g) + 97\ kcal}$

In common fuels it involves the burning of carbon and hydrogen in air and also to a much smaller extent of sulphur.

The presence of moisture in coal is undesirable, because it causes waste of heat; moisture may be present in coal naturally or by adding i.e. moistening the coal before use. The presence3 of some sort of moisture in coal helps to keep the temperature of the fire bars low and prevents the formation of clinkers. The excess presence of moisture leads to heavy smoking and leads to slow starting of combustion process. Optimum free moisture content is 7 to 9% when coal has minimum density. The presence of moisture in combustion makes the combustion process successful.

Calorific value:

The prime property of a fuel is its capacity to supply heat. Fuels essentially consist of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen. Normally when a combustible substance burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions governing the combustion. Further the heat produced is different for different fuels and is termed as its calorific value.

Calorific value of w fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”. Or

“Calorific value is the amount of heat liberated by the complete combustion of a unit weight of the fuel and in usually expressed as cal gm^{-1} or kcal gm^{-1} or B.Th.U. Or

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

There are different units for measuring the quantity of heat. They are:

1. Calorie
2. Kilocalorie
3. British thermal unit (B.Th.U)
4. Centigrade heat unit (C.H.U)

1. Calorie:_It is the amount of heat required to increase the temperature of 1 gram of water through one degree centigrade.

2. Kilocalorie:_This is the unit of heat in metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

1 k.cal = 1000 cal

1 k.cal = 3.968 B.Th.U

3. British thermal unit (B.Th.U):_This is the unit of heat in English system, it is defined as “the quantity of heat required to increase the temperature of one pound of water through of one degree of Fahrenheit.

1 B.Th.U = 252 cal = 0.252 k.cal

4. Centigrade heat unit (C.H.U): It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

1 k.cal = 3.968 B.Th.U = 2.2 C.H.U

Inter conversion of various units of heat:

On the basis that 1 kg = 2.2 lb and 1 ^{0}C = 1.8 ^{0}F we have

1 k.cal = 1000 cals = 3.968 B.Th.U = 2.2 C.H.U

1 B.Th.U = 252 cals

Units of calorific value:

For solid or liquid fuels: cal/g or k.cal/kg, B.Th.U/lb

For gaseous fuels: k.cal/cubic meter or k.cal/m^3

B.Th.U/ft^3 or B.Th.U/cubic feet

Relation between various units:

1 k.cal/kg = 1.8 B.Th.U/lb = 1 cal/g

1 k.cal/m^3 = 0.1077 B.Th.U/ft^3

1 B.Th.U/ft^3 = 9.3 k.cal/m^3

Gross calorific value is the heat liberated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature. This heat includes the latest heat of condensation of water. Because when a fuel containing hydrogen is burnt, the hydrogen present is converted to steam. As the products of combustion are cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Thus the latent heat of condensation of steam, so liberated, is included in the gross calorific value.

Higher calorific value (HCV) or gross calorific value is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled down to 60 ^{0}F or 15 ^{0}C.

Net calorific value or lower calorific value (LCV): lower calorific value is defined as “the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape.

Net calorific value is the gross calorific value excluding the latent heat of condensation of water (the weight of water formed is nine times the weight of hydrogen in the fuel).

Therefore,

LCV or NCV = HCV – Latent heat of water vapour formed

Net calorific value = Gross calorific value – (Mass of hydrogen per weight of fuel burnt x 9 x latent heat of vaporization of water).

Latent heat of steam is 587 kcal/g.

Net calorific value = Gross calorific value – 52.83 x %H

Where % H = percentage of hydrogen.

The gross and net calorific values of coal can be calculated by bomb calorimeter.

Calorific value of a fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”.

Air quantity required for complete combustion of fuel:

The amount of volume of air required theoretically for combustion of 1Kg of fuel is give as

$=100/21[32/12\times C+8[H-O/8]+S]Kg$

Or

$[32/12C+16/2H_2+32/12S]-O_2x$

4.15 Numerical problems on combustion:

1. The following data are obtained in a Bomb Calorimeter experiment.

Weight of coal burnt = 0.95g

Weight of water taken = 700g

Water equivalent of calorimeter = 2000g

Increase in temperature = 2.48^0C

Acid correction = 60.0cal

Cooling correction = 0.02^oC

Fuse wire correction = 10.0cal

Latent heat of condensation = 587 cal/g

Calculate the GCV and NCV of the fuel if the fuel contains 92% of C. 5% of H and 3% of ash.

Sol:

$$GCV = \frac{(W+w)\ (T_2 - T_1 + T_c) - (T_A + T_f + Tt)}{X}$$

$$= \underline{(2200+700)\ (2.48+0.02) - (60+100)}$$

$$0.95$$

$$= 7031.6 \text{ cal/g}$$

$$\text{NCV} = \text{GCV} - 0.09\text{H} \times 587$$

$$= 7031.6 - 0.09 \times 5 \times 587$$

$$= 6767.45 \text{ cal/g}$$

2. On burning 0.72g of a solid fuel in a Bomb calorimeter, the temperature of 250g of water is increased from 27.3^{o}C to 29.1^{o}C. If the water equivalent is 150g, calculate the HCV of the fuel.

Sol:

$x = 0.72$g

$W = 250$g

$T_1 = 27.3^{o}$C

$T_2 = 29.1^{o}$C

$w = 150$g

$$\text{HCV of fuel} = \frac{(W+w)\,(T_2 - T_1)}{X} \text{ cal/g}$$

$$= \frac{(250+150)\,(29.1 - 27.3)}{0.72}$$

$$= 1000 \text{ cal/g}$$

3. A sample of coal was found to have the following percentage composition. C= 75%, H= 5.2%, O= 12%, N= 3.2% and ash =4.5%. Calculate the minimum air required for complete combustion of 1 kg of coal.

Sol:

Combustion reactions are:

$C + O_2 \text{-----}\rightarrow CO_2$

$H_2 + \frac{1}{2} O_2 \text{----}\rightarrow H_2O$

Weight of O_2 required for combustion of 12g of C = 32

Hence, weight of O_2 required by 1 kg of carbon = $\frac{32}{12} \times 1$

Weight of O_2 required for combustion of 2g of H = 16

Hence, weight of O_2 required by 1kg carbon = $\frac{16}{2} \times 1$

1 kg of coal contains:

75%C = 750g

5.2%H = 52g

12% O = 120g

3.2% N = 32g

4.5% ash = 45g

The net weight of O_2 required for complete combustion

$= 750 \times \frac{32}{12} + \frac{16}{2} \times 52$ - oxygen present in 1kg of coal

= 2000+416-120

= 2296g

Since air contains 23% oxygen, the weight of air require for complete combustion of 1kg of coal

$$= 2296 \times \frac{100}{33}$$

$$= 9978\text{g}$$

4. In an experiment in a Bomb calorimeter, a solid fuel of 0.90g is burnt. It is observed that increase of temperature is 3.8^{o}C of 4000g of water. The fuel contains 1% of H. calculate the HCV and LCV value (equivalent weight of water = 385g and latent heat of steam = 587 cal/g)

Sol:

Weight of fuel (x) = 0.90g

Weight of water (W) = 4000g

Equivalent weight of water (w) = 385g

Rise in temperature (T_2-T_1) = 3.8^{o}C

Percentage of carbon = 1%

Latent heat of steam = 587 cal/g

$$\text{HCV} = \frac{(W+w)\ (T_2 - T_1)}{X} \text{ cal/g}$$

$$= \frac{(400+385)\ (3.8)}{0.90} \text{ cal/g}$$

$$= 18514.5 \text{ cal/g}$$

$$\text{LCV} = (\text{HCV} - 0.09\text{H} \times 587)$$

$$= 18514.5 - 0.09 \times 1 \times 587$$

$$= 18461.6 \text{ cal/g}$$

10+2 PCM NOTES

BY

JOYOSHISH SAHA

(PDF version handwritten notes of Maths, Physics and Chemistry for 10+2 competitive exams like JEE Main, WBJEE, NEST, IISER Entrance Exam, CUCET, AIPMT, JIPMER, EAMCET etc.)

10+2

With best wishes from Joyoshish Saha

General Organic Chemistry

Formation of Compounds of Carbon, Classification of Organic Compounds, Functional Groups, Trivial Names, Calculation of number of σ and π bonds, Dipole Moment, Hydrogen Bonding in Organic Compounds, Resonance, Electron Movement Representation in Organic Compounds, Purification Process, Qualitative Analysis, Quantitative Analysis, Types of Carbon in Organic Compounds, Structural Isomerism, Stereo Isomerism, Breaking of Covalent Bonds, Reaction Intermediates, Electron Displacement Effects and Applications, Attacking Reagents and their Nature, Acidic Strength-Comparative Discussion, Basic Strength-Comparative Discussion.

Joyoshish Saha

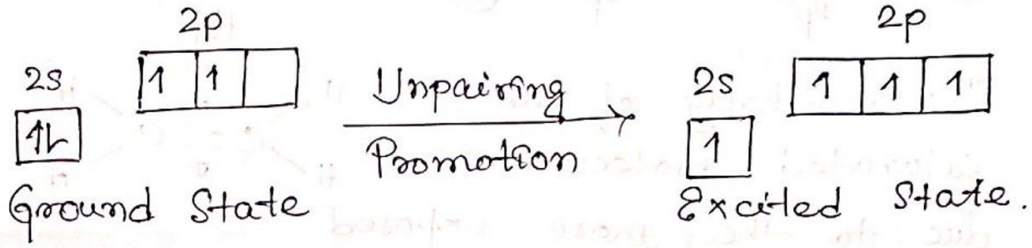
• Some basic principles & techniques

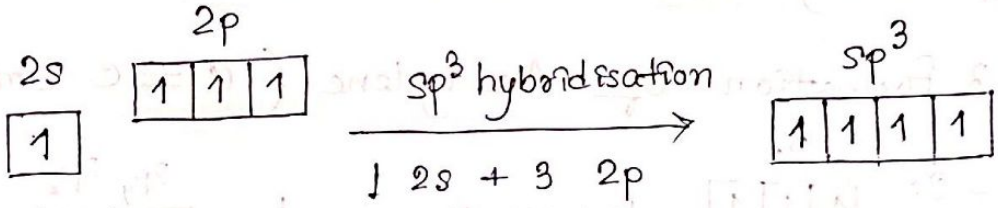
* Formation of Compounds of Carbon:

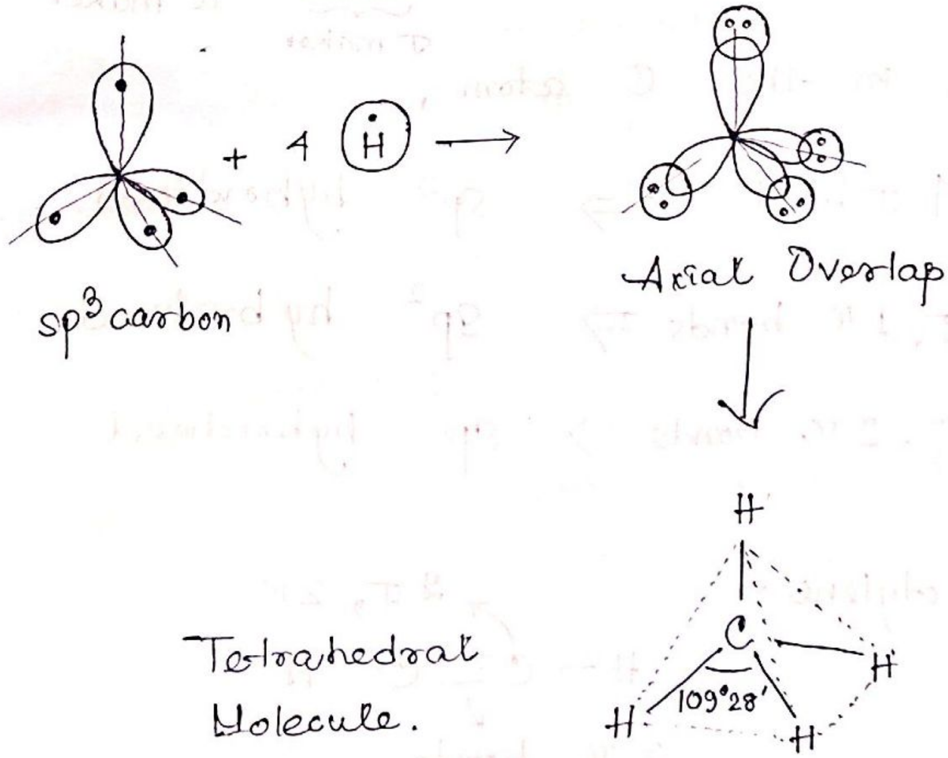
1. Formation of CH_4/Methane (C–C bond):

Bond energy of C–H bond 102 kcal/mol.

C atom – $1s^2 2s^2 2p^2$







Quantitative

Joyoshish Saha

Joyoshish Saha

Joyoshish Saha

14

Metallurgy

INTRODUCTION TO THE STUDY OF METALS

The gold and silver among the metals are probably the first used by man. The art of reducing copper ores and tin ores, and producing bronze dates back to 300 B.C. In history we find 'stone age' followed by 'bronze age' and 'bronze age' followed by 'iron age'.

Today we find the metals are very extensively used in art and industry. Iron in the form of steel, wrought iron and cast iron is used in constructing bridges, dams, pipes, tubes and machine parts. Copper is another important metal being used mainly in electrical articles. Nowadays almost all the metals have some specific uses.

Metals

Metals are the elements, which occupy the left hand side of the periodic table with one, two or three electrons in the outermost shell that takes part in **bonding** and **chemical reactions**.

Physical Properties of Metals

Metals are:

- Shiny when freshly polished and free of corrosion.
- Good conductors of heat and electricity.
- Malleable and ductile.
- Generally solids are with high m.p. and b.p. (only six metals melt below 100 °C—Hg which is a liquid and four group I metals: Na, K, Rb, Cs).

Major Chemical Properties of Metals

Chemically, metals tend to:

- Lose electrons to form cations or positive ions *i.e.,* metals are reducing agents.
- Form basic or amphoteric oxides.
- Form solid ionic chlorides.

The more an element exhibits these properties, the greater is its "**metallic character**".

Metallic Bonds

Metallic bonds are strong bonds in metal crystals. Each metal atom in a metal crystal contributes electrons from its outermost shell to form a "sea of delocalised electrons". Only elements with low first ionisation potential form metallic crystals. When a metal atom looses electron it becomes positively charged. So, it is quite likely that a metal crystal consist positively charged metal atoms embedded in a sea of shared electrons.

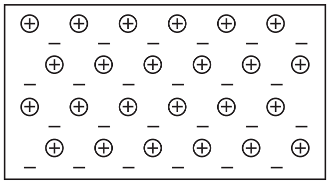


Fig. 14.1 Simplified picture of metallic bonding.

Metals conduct electricity because these shared bonding electrons can drift through the crystal structures from atom to atom when there is an electrical potential difference between the two ends. Metals can bend without breaking because metallic bonding is not highly directional. Lines or layers of metal atoms can shift their positions in a crystal without breaking the metallic bonds.

Mineral Resources of India

The sound economy of a country depends upon its mineral wealth. The most important among the mineral products in India is **coal**, about 58% of the total output is available from Jharia and Raniganj. **Iron ores** occur abundantly in India. The deposits of huge iron ore are in Singhbhoom, Keonjhar and Mayurbhanj. The next important mineral is manganese. Manganese ores are found in Chotanagpur, Mysore, Mumbai and Tamil Nadu. Copper is chiefly found in Chotanagpur and Sikkim. The bauxite deposits are largest in India. Chromite is found in Mysore and Orissa. India occupies the first place in producing mica in the world. Borax, kaoline, limestone, gypsum, pitch-blende, monazite sand are other minerals, which are found in India.

Occurrence of Metals in Nature

Some metals occur in nature in 'native' or 'free state'. A metal is said to occur native or free when it is found in nature in the metallic state. As for example gold and platinum occur in nature in the metallic state. We can say that these metals are not readily attacked by the moisture, oxygen, and carbon dioxide of the air. While those metals which are readily attacked by moisture, oxygen and carbon dioxide occur in the **combined state** or as a compound. These metallic compounds generally occur in the form of hard stones either in the underneath or in the earth surface. **These naturally occurring inorganic compounds are known as minerals**. Minerals are always associated with sand, soil or other impurities. These impurities are known as **Gangue**. The percentage of gangue in a mineral is always higher than the mineral itself.

Common Minerals

- Oxide — [Bauxite, $Al_2O_3\ 2H_2O$] for Aluminium
  [Hematite, Fe_2O_3] for Iron
- Carbonate — [Limestone, $CaCO_3$] for Calcium
  [Magnesite, $MgCO_3$] for Magnesium
- Sulphide — [Zinc blende, ZnS] for Zinc
  [Galena, PbS] for Lead
- Sulphate — [Gypsum, $CaSO_4.2H_2O$] for Calcium
- Nitrate — [Chile saltpetre, $NaNO_3$] for Sodium

- Halide — [Fluospar, CaF_2] for calcium
- Silicate — [Mica, $KHMg_2Al_2(SiO_4)_3$] for Magnesium
- Phosphate — [Phosphorite, $Ca_3(PO_4)_2$] for Calcium

Some minerals of common metal are listed below in tabular form:

Form	*Metal*	*Name of ores and minerals*
Oxides and hydrated oxides	(*i*) Aluminium (Al)	(*i*) Claysilicate ($Al_2O_3.2SiO_2.2H_2O$) Diaspore ($Al_2O_3.H_2O$)
	(*ii*) Copper (Cu) IB (Coinage metal)	(*ii*) Cuprite (Cu_2O)
	(*iii*) Zinc (Zn) IIB (Amphoteric metal)	(*iii*) Zincite (ZnO)
	(*iv*) Manganese (Mn) VIIB (Transition metal)	(*iv*) Pyrolusite (MnO_2) Braunite (Mn_2O_3)
	(*v*) Chromium (Cr) VIB (Transition metal)	(*v*) Chromechre (Cr_2O_3)
	(*vi*) Tin (Sn) IVA (Amphoteric metal)	(*vi*) Tin stone or cassiterite (SnO_2)
	(*vii*) Potassium (K) (Alkali metal)	(*vii*) Felspar ($K_2O.Al_2O_3.6SiO_2$)
Sulphides	(*i*) Copper (Cu) IA (Coinage metal)	Copperglance (Cu_2S); Copperpyrite (CuS, FeS)
	(*ii*) Zinc (Zn)	Zinc blende (ZnS)
	(*iii*) Lead (Pb) IVA (Amphoteric metal)	Galena (Pbs)
	(*iv*) Mercury (Hg) IIB (Liquid metal)	Cinnabar (HgS)
	(*v*) Tin (Sn)	Stannite (Cu_2S, FeS, SnS_2)
	(*vi*) Iron (Fe)	Iron pyrite (FeS_2)
	(*vii*) Silver (Ag) IB (Best conducting metal)	Silver glance (Ag_2S); Rubby silver $3Ag_2S.Sb_2S_3$
Carbonates	(*i*) Iron (Fe)	Siderite ($FeCO_3$)
	(*ii*) Copper (Cu)	Malachite ($CuCO_3$ $Cu(OH)_2$)
	(*iii*) Calcium (Ca) IIA (Alkaline earth metal)	Calcite ($CaCO_3$); Dolomite ($CaCO_3.MgCO_3$)
	(*iv*) Magnesium (Mg) IIA (Bridge metals)	Magnesite ($MgCO_3$); Dolomite ($MgCO_3CaCO_3$)
	(*v*) Manganese (Mn)	Manganese spar ($MnCO_3$)
	(*vi*) Lead (Pb)	Cerussite ($PbCO_3$)
	(*vii*) Zinc (Zn)	Calamine ($ZnCO_3$)
Sulphates	(*i*) Calcium	Gypsum ($CaSO_4.2H_2O$) Anhydrite ($CaSO_4$)
	(*ii*) Lead	Anglesite ($PbSO_4$)
	(*iii*) Aluminium	Alum (K_2SO_4; Al_2 $(SO_4)_3.24H_2O$)
	(*iv*) Barium IIA (Alkaline earth metal)	Heavy spar ($BaSO_4$)

	(*v*) Magnesium	Epsomite ($MgSO_4.7H_2O$) Kisserite ($MgSO_4.H_2O$)
Halides	(*i*) Sodium	Rocksalt (NaCl)
	(*ii*) Potassium	Sylvine (KCl)
	(*iii*) Silver IB (Conductive metal)	Horn silver (AgCl)
	(*iv*) Calcium	Fluoropalite ($3CaF_2$ $Ca_3(PO_4)_2$); Chloropative ($3COCl_2.Ca_3(PO_4)_2$)
	(*v*) Magnesium	Carnallite KCl, $MgCl_2$ $6H_2O$
	(*vi*) Aluminium	Cryolite (3NaF, AlF_3)
Silicates	(*i*) Sodium	Sodium silicate (Na_2SiO_3)
	(*ii*) Potassium	Felspar ($K_2O.Al_2O_3.6SiO_2$)
	(*iii*) Zinc	Willemite ($ZnSiO_2$)
	(*iv*) Aluminium	Felspar ($K_2O.Al_2O_3.6SiO_2$)

Ores

Generally all minerals cannot be considered important for extraction of metal from them. The process of extraction though costly may not be impossible from these minerals. **Particularly, the minerals from which metals can be extracted easily and cheaply are known as ores**. As for example, haematite is the ore of iron, bauxite is the ore for aluminium etc.

Metallurgy

The process by which the metals are extracted from their respective ores is known as metallurgy. An ore is naturally occurring substance or mineral from which the metal can be extracted economically.

Concentration of the Ore

Almost all ores are associated with gangue or matrix. Before the proper extraction of the metal the ore is freed from gangue or matrix to get it in the concentrated form. As a matter of fact, the ore is enriched with the desired metallic compound. This process of removal of gangue is known as the concentration of the ore. There are several processes of the concentration of ores, which are described below. This process of concentration of ore makes the extraction of the metal easier and cheaper. The main steps for the extraction of metals are generally as follows:

1. **Crushing and grinding**
2. **Concentration of the ore**
3. **Calcination/Roasting**
4. **Reduction**
5. **Purification**

Crushing and Grinding. This is one of the crucial steps of concentration process. The step provides breaking of big masses of rocks containing the ore into small lumps by conventional crushing and grinding with machines *viz.*, Jaw crusher, Gyratory crusher etc.

Sometimes, the concentration and further treatment of some ores demand their reduction of size into a very fine state of division. This is effected in **grinding** and **pulverising mills** (Figs. 14.2 and 14.3).

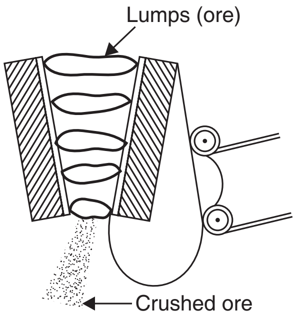


Fig. 14.2 Crushing.

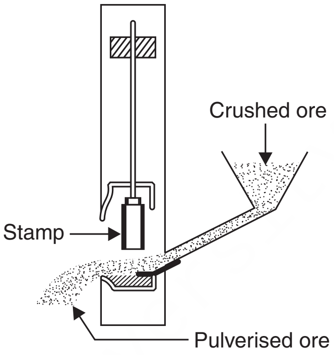


Fig. 14.3 Pulverisation.

Concentration of the Ore

(*i*) *Washing.* This process includes all methods of concentrations in which water in motion is used. From the pulverised ore in stream of water the lighter particles float away with water and thus some gangues are removed.

(*ii*) *Floatation.* Here concentration of the pulverised ore is effected by taking the advantage of the difference in its behaviour towards oil or water. Sulphide ores, as a rule, do not get wet as do silica and most oxides when treated with water. Therefore, sulphide ores will float on the surface while silica and other materials will sink.

(*iii*) *Oil floatation process.* Oils have just the opposite effect, they are attracted by sulphide ores. Oils form a film over the sulphide ore. The pulverised sulphide ore is taken in a tank and some pine oil and water are used. Generally some xanthates are used with pine oils. Air is made to bubble through a perforated pipe from the underneath of the tank. A foam is produced and floats along with the sulphide ore over the surface of water. But the sand and soil are settled down. The concentrated ore is collected from foam (Fig. 14.4).

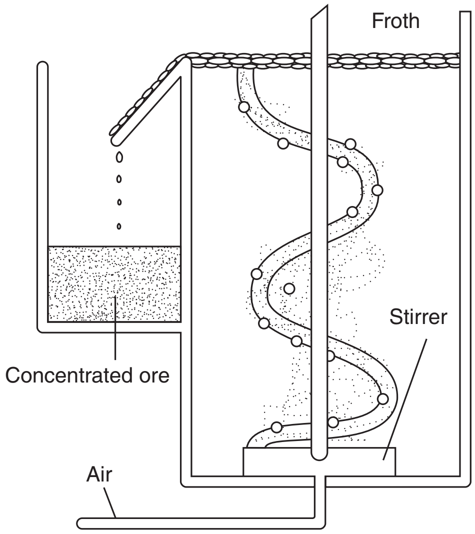


Fig. 14.4 Concentration of ore by oil floatation.

(*iv*) *Magnetic separation.* Ferromagnetic ores can be separated by passing the ore through a strong magnetic field, whereby ferromagnetic substances are separated from the ore. The tungsten or tin ore is separated by this method.

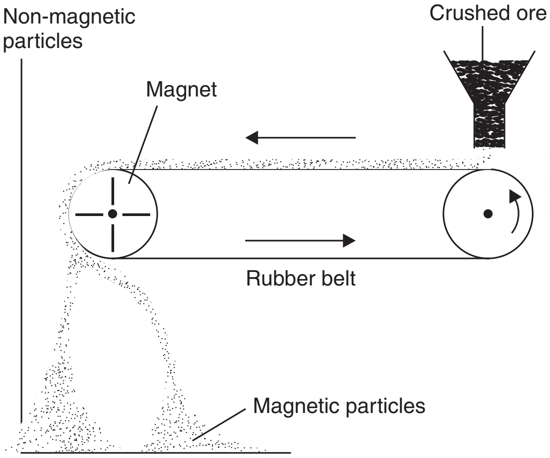


Fig. 14.5 Magnetic separation.

Calcination and roasting. These two terms are used, somewhat interchangeable, among the metallurgists, though a distinction exists between them.

- **Roasting:** To roast a material is to heat it at a temperature insufficient to melt it *i.e.,* below the point of fusion but **always in presence of air** with a view to oxidising the material. The term is usually applied in case of oxidising the ores. As for example, metallic sulphides are roasted to oxides before reduction to extract the metal.

$$2MS + 3O_2 = 2MO + 2SO_2$$
$$MS + 2O_2 = MSO_4$$

- **Calcination:** To calcine a material is to heat it very strongly but at **a temperature insufficient to melt it**; with a view to driving of volatile matters leaving some pores on the rocky ore to facilitate the reduction process, so that reducing gas *viz*., CO can enter into pores and make reduction complete. As for example,

$$M_2O_3.x\,H_2O \xrightarrow{\Delta} \underset{\text{(Calcined)}}{M_2O_3} + x\,H_2O \uparrow$$

$$MCO_3 \xrightarrow{\Delta} \underset{\text{(Calcined)}}{MO} + CO_2 \uparrow$$

Fluxes

Before the extraction of metals from their ores and in their subsequent purification, the impurities (gangue) present in the ores are to be removed. They are often refractory in nature and remain unfused which may disturb efficient extraction of the metal. So, gangue must be removed. They become easily fusible when heated with other substances, those substances are known as **fluxes**.

So, **flux is a material, which when added to an ore and heated gives a fusible mass known as slag.**

$$\text{Gangue + Flux} \xrightarrow{\text{heat}} \text{Slag (fusible)}$$

Selection of Flux

The nature of flux to be used depends on the nature of gangue. If it is acidic, basic flux is to be used *viz*. lime, magnesia etc. If the gangue is basic in character, then an acid flux like sand (SiO_2) must be employed.

There are three kinds of fluxes:

- **Acidic** (SiO_2)
- **Basic** (CaO, MgO)
- **Neutral** (fluorspar)

Fuels

Almost all industries require a fuel. Large scale industries, like metal extraction, need economy of fuel consumption.

Furnaces

- **Reverberatory furnace.** This is a special type of furnace much used in metallurgy. In this furnace, the material is heated not directly over fire, but by the hot gases produced in the fire place (Fig. 14.6).

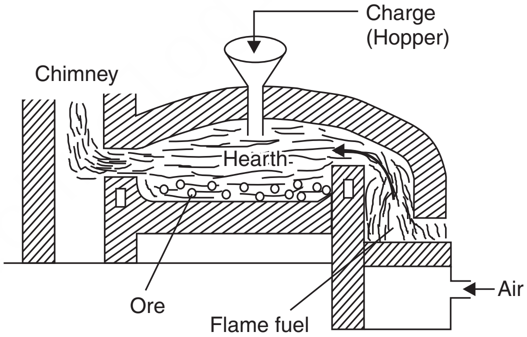


Fig. 14.6 Reverberatory furnace.

- **Muffle furnace.** It is a type of furnace consisting of an enclosed chamber, made of refractory materials, from which the fuel and its products of combustion cannot come in contact with the materials heated in it (Fig. 14.7).

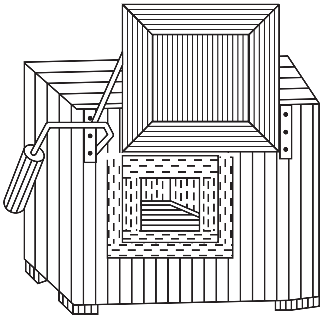


Fig. 14.7 Muffle furnace.

- The other furnaces are **blast furnace** (for iron extraction), **open hearth furnace** (for steel manufacture) and **electric furnace** (for Phosphorus extraction).

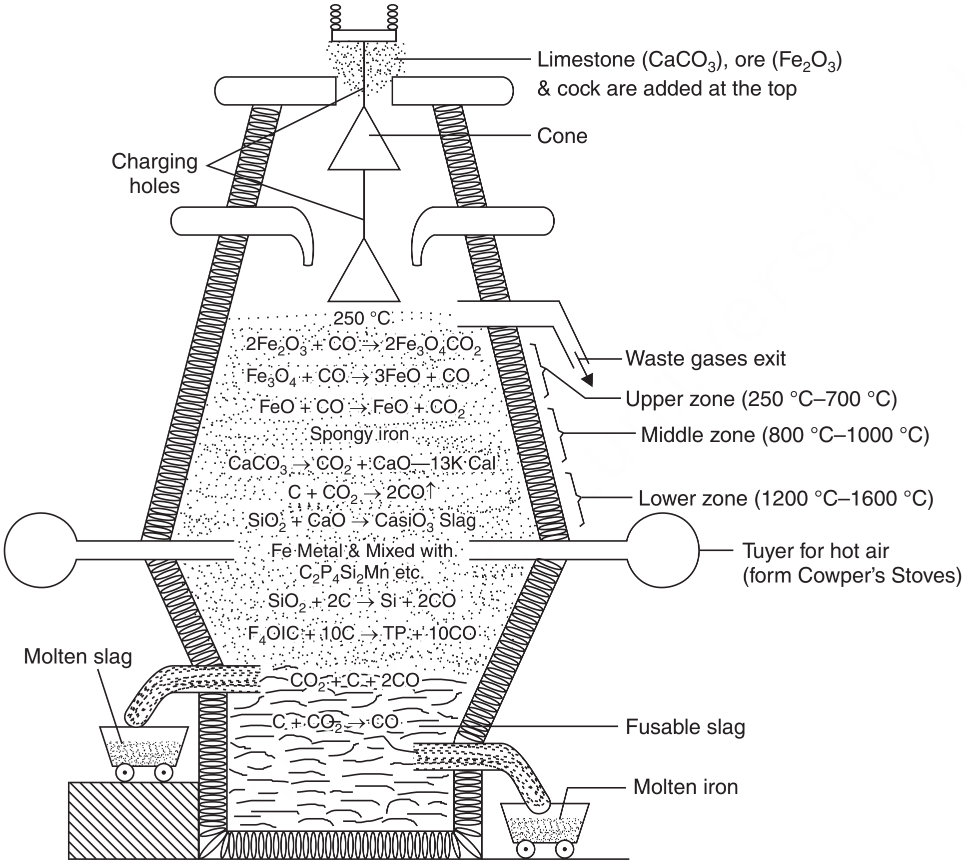


Fig. 14.8 Blast furnace (displaying reactions of iron extraction in various zones of the furnace).

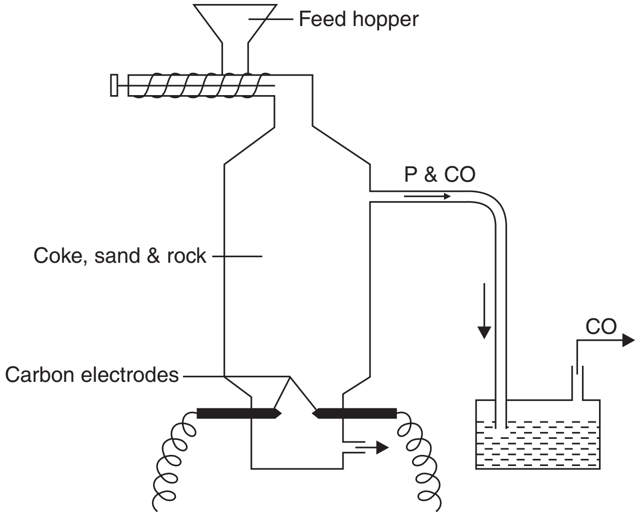


Fig. 14.9 Electric arc furnace.

Smelting. The process by which a metal is extracted in the fused state is called smelting.

Welding. It is the operation of joining the two pieces of a metal either by pressure or by fusion to one compact mass.

Alloy. An alloy is a mixture or compound or both of two or more metals. When one of these metals is mercury, the alloy is called an **amalgam**. So, an alloy may be considered as solid solution or an intermetallic compound or both. Steel is an alloy of iron and carbon, a non-metal. An alloy is often more useful than a pure metal. Controlling the composition of an alloy makes it possible to vary its properties. Generally, alloys are classified as:

- **Non-ferrous alloys**
- **Ferrous alloys**

Non-ferrous alloys do not contain iron as one of the constituents of the alloys, *e.g.*, Brass which is composed of Zn and Cu. Whereas ferrous alloys always contain iron as one of the constituents of the alloys, *e.g.,* Stainless steel contains Fe, Ni, Cr.

Importance of alloy preparation

- to increase the hardness and tensile strength
- to improve the casting property
- to increase the resistance to corrosion
- to decrease the thermal and electrical conductivities.
- to lower the melting and boiling points of individual metal.

General methods of preparation of alloys

- **By fusion.** Component metals are mixed together in the desired ratio and melted followed by cooling.
- **By compression.** Finely divided metals are compressed in the desired ratio.
- **By reduction** of the mixture of oxides to get mixture of metals in the proper ratio.

Examples of important alloys are

- **Mild steel.** An alloy of iron with carbon (0.1-0.25%). It is relatively cheap, can be easily rolled into sheets, and can be pressed into shape.
- **Stainless steel** (Chromium steel) (10-15% Cr, 90-85% Fe). It is mainly used in making utensils as well as reactors in industries.
- **Manganese steel** contains Mn 12-14% and the rest is iron. It is used in making rolls.
- **Molybdenum and Tungsten steel or High speed tool steel** are mainly used for high speed machines.
- **Wrought iron** (C = 0.1-0.25%), is mainly used in making household furnitures.
- **Ferro-titanium** is used as deoxidisers to avoid formation of 'blow holes' from molten steel.
- **Brass,** an alloy of copper (Cu:Zn = 60:40), has a gold colour and does not corrode.
- **Bronze,** an alloy of copper with upto 12% tin (Sn), a strong, hard wearing and resistant to corrosion.
- **Solder.** An alloy of Pb and Sn that melts at low temperature, can be used to join metals.
- **Duralumin.** An alloy of 95% Al with 4% Cu and smaller amounts of Mg, Fe, Si, it is stronger, harder, more resistant to corrosion than pure Al, used mainly in making the body of aeroplanes.

- **Magnalium.** An alloy of Al and Mg (98:2) used in making light machine parts.
- **Alnico.** (Composition—Steel:Al:Ni:Co = 5:2:2:1) Used for making permanent magnets.

Cementation

When a metal is heated in contact with a powder, the powder is slowly absorbed by the metal without melting whereby the property of the metal changes to a certain extent. This process is called **cementation** and the powder is called the **cement**.

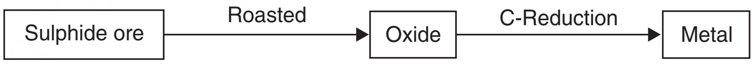
General Methods of Extraction of Metals from their Ores

- Metals like gold (Au), platinum (Pt) etc., are obtained in nature in the free state. So their method of extraction practically consists of separating them efficiently from the rocky and other impurities.
- But, most of the metals occur as their compounds such as oxides, hydroxides, carbonates, sulphides, halides etc. Then we can say, there are two broad steps in their extraction process:

  (*i*) Preliminary **calcination** and **roasting**

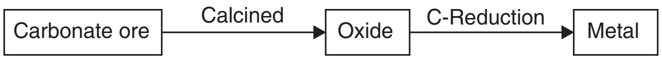
  (*ii*) Reduction.
- When the ore is an oxide, hydroxide, or carbonate it is first calcined to get porous oxides and then the calcined ore is reduced to the metal, generally, by **carbon reduction process**. The principle and processes of reduction will be discussed later on.
- When the ore is a sulphide, it is first heated in the presence of air *i.e.,* roasted to get metallic oxide and then reduced to get the metal.

Scheme I:



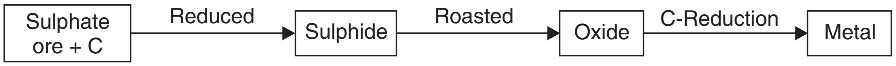
- When the ore is a carbonate or hydroxide:

Scheme II:



- When the ore is a sulphate:

Scheme III:



- When the ore is a halide or metallic oxide or is not reducible by carbon, electrolytic process of reduction is followed.

Methods of Reduction of the Processed Ore

Metal extraction involves two main types of processes for the reduction of the metallic compounds.

(*i*) **Pyrometallurgy:** It means **reactions at high temperature often above 1000°C.**

(*a*) Electrolytic reduction at high temperatures of the fused salts especially halides (for example Na, Al).

(*b*) Chemical reduction by coke at high temperatures (for example, iron, lead)

$$\text{MO} + \text{C} \xrightarrow{\Delta} \text{M} + \text{CO}$$

(*c*) Chemical reduction by a more reactive *i.e.,* electropositive metal (for example, chromium and titanium extraction).

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr \text{ (Goldschmidt Thermit process)}$$

(*ii*) **Hydrometallurgy:** It means, **reactions at low temperature in solution in water.**

(*a*) Electrowinning at low temperature in solution in water (for example, Zn extraction for $ZnSO_4$ solution).

(*b*) Cementation using a displacement reaction (for example, using iron to displace copper from a solution of $CuSO_4$)

$$CuSO_4 + Fe = Cu + FeSO_4$$

Goldschmidt Thermit Process

The metallic aluminium has a strong affinity for oxygen at 1000°C. The combination of oxygen with aluminium at that temperature evolves much heat, which is utilised in **Goldschmidt Thermit process** or **Aluminothermic process** for the reduction of metallic oxides *e.g.,* MnO_2 or Cr_2O_3 and for the separation of molten metals.

Goldschmidt Thermit process is nowadays mostly used for welding rails and machine parts (Fig. 14.10). Thermite, a mixture of aluminium powder and iron oxide in the ratio 3:1 by weight, is ignited in a crucible by a ribbon of magnesium, when a violent reaction takes place producing molten iron at 2500°C.

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe + 199 \text{ kcal}$$

The liquid iron is dropped on the two pieces directly to the joint to be welded.

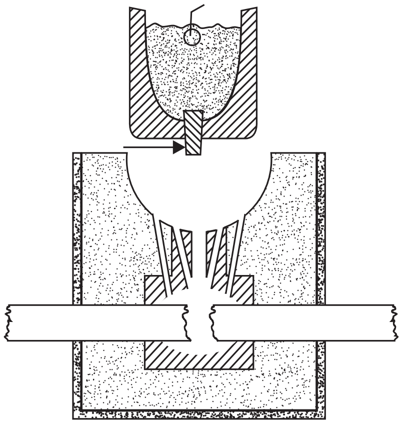


Fig. 14.10 Goldschmidt Thermit process.

Purification of the Metals Extracted

Almost all metals obtained by reduction processes contain some impurities. The impurities are to be removed to get the pure form of metal. The purification processes are:

1. Thermal refining and
2. Electro-refining

1. **Thermal refining**

- *Oxidation of impurities by air poling.* The impure metal is melted and a stream of air is purged through the bottom, as a result of which the easily oxidisable impurities are converted to oxides. The volatile oxides escape and a non-volatile oxide forms a scum over the molten metal, which is removed with the help of a laddle.
- *Fractional distillation.* Easily volatile metals can be removed with the help of fractional distillation. The crude zinc, which is known as spelter, contains about 2% of lead and traces of iron, cadmium, arsenic as impurities. The spelter is at first heated in a retort at a temperature slightly above the boiling point of zinc (920°C). When zinc together with cadmium distils over leaving behind lead (b.p. 1620°C) and iron (b.p. 2800°C). The distillate *i.e.,* molten mixture of zinc and cadmium is redistilled in another retort at a temperature slightly above 767°C when more volatile cadmium (b.p. 767°C) distils out and 99.9% of zinc is left in the retort.
- *Liquation.* An easily fusible metal such as tin or lead can be refined by this process. The impure metal containing infusible impurities is heated on the sloping hearth of a special type of furnace (Fig. 14.11), as a result the metal melts and the molten metal flows down the sloping hearth leaving behind the infusible impurities on the top.

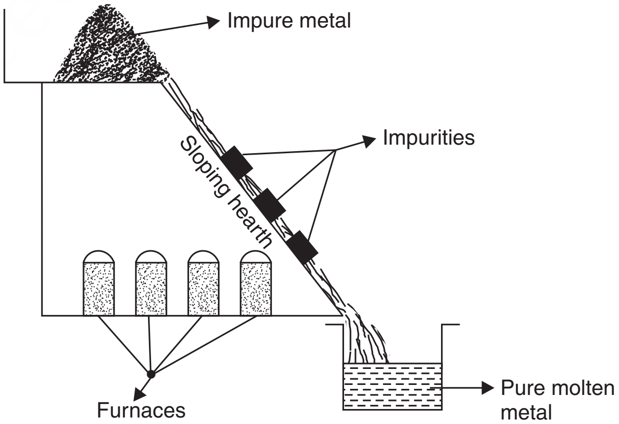


Fig. 14.11 Refining of metal by Liquation.

- *Zone refining* (Fig. 14.12). This process of purification is employed effectively in some special cases. The advantage is taken out of the fact that the impurities are more soluble in the molten metal than the solid metal and the molten metal on resolidification crystallises out as a pure metal. The actual process is: a narrow rod of impure metal is taken and a small portion of it at one end is almost melted by application of heat. This small molten zone is gradually and slowly shifted to the other end of the rod by gradual shifting of the source of heat. At last the molten zone containing all the impurities reach the other end. The rod is allowed to cool and the impure zone is cut off and removed. The remaining portion of the rod consists of the pure metal.

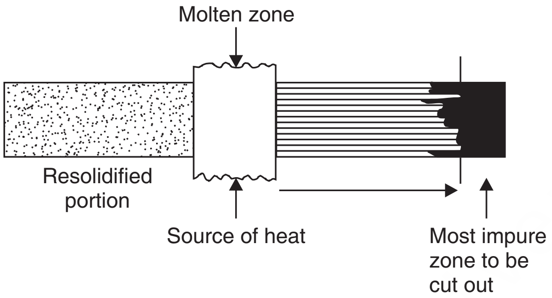


Fig. 14.12 Zone refining.

2. **Electro-refining.** This method is widely used. Usually an electrolytic cell is set up using thin sheets of pure metal as the cathode and comparatively thick impure metal slag as anode. The electrolyte used is an aqueous solution of a suitable salt. During electrolysis, pure metal from the electrolyte gets deposited on the cathode and the equivalent amount of metal from the anode passes into the solution. The impurities either remain in solution or are deposited down the anode. This deposit is known as **anode mud**. Sometimes some valuable metals are recovered from anode mud. A typical example of electrolytic refining is of copper (Fig. 14.13).

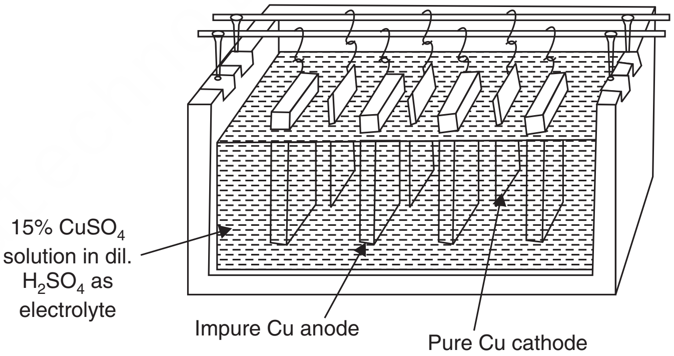


Fig. 14.13 Electrolytic refining of copper.

POWDER METALLURGY

Powder metallurgy (Fig. 14.13) is a technique or operation or process to produce metallic or alloy articles. In this technique, the metal powders or alloy constituents are compacted in a die with melting or no melting followed by sintering. The simultaneous method of compacting and sintering is called *pressure sintering.*

The article is made into the desired shape by powder metallurgy in the following steps:

(*i*) *Pulverisation of metallic powders*
(*ii*) *Mixing and blending*
(*iii*) *Compacting*
(*iv*) *Pre-sintering, and*
(*v*) *Sintering*
(*vi*) *Finishing operation.*

(*i*) **Pulverisation of metallic powders.** For pulverisation of metals techniques adopted are:

(*a*) *Mechanical:* This method may be adopted in the case of Mg, Al, Zn, and Pb. For pulverisation ball mills can be employed.

(*b*) *Atomisation:* This method involves forcing molten metal through a nozzle or spinnerette in a stream of water or compressed air, when fine powder of metals are obtained. This method requires control of pressure and temperature and the oxidation of metal into an atmosphere of inert gas. This method is commonly employed for metals like Mg, Cd, Zn, Pb, Sn etc.

(*c*) *Chemical:*

1. By reduction,

$$WO_2 + 2H_2 \xrightarrow{\Delta} W + 2H_2O$$

2. By decomposition,

$$Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO\uparrow$$

The metals are obtained in a state of fine powders in both cases.

(*ii*) **Mixing and blending.** This operation is required when a combination of metallic powders are used. They are uniformly mixed in right proportions. Lubricants may be added if necessary.

(*iii*) **Compacting.** The metal powder in right proportions is then taken in a die into the cavity (female joint) of accurate dimensions and then compressed (100–1000 N/m^2) by the male joint of the die. The solid in this stage is known as '*green compact*'.

(*iv*) **Pre-Sintering.** It involves heating the green compact to a temperature below the sintering temperature. This step increases the strength of green compact as well as removes the lubricant if used. This step is essential for tungsten.

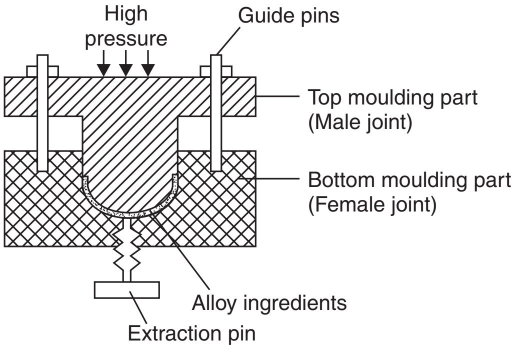


Fig. 14.14 Technique of powder metallurgy adopted in a die.

(*v*) **Sintering.** Compacted pieces are heated to a temperature below and very close to the melting point of the metal in a furnace, preferably in an atmosphere of hydrogen, whereby metal particles sinter to a coherent mass. Time and temperature of sintering depend upon the nature of the metal.

(*vi*) **Finshing operations.** The sintered articles require operations like machinery, plating etc., to get accurate shape of the work pieces.

Uses

In making:

(*i*) Porous bearings ; (*ii*) Tungsten filaments for electric bulbs ; (*iii*) Sewing machines (*iv*) Gears ; (*v*) Clutches, breaks etc.

Advantages

(*i*) Articles of any intricate shape can be produced with desired accuracy and smooth finish.

(*ii*) Clean and smooth operations.

(*iii*) Metals and non-metals can be mixed to give the desired property to the article as for example W and C can be mixed to produce W_2C (tungsten carbide) for cutting tools.

(*iv*) Articles with impregnated lubricants can be produced which would be self-lubricating for ever.

(*v*) 100% raw material is consumed with no loss.

Disadvantages

(*i*) Dies of desired precision are required which are very much expensive.

(*ii*) Ejection of the articles from the die is necessary, which limits the production of very very intricate articles.

SOME SPECIFIC EXAMPLES OF EXTRACTION OF METALS

Titanium (Ti)

Titanium is a very strong metal and has a density much less than that of steel. It melts at a very high temperature of 1675 °C. The metal is being protected like aluminium by a thin oxide layer formed on the surface of the metal.

Titanium is an element of *d*-block in the periodic table and its electronic configuration is [Ar] ... $3d^2.4s^2$. It can exhibit three oxidation states +2, +3 and +4, but only +4 oxidation state is common. Titanium (IV) chloride is a colourless liquid produced as an intermediate in titanium extraction and is used in the manufacture of titanium (IV) oxide.

Smoke grenades produce dense clouds of titanium (IV) oxide due to rapid hydrolysis of titanium (IV) chloride.

Extraction

The ores of titanium used for extracting metal are *rutile* (TiO_2) and *ilmenite* ($FeTiO_3$). Among the most abundant metals in the earth's crust Titanium achieves the fourth place. But as the extraction process is difficult and expensive, it is not widely used.

After the purification of the ore, it is heated with carbon in a steam of chlorine gas at about 1100 K.

$$TiO_2 + C + 2Cl_2 \longrightarrow TiCl_4 + CO_2$$

In **Kroll process**, the titanium (IV) chloride condenses as a liquid that can be purified by fractional distillation.

The chloride of the metal is then allowed to react with molten sodium or magnesium at 800 K in an inert argon atmosphere, the reaction is exothermic and so temperature rises.

$$TiCl_4 + 4Na \longrightarrow Ti + 4NaCl$$

The reactor is kept hot for about two days then the mass is removed from the furnace and is allowed to cool. The solid product is then crushed and leached with dilute hydrochloric acid, which dissolves the sodium chloride, leaving behind the metal Ti which is then washed and dried. Extremely pure Ti can be obtained by decomposition of TiI_4 vapour on an electrically heated tungsten (W) filament in vacuum.

Uses

(*i*) Titanium is used mainly for making aircraft engines and airframes.

(*ii*) Other major uses are the production of chemical components of chemical plants such as heat exchangers.

Chromium (Cr)

Chromium is mainly extracted from Cr_2O_3 *i.e.,* Chromium (III) oxide in a batch process employing aluminium as the reducing agent. **The commercial ore is chromite**. Chromite contains other metals like iron besides chromium. The first step is to convert the ore to pure Cr_2O_3. A mixture of the oxide with powdered aluminium is then ignited in a reaction vessel. The **exothermic reaction** produces pure metal (99 %).

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr_2(s) + Al_2O_3(s)$$

Carbon can reduce Cr_2O_3 but the produced metal then contains carbon as impurity. The presence of carbon in the metal makes the metal brittle and less resistant to corrosion.

Chromium, like aluminium, is protected from corrosion by a thin layer of oxide on the metal surface. The main use of chromium is to make **alloys** with iron (**stainless steels**).

Electroplating with chromium gives a shiny, corrosion resistant finish to metals.

Uses

(*i*) The chief uses of chromium are in the manufacture of chrome steel and chromium plating.

(*ii*) Chrome steels are employed in the form of alloy “ferrochrome” containing 60–70% Cr. This is very hard and used in making cutting tools. Stainless steel is ordinary steel with 14% Cr. Steels with 18% Cr and 7–8% Ni are superior corrosion resistant. Chromium-vanadium steel is very hard and is used in axle, shafts, locomotive wheels etc.

(*iii*) Chromium plating unlike nickel plating is resistant to sulphur compounds of the atmosphere.

Nickel (Ni)

Nickel is a hard, grayish but shiny *d*-block metal with the electronic configuration ... $3d^8.4s^2$ [Ar]. The common oxidation state of nickel is +2. Nickel (II) salts, like nickel sulphate ($NiSO_4$) are green.

Uses

(*i*) Nickel is so unreactive that it is used to make spatulas and crucibles.

(*ii*) Nickel is a constituent of many alloys including some alloy steels and the ferromagnetic alloy and also of Alnico which is used in making permanent magnet.

(*iii*) Nickel in finely divided form acts as a good catalyst in hydrogenation reactions.

(*iv*) It is a heterogeneous catalyst and is used to harden unsaturated vegetable oils by addition of hydrogen across the double bond.

Manganese (Mn)

Manganese is a hard, gray, brittle d-block metal having electronic configuration ...$3d^5.4s^2$ [Ar]. The main oxidation states of manganese are:

+7 in MnO_4^- — the purple manganate (VII) ion, which is a strong oxidising agent in acid medium.

+4 in MnO_2 — an insoluble black compound and acts as an oxidising agent in acid solution.

+2 as Mn^{2+} — the pink manganese (II) ion in salts such as manganese (II) sulphate.

Uses

(*i*) Manganese is added in steel to modify its mechanical characteristics.

(*ii*) The metal is mainly used in steel industry in making alloy steels and as a deoxidant.

(*iii*) Manganese steel containing 13% Mn is extremely hard and tough and is used in making jaws or rock crushers.

(*iv*) An alloy of copper, aluminium and manganese (Heusler's alloy) is ferromagnetic.

(*v*) An alloy of copper, manganese and nickel, known as Manganin, is used for resistance coils since its electrical resistance is very slightly affected by temperature.

Cobalt (Co)

Cobalt is a hard, shiny d-block metal and is less reactive than iron. It has the electronic configuration ... $3d^7.4s^2$ [Ar].

In solution cobalt forms ions in the +2 and +3 oxidation states. Cobalt (II) is a more stable state.

Uses

(*i*) Cobalt is used in making the so called 'hard alloys' which are superior to high speed tool steel as regards the life of the tools.

(*ii*) Steels containing about 35% cobalt is used for permanent magnet.

(*iii*) Cobalt may be used for electroplating iron, steel and brass etc.

(*iv*) Cobalt oxide is used as a colouring agent in the glass and ceramic industry *i.e.*, in making blue glass and blue enamels for coating iron.

(*v*) Some cobalt salts with organic acids are used as driers in paints and varnishes.

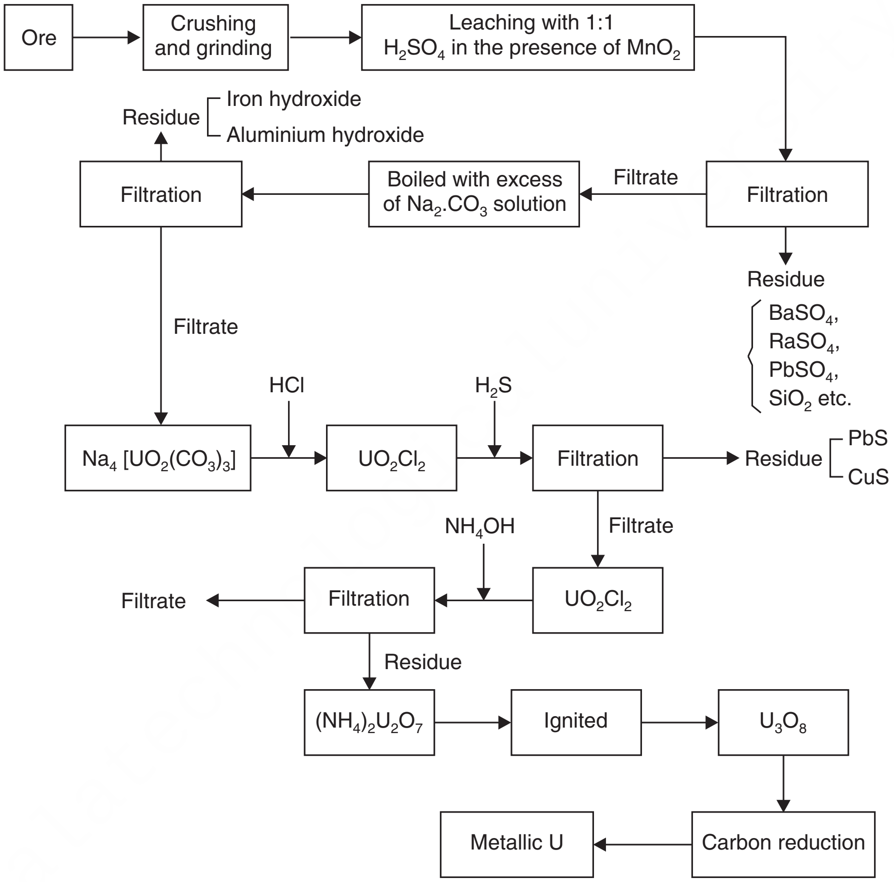
(*vi*) The radio-active isotope Co-60 is a strong γ-radiation emitter. Cobalt-60 capsules are used to kill cancer tissues by radiation.

Uranium (U)

Uranium is not obtained in free state in nature. It occurs in the form of compounds. The important ores of uranium are:

(*i*) Pitchblende (uranite—U_3O_8) (*ii*) Carnolite—$K_2O.2UO_3.V_2O_5.3H_2O$.

Uranium is extracted from pitchblende and a flow diagram for the extraction of uranium is shown below:



Uses

(*i*) Its principal use is as atomic fuel in nuclear reactors. U^{235} releases 200 meV per fission with neutrons.

$$U^{235} + {}_{0}^{1}n = Ba^{140} + Kr^{92} + 200 \text{ meV}.$$

(*ii*) In ceramics uranium compounds are sometimes used to form coloured glasses (yellow or orange).

(*iii*) Uranium steels are also important technically.

Zirconium (Zr)

Occurrence

The main ores of zirconium are:

(*i*) *Zircon—Zr* SiO_4

(*ii*) *Baddeleyite* (ZrO_2)

The ores are found in the USA, Brazil and Australia. Zirconium also occurs in alluvial sands of Kerala and Sri Lanka.

Extraction

(*i*) Zirconium is produced commercially by Kroll process. (See extraction of Titanium.)

(*ii*) *Van Arkel-de Boer process.* In this process, crude zirconium is heated with a little iodine under vacuum at 200 °C when ZrI_4 volatilizes. A tungsten or Zirconium filament is heated to 1300 °C in the same vessel. This filament decomposes ZrI_4 to pure Zr which is deposited on the filament.

$$ZrI_4 = Zr + 2I_2$$

Properties

Zirconium is a lustrous, silvery metal with m.p. 1857 °C. Zirconium is a good conductor of heat and electricity. The traces of impurities like O, N and C make the metal brittle.

Chemical: If heated to high temperatures, zirconium reacts directly with most non-metals *viz.*, O_2, H_2; when finely divided, the metal is pyrophoric. So, care should be taken during machining and the production waste chips should be avoided. Despite this inherent reactivity, the metal has got outstanding resistance to corrosion, which is due to the formation of a dense, self-heating oxide film over the metal surface. With the exception of HF, other mineral acids react at elevated temperatures with the metal. The most important oxidation state of the metal is +4.

Uses

(*i*) Zirconium has a high corrosion resistance and it is sometimes preferable to stainless steel in certain chemical plants.

(*ii*) It is used in a variety of alloy steels; a notable superconducting alloy is with niobium which retains its superconductivity even in strong magnetic fields.

(*iii*) The small percentage of hafnium (Hf), which is almost always present with zirconium, is not detrimental at all and may even improve the property of Zr. Zirconium's major use is as a cladding for uranium dioxide fuel rods in water-cooled nuclear reactors for its low absorption of 'Thermal' neutrons. Here the presence of Hf is disadvantageous, as Hf is a powerful absorber of 'Thermal neutrons'. So Hf content of Zr is reduced to less than 100 ppm.

EXERCISES

1. Define metal and mention some of its characteristics.
2. What do you mean by metallic bonds? Explain electrical conductivity of metal in the light of metallic bonds.
3. What do you mean by minerals and gangue? Give relations between them.
4. Distinguish between ores and minerals.

5. What do you mean by the study of metallurgy?

6. What is the concentration of ore?

7. Write down the different steps involved in the extraction of metals from corresponding ores.

8. Write short notes on:

(*i*) Crushing and Grinding
(*ii*) Oil floatation process
(*iii*) Calcination
(*iv*) Roasting

9. Briefly discuss the stages involved in concentration of ores.

10. What is flux? State the factors on which the selection of flux is based.

11. Describe different types of furnaces with their uses in metallurgy.

12. Write short notes on:

(*i*) Smelting
(*ii*) Welding

13. What is an alloy? Write (*a*) the importance of preparation of an alloy (*b*) general methods of preparation of alloys. Give the composition and uses of the following alloys:

(*i*) Mild steel
(*ii*) Stainless steel
(*iii*) Manganese steel
(*iv*) Duralumin
(*v*) Alnico
(*vi*) Wrought iron
(*vii*) Magnelium
(*viii*) Brass
(*ix*) Bronze
(*x*) Solder

14. What is cementation?

15. Give general method of extraction of metals from their ores.

16. Write notes on:

(*i*) Pyrometallurgy
(*ii*) Hydrometallurgy
(*iii*) Goldschmidt thermit process
(*iv*) Electro-refining
(*v*) Zone refining

17. Briefly describe the methods involved in purification of metals extracted.

18. Write a short review on powder metallurgy.

19. Mention four advantages of powder metallurgy.

20. Discuss the various steps involved in powder metallurgy and mention its application.

21. (*a*) How is metal powder prepared? Describe any two applications of powder metallurgy.

(*b*) What is sintering in powder metallurgy?