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NARSIMHA REDDY
ENGINEERING COLLEGE
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CHEMISTRY

UNIT I

WATER & ITS TREATMENT

- BY p chalapathi

Sources of water

- Surface water :-The water which comes from surface through rain. eg :- rain water, river water & sea water.

- Underground water :- This water comes from rain that falls on earths surface & then goes into the ground water & travel down the impervious (cracks) layers of earth, thus forming ground water. eg :- spring water & well water.

Impurities in Water

- Silica, clay etc
- CO_2, O_2, H_2S
- Bacteria & other Micro-organisms like algae & fungi
- Carbonates, Bicarbonates, Chlorides & Sulphates of Ca, Mg.

Types Of Water

HARD WATER

SOFT WATER

HARD WATER	SOFT WATER
Does not form lather with soap easily	Forms lather with soap easily
Contains dissolved salts of Ca & Mg	Does not contain dissolved salts of Ca & Mg
More wastage of time & fuel as boiling temp. of water gets increased due to impurities	Less wastage of time & fuel
More consumption of soap by hard water	Less consumption of soap by soft water

Hardness of water

- Hardness is the soap consuming capacity of water

- Hardness of water is due to the presence of Ca and Mg salts in it. Other ions responsible for hardness are Al^{3+}, Fe^{3+} and Mn^{2+}

- If Ca and Mg salts are present in water then they react with the soluble sodium soap to form insoluble salts calcium and magnesium.

- $2C_{17}H_{35}COONa + CaSO_4 \dashrightarrow (C_{17}H_{35}COO)_2Ca + Na_2SO_4$
  Sodium stearate Insoluble salt
- $2C_{17}H_{35}COONa + MgCl_2 \dashrightarrow (C_{17}H_{35}COO)_2Mg + 2NaCl$

Types Of Hardness

TEMPORARY

PERMANENT

Temporary Hardness

- Caused by the presence of dissolved bicarbonates of Ca, Mg and. This hardness is also known as alkaline hardness.
- Easily removed by heating :
- $Ca(HCO_3)_2 \xrightarrow{\text{Heat}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$
- $Mg(HCO_3)_2 \xrightarrow{\text{Heat}} Mg(OH)2 \downarrow + CO_2 \uparrow$

Permanent Hardness

- Due to the presence of sulphates and chlorides of Ca & Mg
- Cannot be removed simply by boiling.
- Special methods like lime soda process, zeolite process, ion-exchange method are used for the removal of permanent hardness.

Degree of Hardness in terms of $CaCO_3$ equivalent

- Hardness is expressed in terms of CaCO3 equivalents.

- Reasons for choosing $CaCO_3$ as the reference standard for calculating hardness of water is :

- mol. wt. is 100 that makes mathematical calculation easier.

- The most insoluble salt and can be easily precipitated in water treatment process.

How to calculate harness in terms of $CaCO_3$ equivalent

Hardness in terms of CaCO3 equivalents

$$= \text{wt. of hardness producing sub.} \times \frac{\text{mol. mass of CaCO3}}{\text{mol. mass of hardness producing sub.}}$$

Units of Hardness

a)	parts per million	ppm	parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.
b)	Milligrams per litre	Mg/l	no. of milligrams of $CaCO_3$ equivalent hardness per litre of water.
c)	Degree Clark	°Cl	parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.
d)	Degree French	°Fr	parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

Relation between various units of hardness

$$1\text{ppm} = 1\text{mg/l} = 0.1\,°\text{Fr} = 0.07\,°\text{Cl}$$

Units of Hardness

- Parts per Million (ppm): The number of parts of calcium carbonate equivalent hardness presents in 106 parts of water.

1ppm = 1 part of CaCO3 eq hardness in 106 parts of water

- Milligrams per litre (mg/l): The number of milligrams of calcium carbonate equivalent hardness presents in litre of water

1 mg/L = 1 mg of CaCO3 eq hardness in 1 litre of water
But one litre of water weights =1 kg =1000g = 1000 x 1000 mg = 106 mg = 1 ppm.

- Clark’s degree (° Cl): The number of parts of calcium carbonate equivalent hardness presents in 70,000 or (7×104) parts of water

1° Clarke = 1 part of CaCO3 eq hardness per 70,000 parts of water.

Units of Hardness

- Degree French (° Fr): The number of parts of calcium carbonate equivalent hardness presents in 105 parts of water.

1° Fr = 1 part of CaCO3 hardness eq per 105 parts of water.

Relationship between various units of hardness:

1 ppm = 1 mg/L = 0.1° Fr = 0.07° Cl

1 mg/L = 1 ppm = 0.1° Fr = 0.07° Cl

1 ° Cl = 1.433° Fr = 14.3 ppm = 14.3 mg/L

1 ° Fr = 10 ppm = 10 mg/L = 0.7° Cl

Boiler feed water

- For steam generations, boilers are used
- if hard water is fed to the boiler, various problems are faced by boiler :

- Scale and Sludge formation
- Priming and Foaming
- Boiler corrosion
- Caustic embrittlement

Sludge

❖ FORMATION:

- Where flow of water is slow
- At colder region
- By substances which have greater solubility in the hot water.
- $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

❖ DISADVANTAGES:

- Poor conductor of heat hence more consumption of time and fuel.
- Disturbs functioning of boiler & settles in the regions of poor water circulation.

❖ PREVENTION :

- By using soft water
- By using blow down pipe operation .

Scale

❖ FORMATION :

➢ Decomposition of $Ca(HCO_3)_2$:

- $Ca(HCO_3)_2 \longrightarrow \underset{\text{Soft Scale}}{CaCO_3} + H_2O + CO_2$
- $CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2$

➢ Deposition of $CaSO_4$:

- Soluble in cold water
- As temp. ↑ solubility of $\underset{\text{hard scale}}{CaSO_4}$ ↓

➢ Hydrolysis of Mg salts

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

➢ Presence of (SiO_2)

Scale

DISADVANTAGES

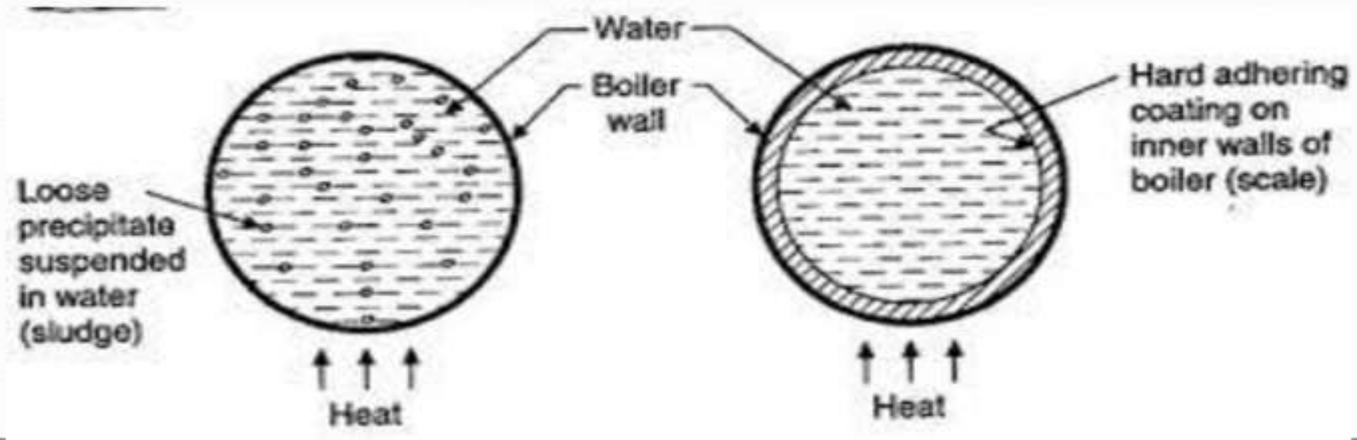
- Fuel Wastage
- Lowering of boiler safety
- Decreased efficiency
- Danger of explosion

Removal

- Using wire brush
- By using chemicals :
- $CaCO_3$ scales by 5-10% HCl
- $CaSO_4$ scales by EDTA
- Blow down pipe operation
- By giving thermal shocks

Sludge & Scale

- Continous evaporation of water takes place & conc. of dissolved salts gets increased & at saturation point forms ppts. on the inner walls of the boiler.
- Sludges : If loose & slimy ppts formed.
- Scales : If sticky, hard & adhernt coat formed.
-
- Sludge Scale



Scale

- **Prevention**

External Treatment

- By using soft water

INTERNAL TREATMENT

- Colloidal conditioning :
  - Addition of organic substances such as tannin, Agar- Agar
- Phosphate conditioning :
  - $CaCl_2 + Na_3PO_4 \longrightarrow$ Calcium phosphate $+ 6NaCl$
- Carbonate conditioning
  - $CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$
- Calgon conditioning
  - $CaSO_4 +$ calgon $\longrightarrow$ Soluble complexes of Ca ions
- Treatment with sodium aluminate :
  - $NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$

Difference between Sludge & Scale

Sludge	**Scale**
Soft, loose & slimy precipitates.	hard deposits.
Non-adherent deposits & can be easily removed.	Stick very firmly to the inner surface of boiler and are very difficult to remove.
Formed by substances like $CaCl_2$, $MgCl_2$, $MgSO_4$ & $MgCO_3$.	Formed by substances like $CaSO_4$, $Mg(OH)_2$, $CaCO_3$ & $CaSio_3$.
Formed generally at colder portions of the boiler.	Formed generally at heated portions of the boiler.
Decrease the efficiency of boiler but are less dangerous.	Decrease the efficiency of boiler & chances of explosions are also there.

Boiler Corrosion

- The chemical or electro-chemical eating away of metal by its environment in a boiler

❖ Cause

- Dissolved Oxygen :
- $2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2 + O_2 \longrightarrow 2(Fe_2O_3 . 2H_2O)$
- Dissolved CO_2 :
- $CO_2 + H_2O \longrightarrow H_2CO_3$
- Acids from dissolved salts :
- $MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$
- $Fe + HCl \longrightarrow FeCl_2 + H_2$
- $FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$

Boiler Corrosion

- **Disadvantages**
- Shortening of boiler life
- Leakages of joints and rivets
- Increased cost of repairs and maintenance
- **Removal of boiler corroision** :
- Removal of O_2 :
- $2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$
- $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$
- Removal of CO_2 :
- $2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$
- Removal of acids :
- By adding alkali

Caustic Embrittlement

- formation of brittle and incrystalline cracks in the boiler shell due to the accumulation of caustic substances

Cause

- Presence of alkali-metal carbonates and bicarbonates in feed water
- presence of sodium sulphate.
- Sodium carbonate is used in softening of water by lime soda process, due to this some sodium carbonate may be left behind in the water.

Process

- Na_2CO_3 used for softening of water & some of which remain unreacted

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$

- As Conc. of NaOH increases, water flows into minute hair cracks by capillary action.
- As water evaporates, conc. of NaOH increases further and react with iron of boiler, (thereby dissolving Iron of boiler as Sodium ferroate), hence cause Embrittlement.
- This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail.etc.

prevention :

- Use of Na_3PO_4 instead of Na_2CO_3
- By adding tanin & lignin that blocks the hair cracks
- By adding $NaSO_4$ that also blocks the cracks

Internal Treatment of Water

Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into compounds is called internal treatment of the boiler feed water. Internal treatment can be done following types.

Colloidal conditioning:

The addition of organic substances such as Kerosene, tannin, Gel. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

Internal Treatment of Water

Phosphate conditioning: The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation.

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaCl$$

$$3MgSO_4 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 3Na_2SO_4$$

Generally three types of Phosphates are employed.

i. Trisodium Phosphate (Na_3PO_4): is too alkaline used for treat to too acidic water.

ii. Disodium Phosphate (Na_2HPO_4): is weakly alkaline used for treat to weakly acidic water.

iii.Sodium dihydrogen Phosphate ($Na\ H_2PO_4$): is too acidic used for treat to too alkaline water.

Internal Treatment of Water

Calgon conditioning: Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$. Calgon = Sodium hexametaphosphate = $Na_2[Na_4(PO_3)_6]$

$$Na_2[Na_4(PO_3)_6] \rightarrow 2Na^+ + [Na_4P_6O_{18}]^{-2}$$

$$2CaSO_4 + [Na_4P_6O_{18}]^{-2} \rightarrow [Ca_2P_6O_{18}]^{-2} + 2Na_2SO_4$$

Softening Methods

The following methods are used :

- Lime soda Process
- Zeolite softening process
- Ion exchange process

Ion Exchange or De-ionization or De-mineralisation process

- Hard water is allowed to pass through ion exchangers when soft water, free from all the minerals and hardness causing as well as the other ions is obtained.

- Types
  - Cation Exchange Column represented with its H^+ ions
  - Anion Exchange Column represented with its OH^- ions

Ion exchange process

Ion exchange process is also known as demineralization process. Ion- Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the “functional Groups” attached to the chains are responsible for the ion-exchanging properties.

- ❖ Resins with acidic functional group are capable of exchanging H+ ions with other cations.
- ❖ Resins with basic functional groups are capable of exchanging OH− ions with other anions.

Resins are classified as:

- ➢ Cation Exchange Resins

Ion exchange process

- **Cation Exchange Resins:**

Cation exchange resins are styrene divinylbenzene co-polymers, which on sulphonation (or) carboxylation, which contains –COOH, –SO3H functional groups which responsible for exchanging their hydrogen ions with cations in water.

- **Anion Exchange Resins:**

Anion exchange resins are Phenol formaldehyde (or) amine formaldehyde copolymers, which contains amino or basic functional groups which responsible for exchanging their OH− ions with anions in water.

Ion exchange process

Process:

In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove Ca+2 and Mg+2 ions and exchange equivalent amount of H+ ions.

Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of OH− ions.

Thus by passing hard water through cation hardness is observed by the following reactions. H + and OH− ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

$$\mathrm{H} + + \mathrm{OH}^- \rightarrow \mathrm{H2O}$$

The water coming out from the exchanger is ion free from anions

Ion exchange process

Cation Exchange Resins:

$2RH + Ca(HCO)_2 \rightarrow R_2Ca + H_2CO_3$

$2RH + Mg(HCO)_2 \rightarrow R_2Mg + H_2CO_3$

$2RH + CaCl_2 \rightarrow R_2Ca + 2HCl$

$2RH + MgCl_2 \rightarrow R_2Mg + 2HCl$

$2RH + MgSO_4 \rightarrow R_2Mg + H_2SO_4$

$2RH + CaSO_4 \rightarrow R_2Ca + H_2SO_4$ (RH = Cation exchange resin)

Anion Exchange Resins:

$ROH + HCl \rightarrow RCl + H_2O$

$2ROH + H_2SO_4 \rightarrow R_2SO_4 + 2H_2O$

$ROH + H_2CO_3 \rightarrow RHCO_3 + H_2O$(ROH = anion exchange resin)

Process

Cation Exchange column :

$$\underset{\text{Cation exchange resin}}{2RH^{+}} + \underset{\text{H. W.}}{Ca^{+2}} \longrightarrow \underset{\text{Cation exchange resin}}{R2Ca^{+2}} + \underset{\text{S. W.}}{2H^{+}}$$

Anion Exchange column :

$$\underset{\text{Anion exchange resin}}{R'OH^{-}} + \underset{\text{H. W.}}{Cl^{-}} \longrightarrow \underset{\text{Anion exchange resin}}{R'Cl^{-}} + \underset{\text{S. W.}}{OH^{-}}$$

$$\underset{\text{Anion exchange resin}}{2R'OH^{-}} + \underset{\text{H. W.}}{SO4^{-2}} \longrightarrow \underset{\text{Anion exchange resin}}{R_2'SO4^{-2}} + \underset{\text{S. W.}}{2OH^{-}}$$

Regneration:

CationExchange column :

$$\underset{\text{Saturated Cation exchange resin}}{R_2Ca^{+2}} + \underset{\text{dil. acidic sol.}}{2H^{+}} \longrightarrow \underset{\text{Regenerated Cation exchange resin}}{2RH^{+}} + \underset{\text{washings}}{Ca^{+2}}$$

Anion Exchange column :

$$\underset{\text{Saturated anion exchange resin}}{R_2'SO4^{-2}} + \underset{\text{dil. Basic sol.}}{2OH^{-}} \longrightarrow \underset{\text{Regenerated Cation exchange resin}}{2R'OH^{-}} + \underset{\text{washings}}{SO4^{-2}}$$

POTABLE WATER

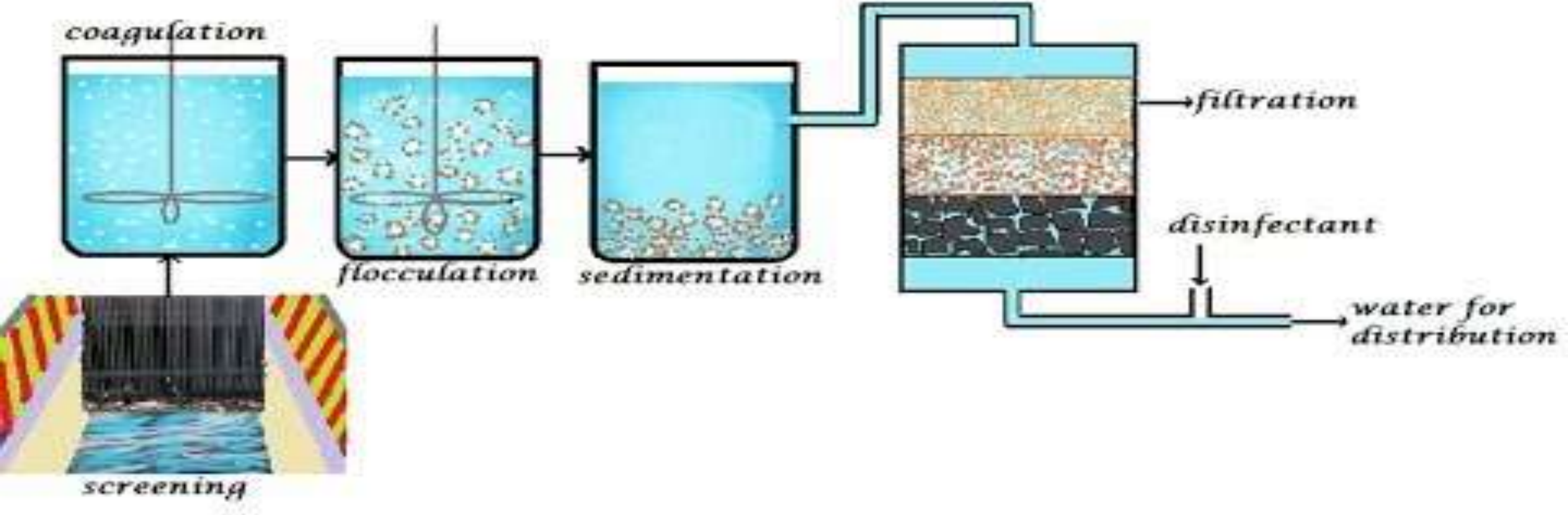
Potable water:

Water which is fit for drinking is called potable water.

Specification for drinking water

- It should be bacteria free
- It should not contain any suspended impurities
- It should not have bad taste.
- It should not contain toxic materials such as lead, arsenic, chromium and copper.
- pH should be in the range 7 to 8.5
- It should be slightly alkaline
- It should be free from dissolved gases like H_2S, CO_2 etc.
- Its turbidity should be less than 10 ppm.
- It should be cool
- It should be reasonably soft.

DRINKING WATER TREATMENT



Steps involved in the treatment of Potable water

Treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria. The following stages are involved in purification.

1. **Screening**: The water is passed through screens having larger number of holes; it retains floating impurities like wood pieces, leaves, heaver objectives etc.

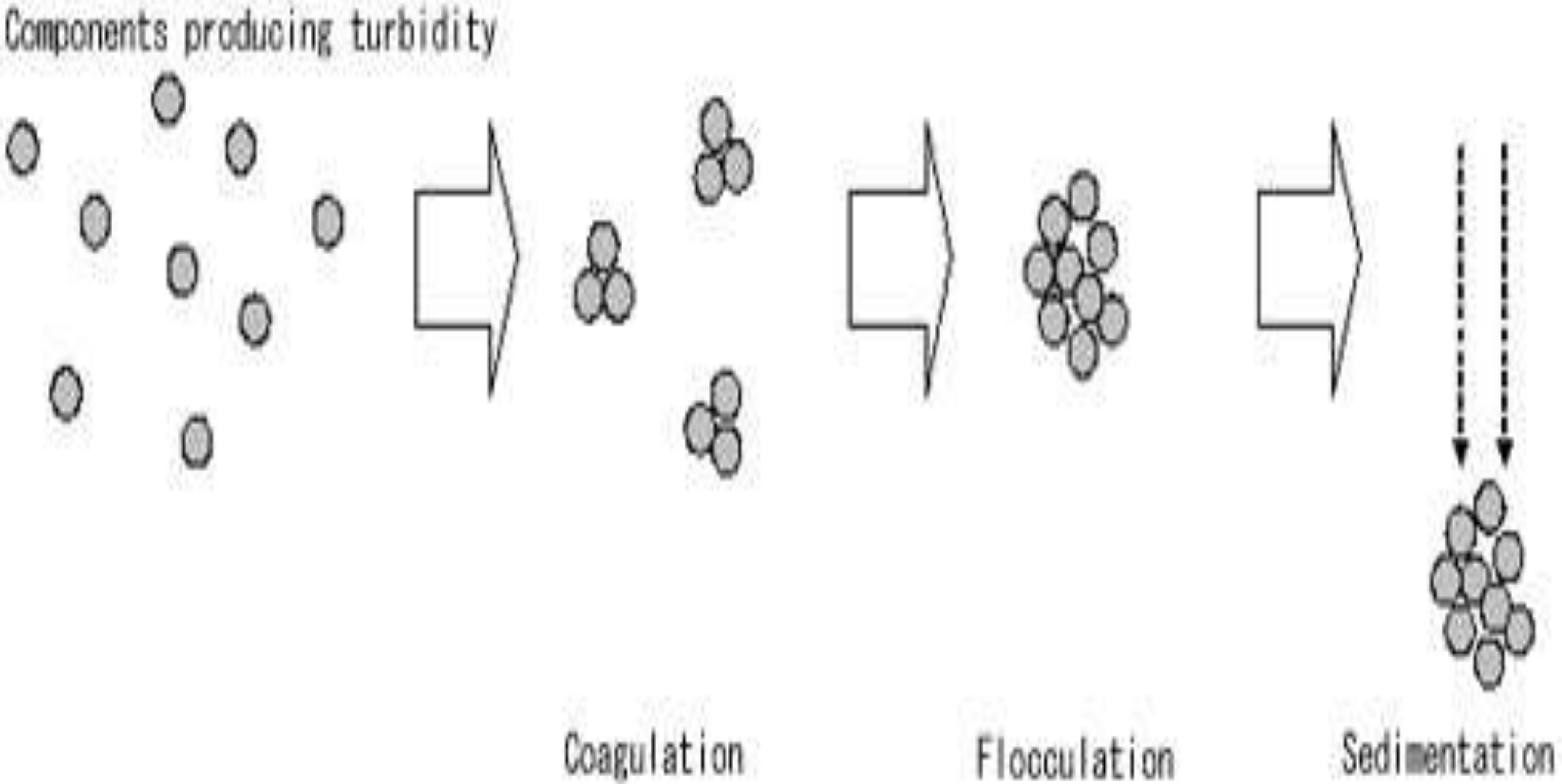
2. **Coagulation**: Coagulants like alum, sodium aluminates and Aluminum sulphate are added which produce gelatinous precipitates called flock. Flock attracts and helps

Steps involved in the treatment of Potable water

Sedimentation: Water is allowed to stand for few hours so that the suspended particles will det settle at the bottom of the tank.

Filtration: Filtration helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually sand filters are employed. In this filtration fine sand layer on the top supported by coarse sand layer, which is supported by gravel.

Disinfection of water by sterilization: The process of destroying the harmful bacteria is known as sterilization or


Components producing turbidity
Coagulation
Flocculation
Sedimentation

Disinfection of Potable water

- **By Ozonization:** Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down to give nascent oxygen.

$$O3 \rightarrow O2 + [O] \text{ nascent oxygen}$$

The nascent oxygen is a powerful oxidizing agent and kills the bacteria. **Disadvantages**: This process is costly and cannot be used in large scale, due to unstable of ozone cannot be stored for long time.

- **By Chlorination:** The process of adding chlorine to water is called chlorination. Chlorination can be done by the

Disinfection of Potable water

By adding Chlorine gas: Chlorine gas is a very good disinfectant, which can be bubbled in the water. In this process calculated amount of chlorine gas is passed in order to destroy the pathogenic bacteria is called chlorination. Chlorine is also reacts with water and generates hypochlorous acid and nascent oxygen, which acts a powerful oxidizing agent and kills the bacteria.

$\mathrm{Cl_2} + \mathrm{H_2O} \rightarrow \mathrm{HOCl}$ (Hypochlorous acid) + HCl

$\mathrm{HOCl} \rightarrow \mathrm{HCl} + [\mathrm{O}]$ nascent oxygen

By adding Chloramine: When chlorine and ammonia are mixed in the ratio 2:1 a compound chloramine is formed.

$\mathrm{Cl_2} + \mathrm{NH_3} \rightarrow \mathrm{ClNH_2} + \mathrm{HCl}$ Chloramin

Disinfection of Potable water

$ClNH_2 + H_2O \rightarrow NH_3 + HOCl$ (Hypochlorous acid)

$HOCl \rightarrow HCl + [O]$ nascent oxygen

Chloramine compounds decompose slowly to give nascent oxygen which will be act as good disinfectant than the Chlorine.

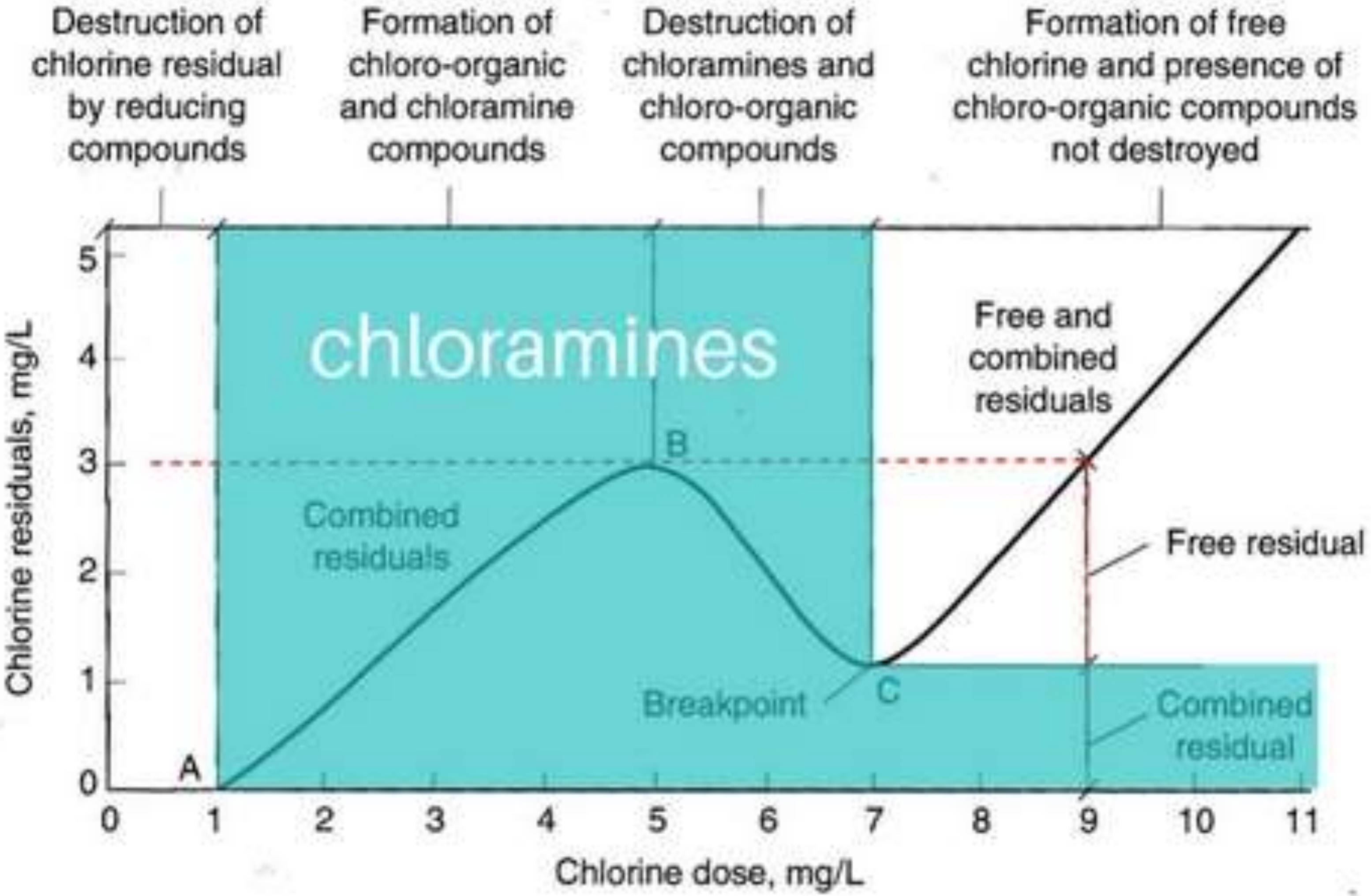
Chloramine gives good taste to the treated water.

BREAK POINT CHLORINATION

Break-point chlorination: The amount of chlorine required to kill bacteria and to remove organic matter is called breakpoint chlorination.

The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted a graph as shown below which gives the break-point chlorination.

From graph it is clear that: ‘a’ gms of chlorine added oxidizes reducing impurities of water.
‘b’ gms of chlorine added forms chloramines and other chloro compounds.
‘c’ gms of chlorine added causes destruction of bacteria.
‘d’ gms of chlorine is residual chlorine. ‘c’ gms is the break point for addition of chlorine to water.
This is called break- point chlorination.


Destruction of chlorine residual by reducing compounds
Formation of chloro-organic and chloramine compounds
Destruction of chloramines and chloro-organic compounds
Formation of free chlorine and presence of chloro-organic compounds not destroyed
chloramines
Free and combined residuals
B
Combined residuals
Free residual
Breakpoint
C
Combined residual
A
Chlorine residuals, mg/L
0
1
2
3
4
5
0
1
2
3
4
5
6
7
8
9
10
11
Chlorine dose, mg/L

BREAK POINT CHLORINATION

Advantages of breakpoint chlorination:
➢ It removes bad taste, colour, oxidizes completely organic compounds, ammonia and other reducing impurities ➢ It destroys completely (100%) all disease producing bacteria.

➢ It prevents growth of any weeds in water.

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UNIT -II

BATTERY CHEMISTRY AND CORROSION

Battery:

A battery is an arrangement of several electrochemical cells connected in series that can be used as a source of direct electric current

Cell: contains one anode and one cathode

Battery contains several anodes and several cathodes

Types of batteries

Primary batteries:

Not rechargeable

Electrode reactions cannot be reversed

Examples : Dry cell, mercury cells, lithium cells

Secondary batteries:

Can be recharged

Electrode reactions can be reversed

Examples: Lithium ion cell, lead acid battery, nickel cadmium battery

Lithium cells

Lithium cells with solid cathode

Anode: Li

Cathode: MnO2

Electrolyte: LiBF4 salt in a solution of propylene carbonate & dimethoxyethane

Lithium cells with liquid cathode

Anode: Li

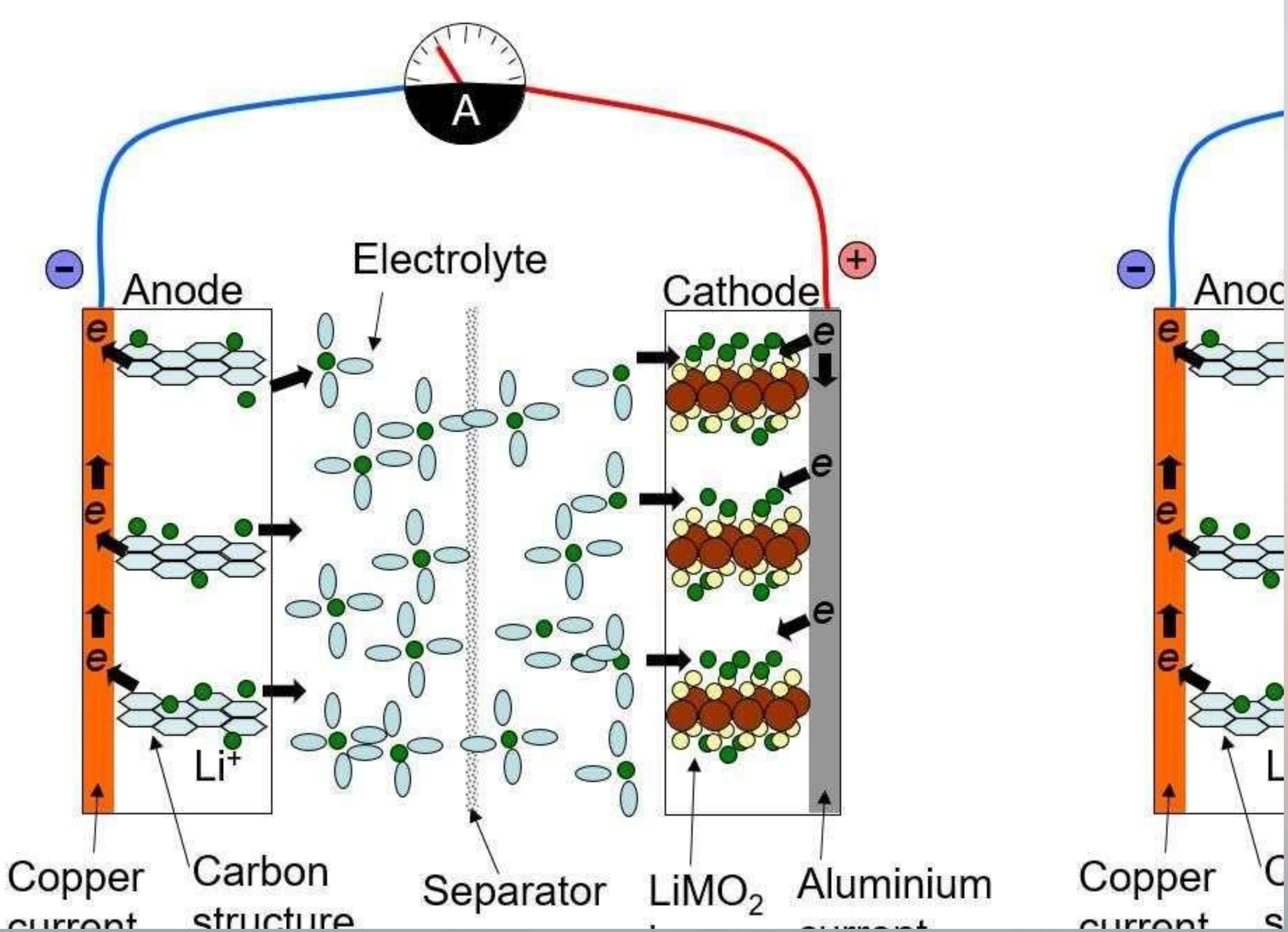
Cathode: SOCl2

Electrode: SOCl2

A LIB is an electrochemical device that stores/delivers electrical energy through a reversible intercalation reaction in which Li+ ions are shuttled between two dissimilar electrode materials separated by the Li+ ion conducting electrolyte solution.

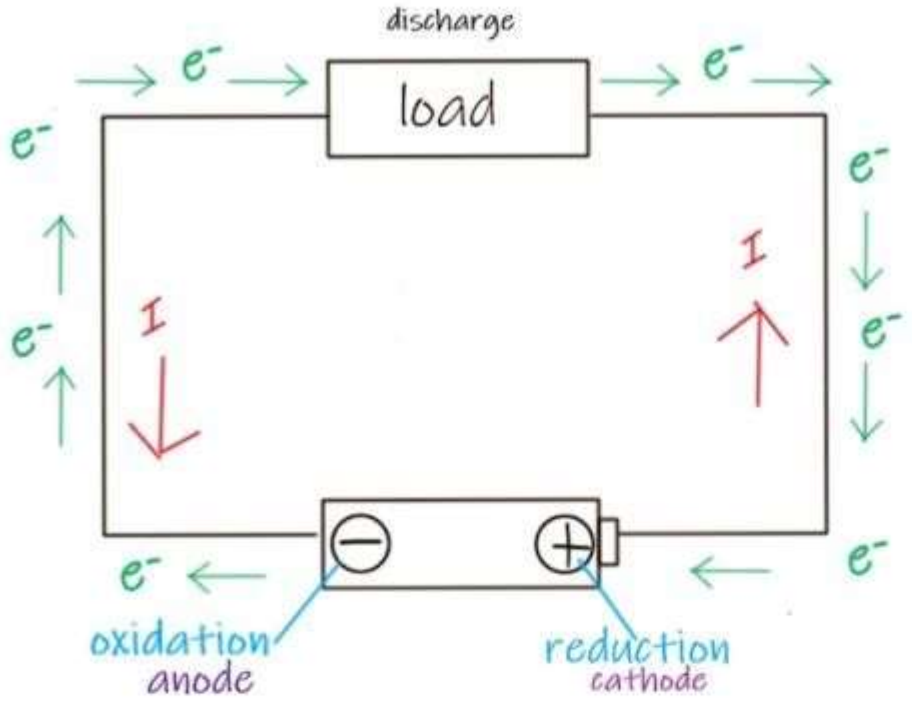
Lithium-ion batteries consisting of LiCoO2 and graphite are popular worldwide as power sources for mobile phones, laptop computers, and other electronic devices. Graphite and LiCoO2 are called lithium insertion materials. In other words, the lithium-ion Battery consists of two lithium insertion materials. The combination of two lithium insertion materials is essential for the basic function of the lithium-ion battery. An advantage of the lithium-ion battery concept is that the operating voltage of the battery can be designed by the choice of insertion reaction in terms of operating voltage and its charge–discharge profile.

Cathode, Anode and Electrolyte are the basic building blocks of Cells and Batteries.


A
−
Anode
Electrolyte
Cathode
+
e
e
e
e
e
e
Li$^+$
Copper current
Carbon structure
Separator
$LiMO_2$
Aluminium current
−
Anoc
e
e
e
Copper current
C
L

Lithium Ion Cells

When discharge begins the lithiated carbon releases a Li+ ion and a free electron. Electrolyte, that can readily transports ions, contains a lithium salt that is dissolved in an organic solvent. The Li+ ion, which moves towards the electrolyte, replaces another Li + ion from the electrolyte, which moves towards the cathode. At the cathode/electrolyte interface, Li+ ions then become intercalated into the cathode and the associated electron is used by the external device.


discharge
e⁻
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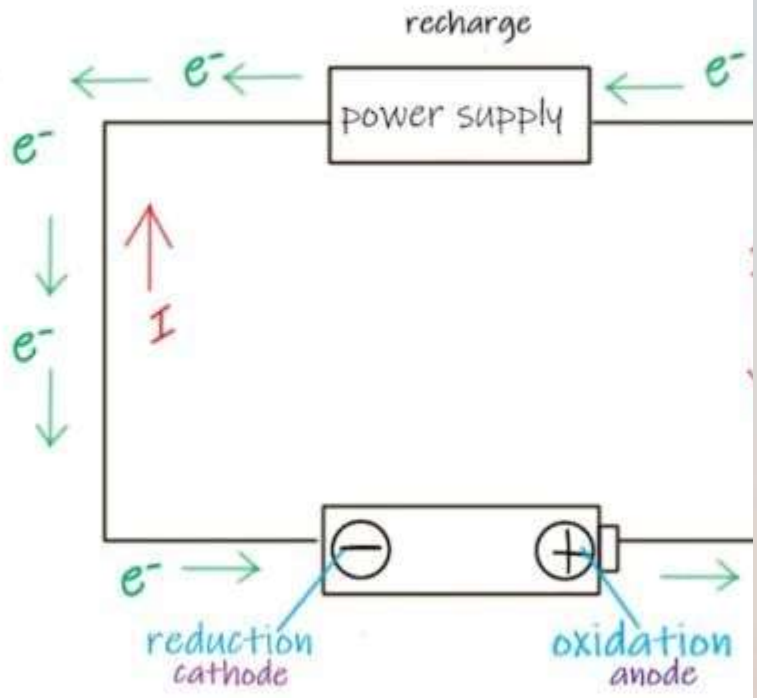
oxidation
anode
reduction
cathode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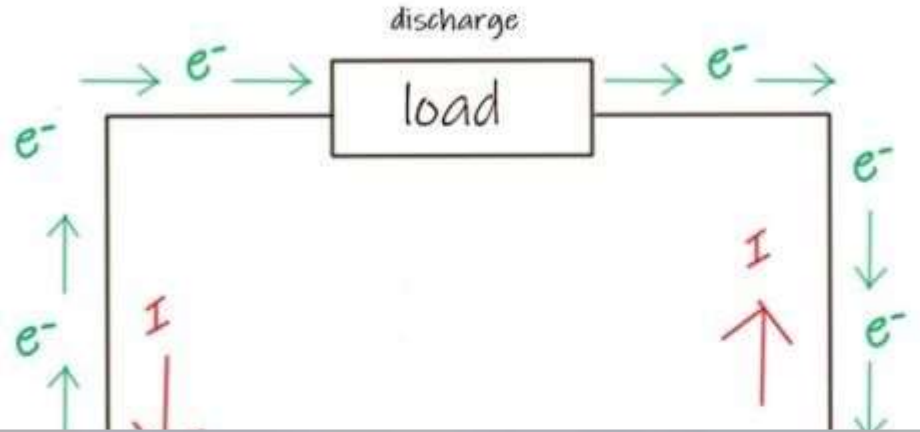
anode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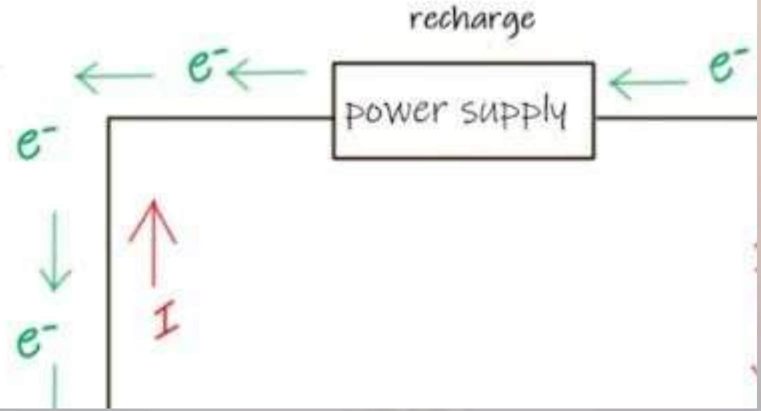
recharge
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power supply
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I

ANODE - CATHODE

Anode and Cathode are not fixed and change positions depending on whether the cell is being charged or discharged. It is therefore incorrect to state that the electrons move from Cathode to Anode during the recharging process. The – and + electrodes (terminals) however stay put. For example, in a typical Lithium ion cobalt oxide battery, graphite is the – electrode and LCO is the + electrode at all times.

Cathode

When discharging a battery, the cathode is the positive electrode, at which electrochemical reduction takes place. As current flows, electrons from the circuit and cations from the electrolytic solution in the device move towards the cathode. Although these processes are reversed during cell charge in secondary batteries, the positive electrode in these systems is still commonly, if somewhat inaccurately, referred to as the cathode, and the negative as the anode.

Cathode active material in Lithium Ion battery are most likely metal oxides. Some of the common CAM are given below

- Lithium Iron Phosphate – LFP or LiFePO4
- Lithium Nickel Manganese Cobalt oxide – LiNiMnCoO2 or NMC
- Lithium Manganese Oxide – LiMnO2
- Lithium Cobalt Oxide – LiCoO2

Many materials in cathode especially Lithium, Cobalt are rare and expensive. One of the ways to improve Lifecycle sustainability of Li Ion Batteries is to recycle the batteries especially to recover the cathode materials.

Cathode materials market was estimated $30Billion in 2023 and expected to grow to $70Billion by 2030. Cathode material today represents 30% approx of EV Battery cost.

Anode

The Anode is the negative or reducing electrode that releases electrons to the external circuit and oxidizes during and electrochemical reaction. In a lithium ion cell the anode is commonly graphite or graphite and silicon.

Anode Components

The anode is not just graphite or graphite and silicon. It needs additives to increase the conductivity and a binder to hold it all together.

Active material

graphite

natural synthetic graphite and

siliconsilicon

conductive additive

1. Carbon Black

Binder

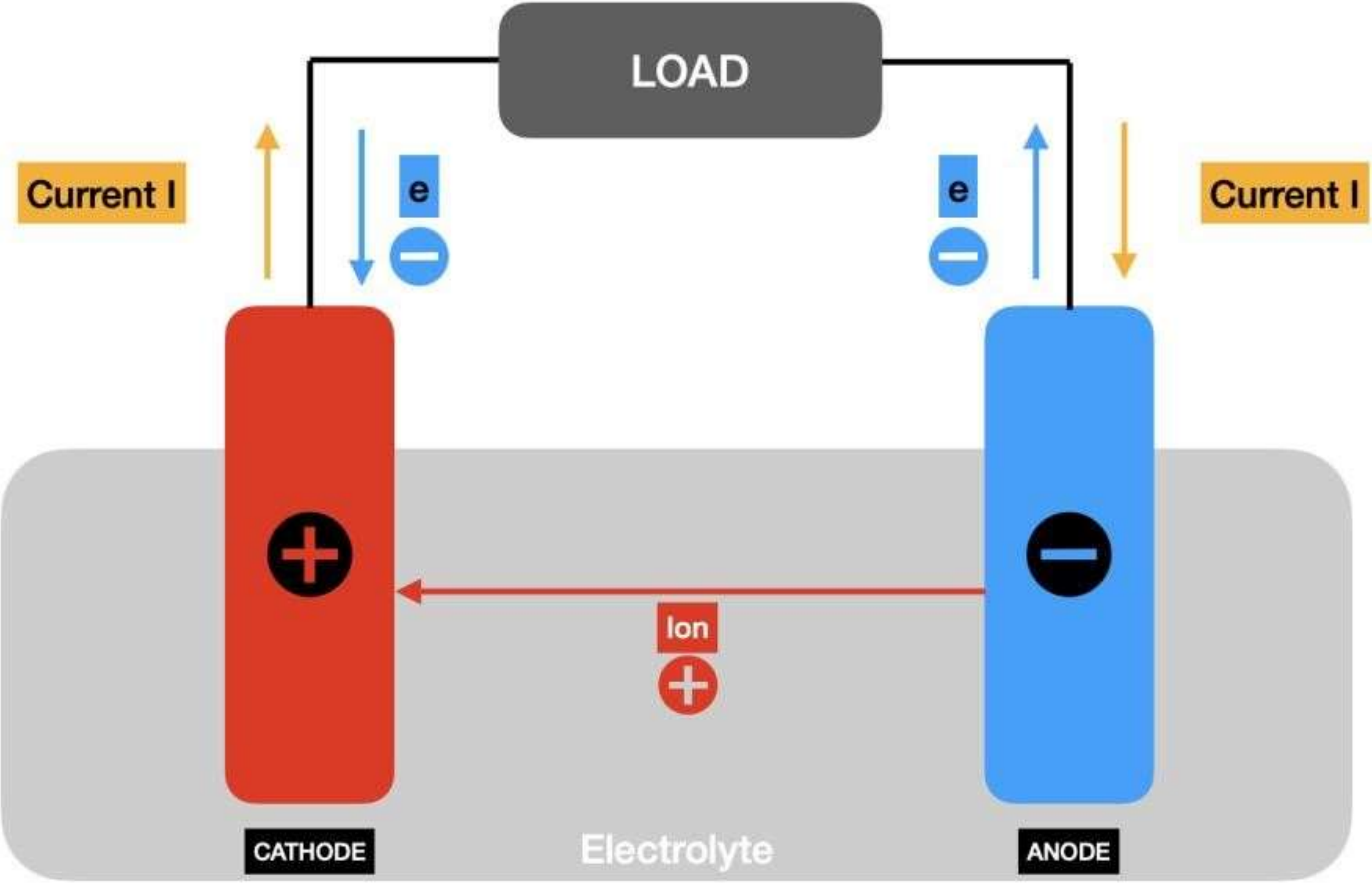
1. Carboxymethyl Cellulose (CMC)
2. Styrene Butadiene Rubber (SBR)

Electrolyte

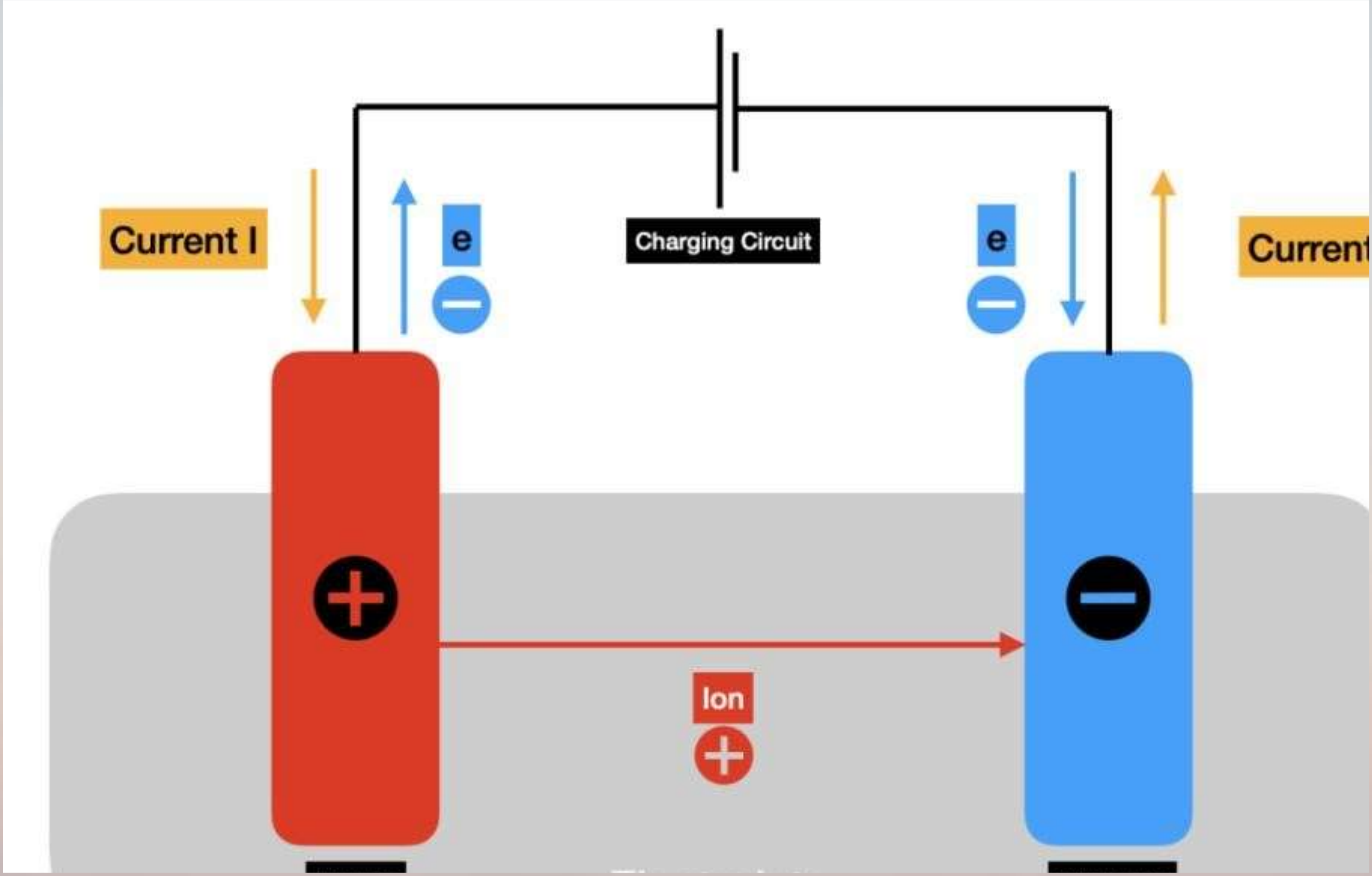
Electrolyte is an ionic transport medium. It can be liquid or solid. Liquid electrolytes transport ions between the electrodes and thus facilitate flow of electrical current in the cell or batteries.

Charging and Discharging cycle

To understand better cathode, anode and electrolyte lets see what role they play in functioning of a cell or battery.



DISCHARGING


Current I
e
Charging Circuit
e
Curren
Ion

What is fuel cell?

- A cell capable of generating electricity by converting chemical energy of the fuel directly into electrical energy.
- In simple words it is a electrochemical device which converts chemical energy into electric energy.

Parts of fuel cell

1. Anode
2. Cathode
3. Catalyst
4. Electrolyte

Cathode

- The cathode is the positive post of the fuel cell.
- It has channels etched into it that distribute the oxygen to the surface of the catalyst.
- It also conducts the electrons back from the external circuit to the catalyst, where they can recombine with the hydrogen ions and oxygen to form water.

catalyst

It is a chemical substance which increases the rate of reaction.

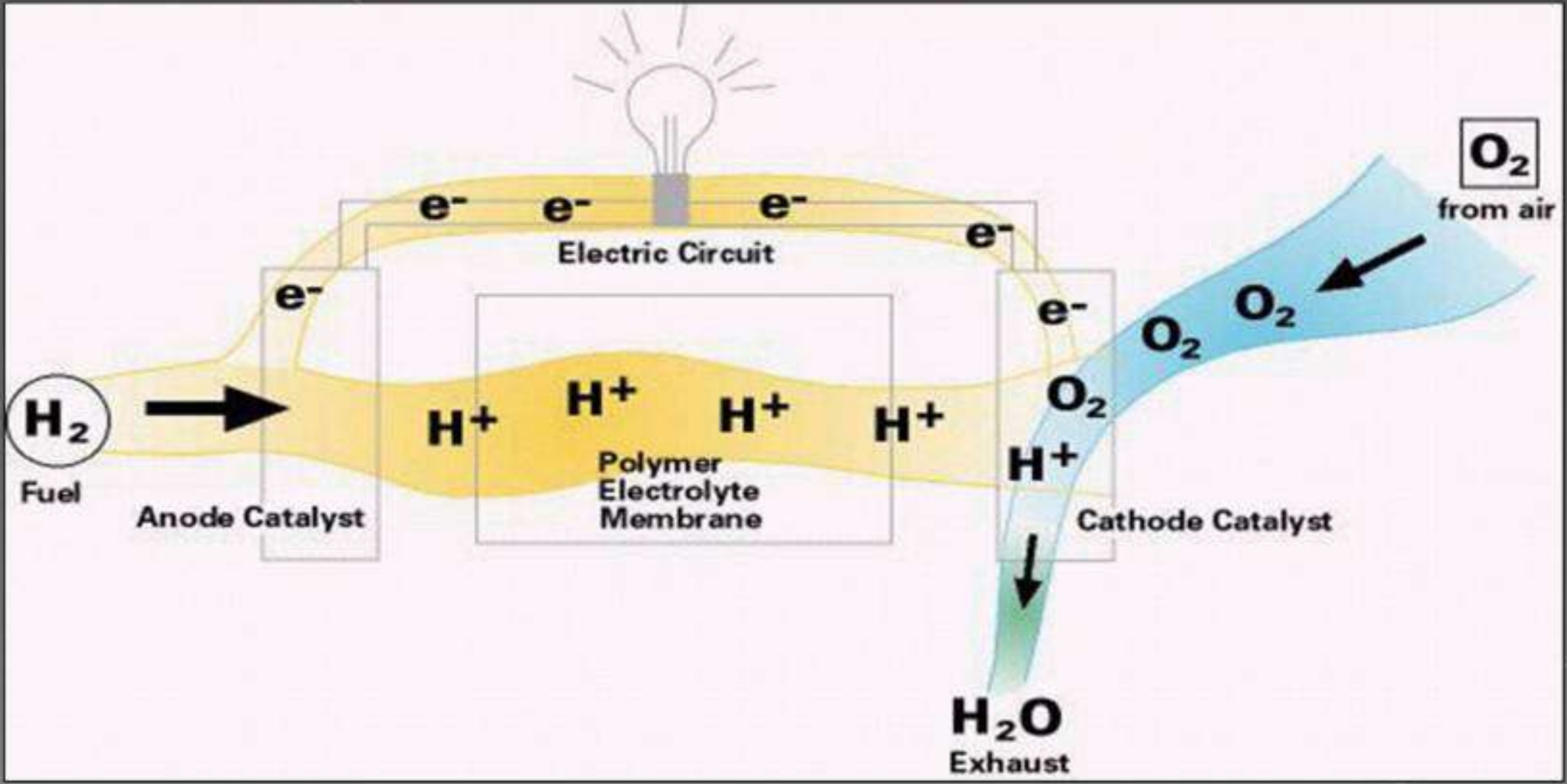
The catalyst is a special material that facilitates the reaction of oxygen and hydrogen.

It is usually made of platinum powder very thinly coated onto carbon paper or cloth. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen.

Mechanism of fuel cell

- A fuel cell consists of two electrodes - Anode and Cathode.
- Hydrogen and Oxygen are fed into the cell.
- Catalyst at Anode causes hydrogen atoms to give up electrons leaving positively charged protons.
- Oxygen ions at Cathode side attract the hydrogen

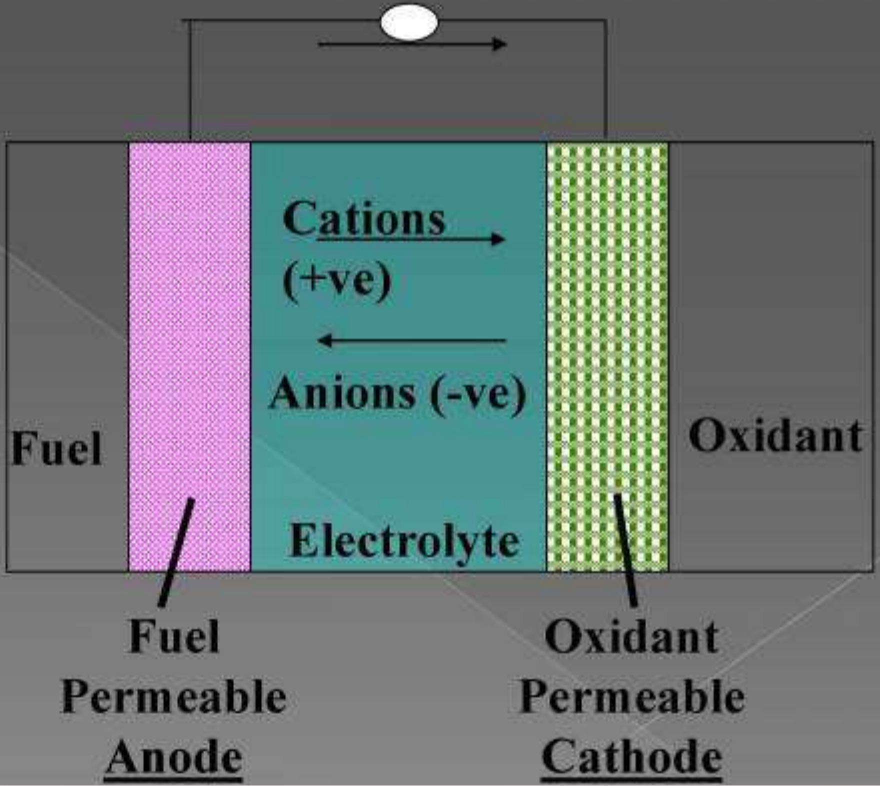
Mechanism of fuel cell



H2-O2 fuel cell

Principle:

- The fuel is oxidized on the anode and oxidant reduced on the cathode. One species of ions are transported from one electrode to the other through the electrolyte to combine there with their counterparts, while electrons travel through the external circuit producing the electrical current.



Working

The Fuel gas (hydrogen rich) is passed towards the anode where the following oxidation reaction occurs:

$$H_2 (g) = 2H^+ + 2e^-$$

The liberated electrons from hydrogen in anode side do not migrate through electrolyte.

Therefore, they passes through the external circuit where work is performed, then finally goes into the cathode.

On the other hand, the positive hydrogen ions (H^+) migrate across the electrolyte towards the cathode.

Continue…

At the cathode side the hydrogen atom reacts with oxygen gas (from air) and electrons to form water as byproduct according to:

The reaction proceeds in two steps:

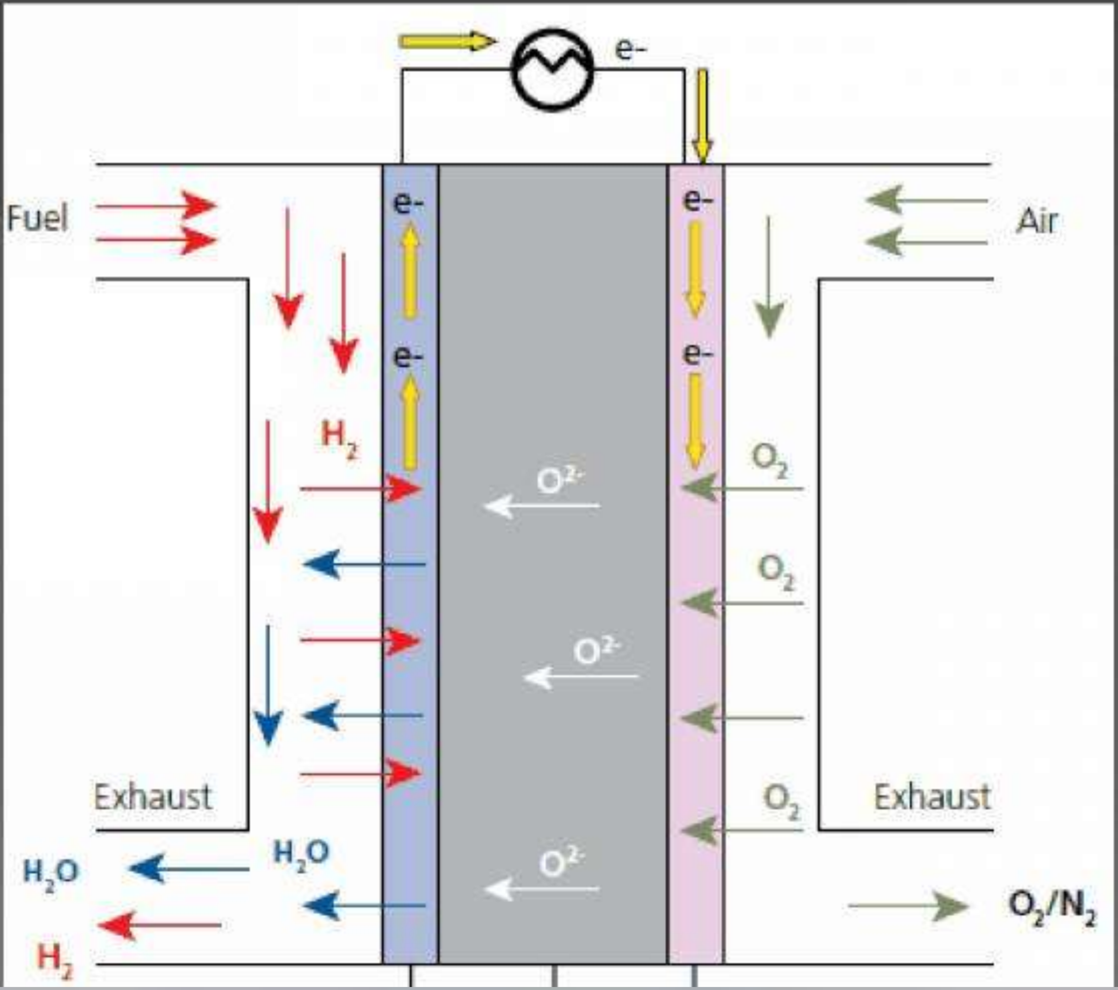
1. $0.5O2 + H2O + 2e^{-} \rightarrow 2OH^{-}$
2. $H+ + OH^{-} \rightarrow H2O$

Overall reaction is given as:
Fuel + oxidant → product + heat
$H2 + 0.5\ O2 \rightarrow H2O + heat$

Solid oxide fuel cell

- Certain solid have tendency to conduct electricity at high temperature and can serves as electrolytes for fuel cell.
- SOFCs are unique since in those, negatively charged oxygen ions travel from the cathode (positive side of the fuel cell) to the anode (negative side of the fuel cell) instead of positively charged hydrogen ions travelling from the anode to the cathode, as is the case in all other types of fuel cells.
- Oxygen gas is fed through the cathode, where it absorbs electrons to create oxygen ions. The oxygen ions then travel through the electrolyte to react with hydrogen gas at the anode. The reaction at the anode produces electricity and water as by-products. Carbon dioxide may also be a by-product depending on the fuel,

Construction and working



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2. $H^+ + OH^- \rightarrow H_2O$

Overall reaction is given as:

Fuel + oxidant → product + heat

$H_2 + 0.5\ O_2 \rightarrow H_2O$ + heat

Advantages of fuel cell

- They can be installed near the use point, thereby reducing the transmission losses.
- They have few mechanical components, so less attention and less maintenance is required.
- Atmospheric pollution is negligible if the primary energy source is hydrogen.
- As fuel cells don't make noise, they can be installed in residential areas.
- The fuel cell takes little time to go under operation.
- Space required by fuel cell in considerably less compared to other conventional methods

Disadvantages of fuel cell

- Main disadvantage of fuel cell is its high initial cost.
- Fuel cell has low service life.
- If hydrocarbon is the energy source in fuel cell then it emits carbon dioxide and no longer a green source.
- It is comparetively expensive.
- It is difficult to handle pure hydrogen.

CORROSION AND ITS CONTROL

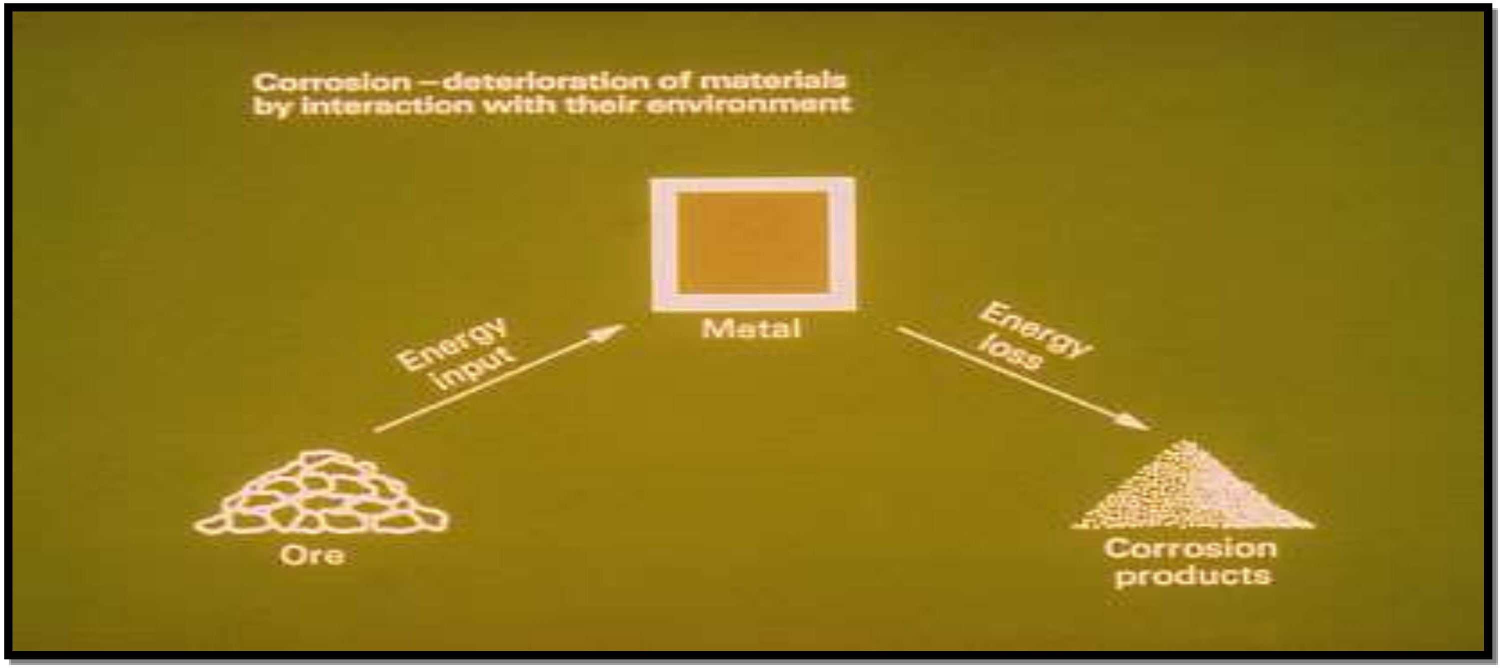
- **INTRODUCTION**
- **CAUSES OF CORROSION**
- **THEORIES OF CORROSION**
- **CORROSION REACTIONS**

- **FACTORS EFFECTING THE CORROSION**
- **TYPES OF CORROSION**
- **CORROSION CONTROL METHODS**

INTRODUCTION

- Destruction of a metal by chemical or electrochemical reaction with its environment.
- Physical or mechanical wearing away of a metal is not called corrosion but is called erosion
- If corrosion and erosion take place together the destruction of the metal takes place very much faster
- Corrosion is an unintentional attack on a material by reaction with a surrounding medium
- The corrosion problem should be very seriously considered in all those cases where the structure or the equipment is meant to last many years say 20 years…

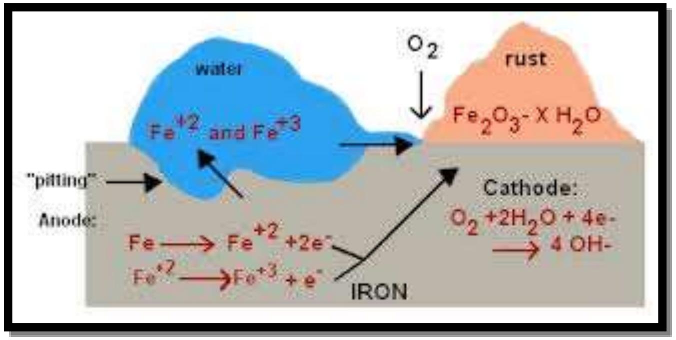
Definition of Corrosion



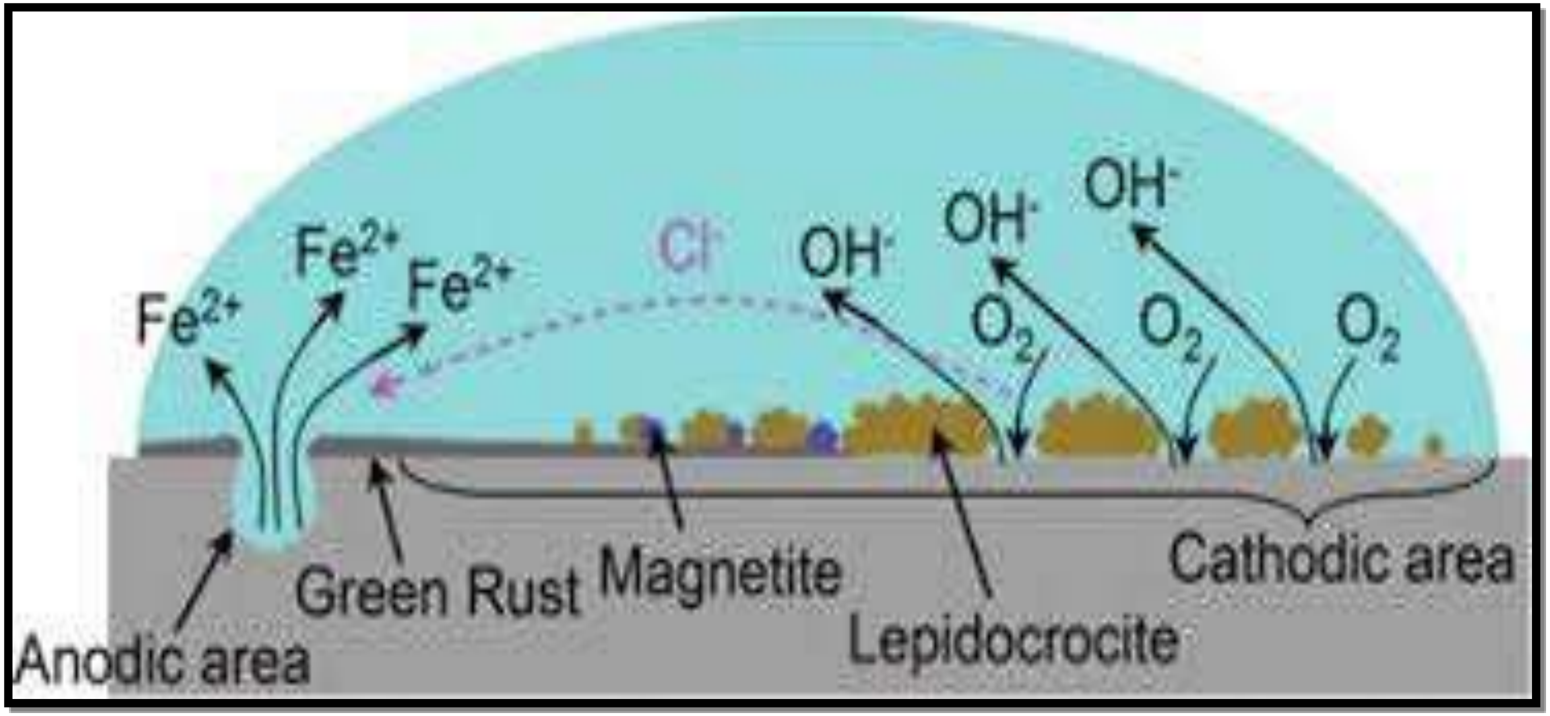
Corrosion – deterioration of materials by interaction with their environment

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals.

Rusting of iron



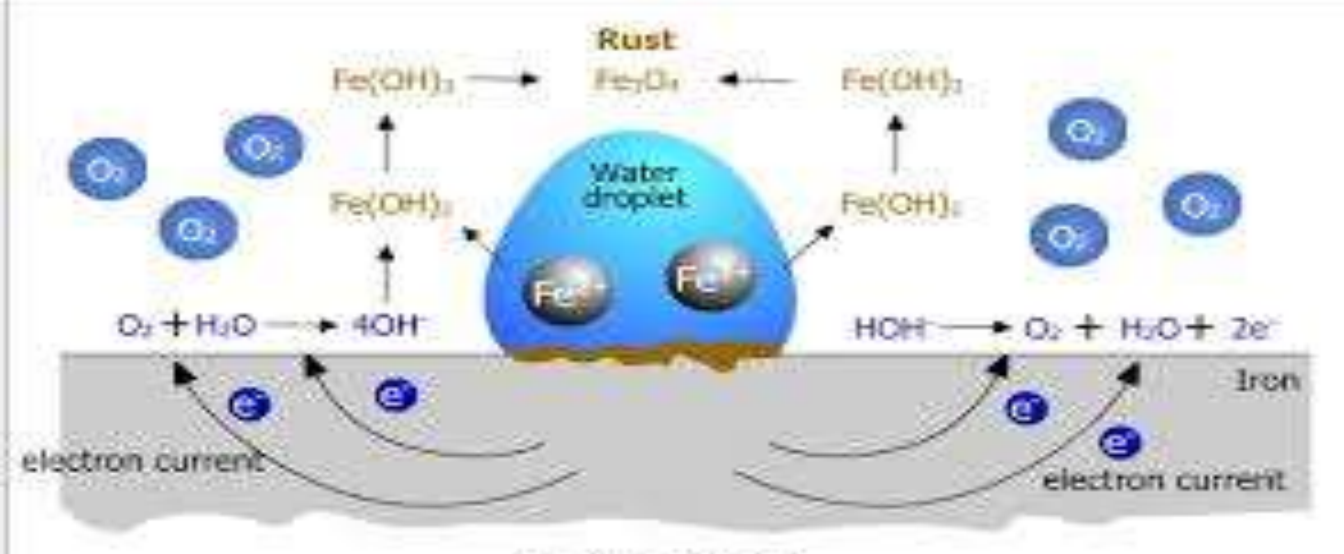
Formation of green rust



CAUSES OF CORROSION

- The chemical combined state of the metal is known as **“ore”**
- The ore has low energy in its thermodynamical state.
- The extracted metal has high energy ,thermodynamically unstable .
- Metal converts itself into stable state by reacting with the environment and undergoes corrosion.
- The corroded metal is thermodynamically stable.

Formation of rust



Formation of Rust.

Effects or disadvantages of corrosion

- The valuable metallic properties like conductivity,malleability, ductility etc are lost due to corrosion.
- Life span of the metallic parts of the machineries is reduced.
- The process of corrosion is very harmful and is responsible for the enormous wastage of metal in the form of its compound.
- The failure of the machinery takes place due to lose of useful properties of metals.
- The approximate estimate of loss of metal due to corrosion is 2 to 2.5 billion dollars per annum all over the world.


1 mm

TYPES OF CORROSION

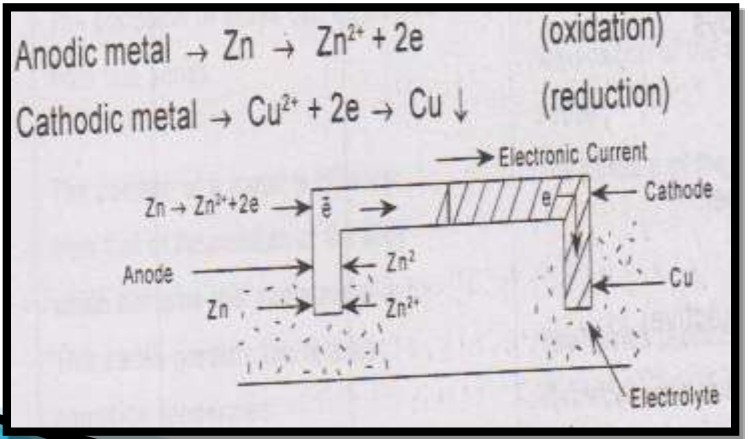
Different types of electrochemical corrosions are

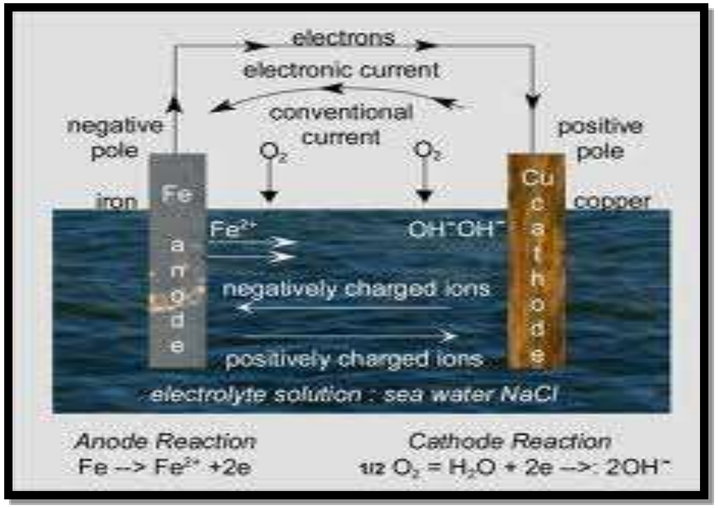
- Galvanic corrosion
- Pitting corrosion
- Intergrannular corrosion
- Water line corrosion

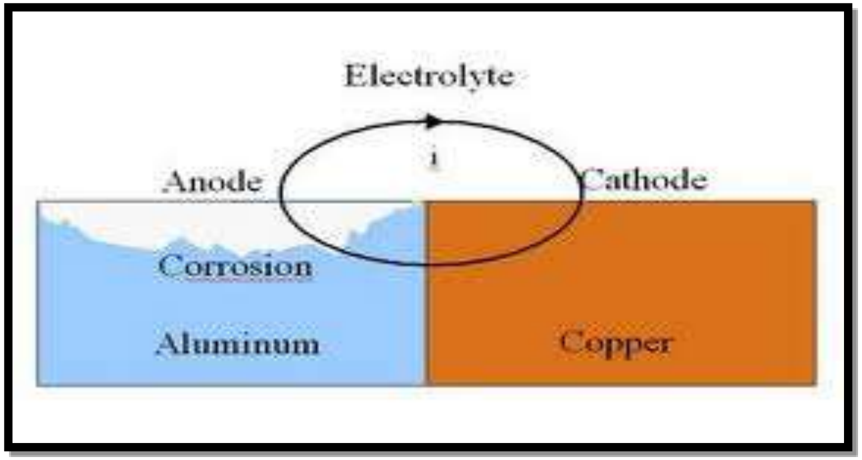
Galvanic corrosion

- This corrosion occurs when different metals are in contact and exposed to corrosive atmosphere.

- The metal which has higher electrode potential value will form anode and undergoes corrosion. Example: Zn-Cu galvanic cell zinc behaves as anode and corrosion occurs, copper behaves as cathode and protected.

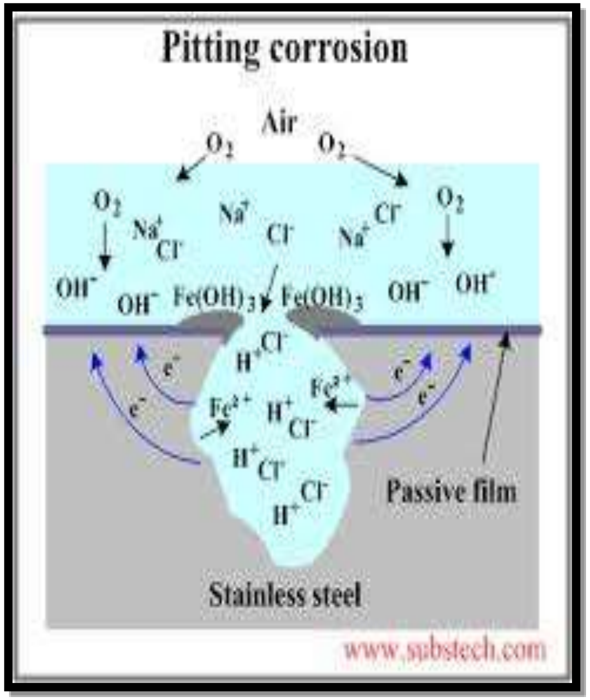


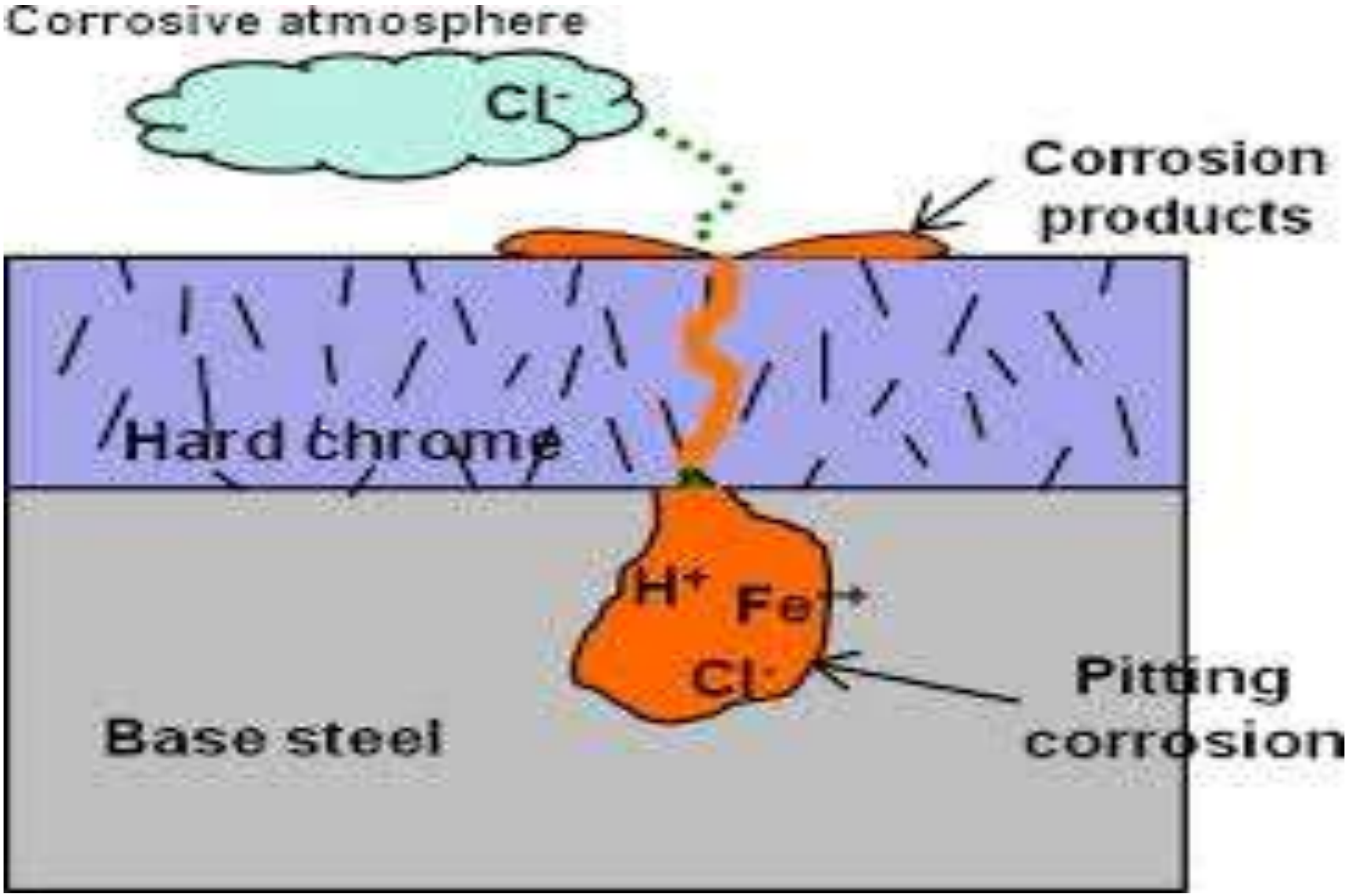



Electrolyte
i
Anode
Cathode
Corrosion
Aluminum
Copper

Pitting corrosion

- When corrosion starts on a metal surface at certain spots they become less open to oxygen with the result that corrosion proceeds faster at those very spots making deeper and deeper cavities.
- Pitting corrosion can be explained on the basis of differential aeration.
- The pit created becomes deeper, its bottom becomes less open to oxygen which makes it more anodic.
- The part which has higher oxygen concentration is cathodic.




Corrosive atmosphere
Cl⁻
Corrosion products
Hard chrome
H⁺
Fe⁺⁺
Cl⁻
Pitting corrosion
Base steel

Water line corrosion

- The concentration of oxygen dissolved in water is greater at the surface than deeper down. This causes formation of a concentration cell.

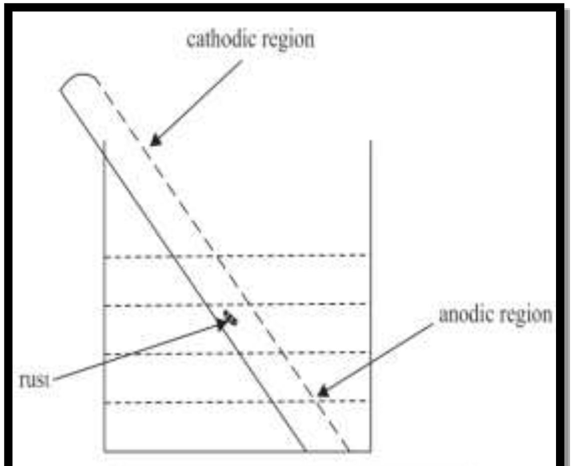


Fig. 13.3 Water line corrosion

- Anode is the lower portion .

- Cathode is at the water level.

- Due to the poor conductivity of water the ions just below the water level are available for reaction, the metal corrodes just below the water level.

Theories of corrosion

THEORIES OF CORROSION

- In atmospheric corrosion the metals tend to revert to the states in which they occur in nature.

- Several theories of corrosion have been proposed from time to time..

- The three theories are
  - i) ACID THEORY
  - ii) CHEMICAL CORROSION (**DRY CORROSION**)
  - iii) ELECTROCHEMICAL CORROSION (**WET CORROSION**)

ACID THEORY

Acid theory of corrosion considers acid to be the main cause.

Rusting takes place faster in acid solutions than in neutral or basic solutions.

Oxygen and water are necessary for rusting of iron.

This is not true for all the metals like Zn etc..

Rate of corrosion in absence of Carbon di oxide is also seen.

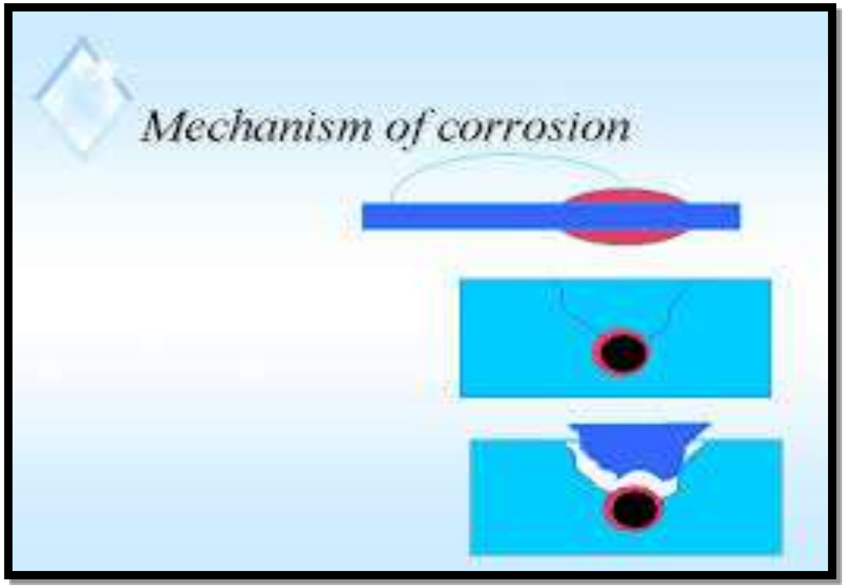
Dry corrosion or chemical corrosion

- The direct chemical reaction of environment/atmospheric gases or inorganic liquids with metal surfaces .
- There are three types of chemical corrosion

i) Oxidation corrosion

ii) Corrosion by other gases

iii) Liquid metal corrosion



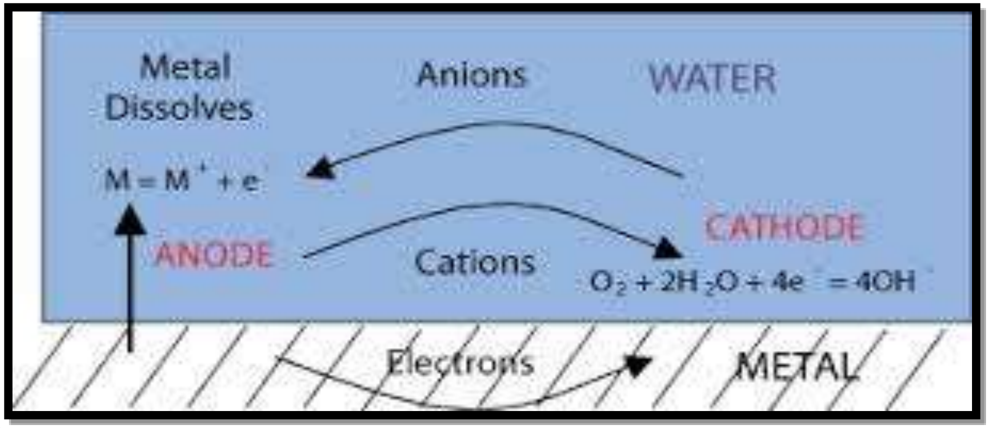
(1.) Oxidation Corrosion: This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture.

Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).

$M \rightarrow M_2^+ + 2e^-$ (Oxidation)

$O_2 + 2e^- \rightarrow 2O_2^-$ (Reduction)

$M + O_2 \rightarrow M_2^+ + 2O^{2-}$ (Metal oxide)



Mechanism:-

1. When temp increases the metal undergoes oxidation and losses e^-

$$2M \rightarrow 2M^{+n} + 2ne^-$$

Metal Ion

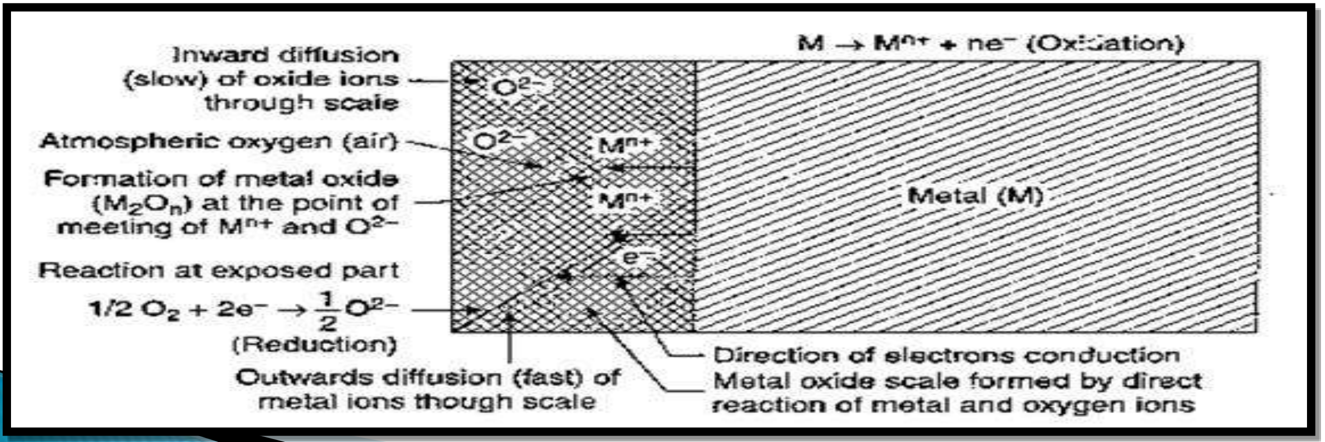
2. Electron are gained by the oxygen molecules forms oxide ions

$$nO_2 + 4ne^- \rightarrow 2n\, O^{2-}$$

Oxide Ion

3. Scale of metal oxide formed $2M + nO_2 \rightarrow 2M + 2n\, O^2$

Metal Oxide



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.

$Ag + Cl_2 \rightarrow 2AgCl$ (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 or Electrochemical corrosion

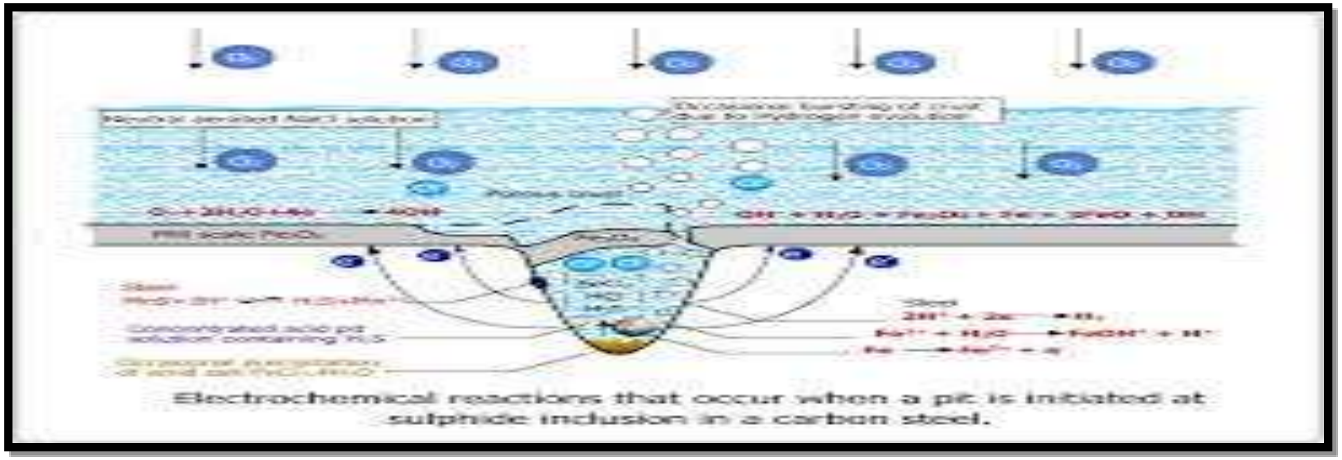
- The electrochemical corrosion occurs when

  i) a conducting liquid is in contact with a metal.

  ii) when two dissimilar metals or alloys are immersed partially in the solution.

- Corrosion occurs due to the presence of anodic and cathodic areas.

- At anode oxidation reactions takes place
- At cathode reduction reactions takes place



Electrochemical reactions that occur when a pit is initiated at sulphide inclusion in a carbon steel.

- Occurs when aqueous solution or liquid electrolytes are present

- Wet corrosion takes place in environments where the relative humidity exceeds 60 %.

- Wet corrosion is most efficient in waters containing salts, such as NaCl (e.g. marine conditions), due to the high conductivity of the solution.

Mechanism Of Electrochemical Corrosion

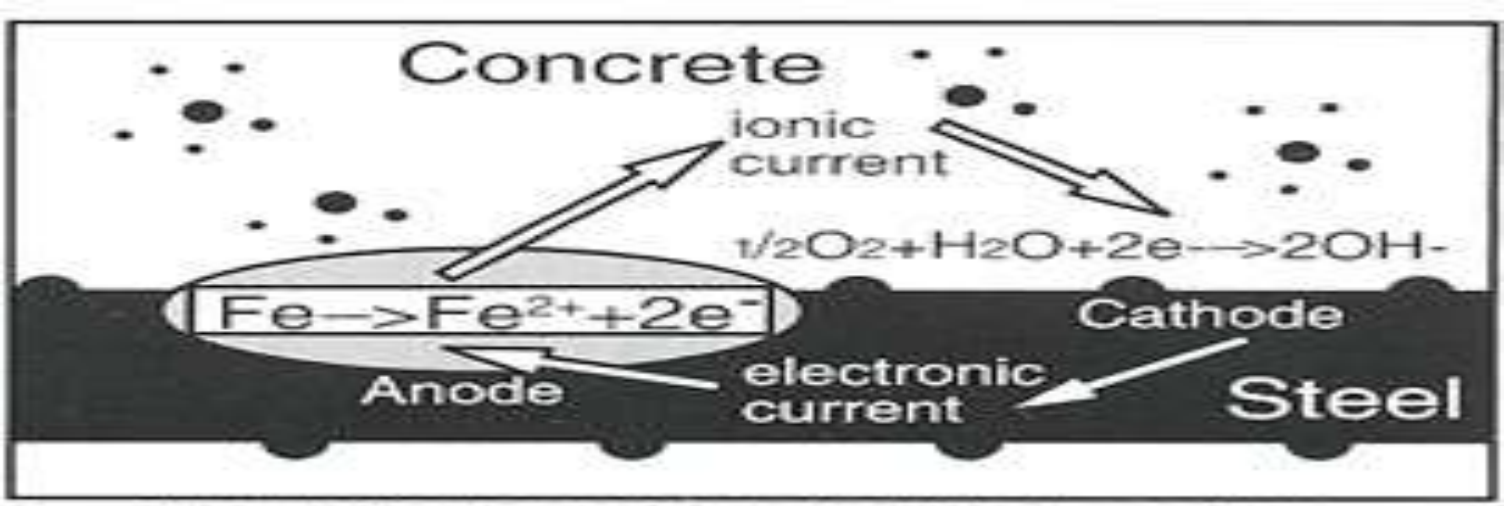


Figure 1: The anodic and cathodic reactions

Mechanism Of Electrochemical Corrosion

Anodic Reaction:

Dissolution of metal takes place.

As result metal ions are formed with the liberation of free electrons.

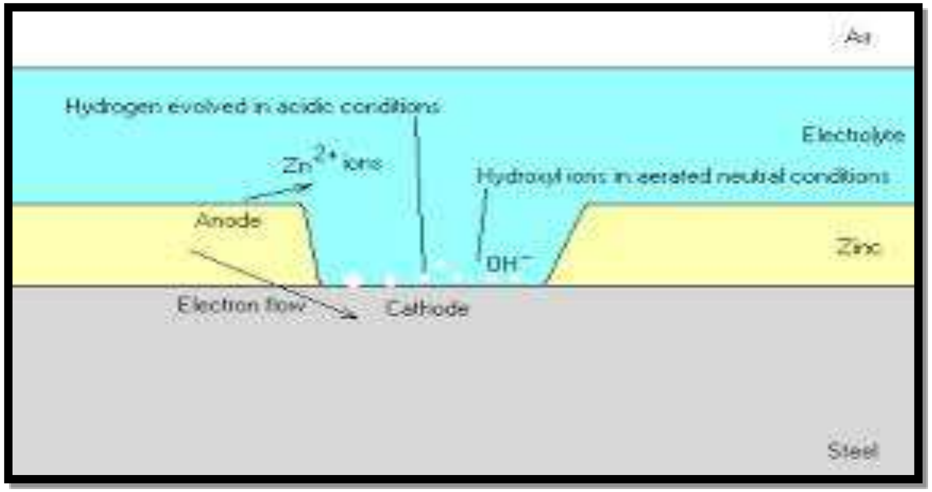
$$M \leftrightarrow M^{+n} + e^{-}$$

Metal Ion

Cathodic Reaction

(i) Hydrogen Evolution :- Occurs usually in acidic medium

$$2H^+ + 2e^- \leftrightarrow H_2\ (g)$$



(ii) Oxygen Absorption :- occurs when solution is aerated sufficiently.

$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ (In acidic medium)

$O_2 + 4H^+ + 4e^- \leftrightarrow 4OH^-$ (In basic medium)

Wet corrosion takes by the following ways.

- Hydrogen gas evolution
- Oxygen gas absorption

This type of corrosion occurs in acidic medium.

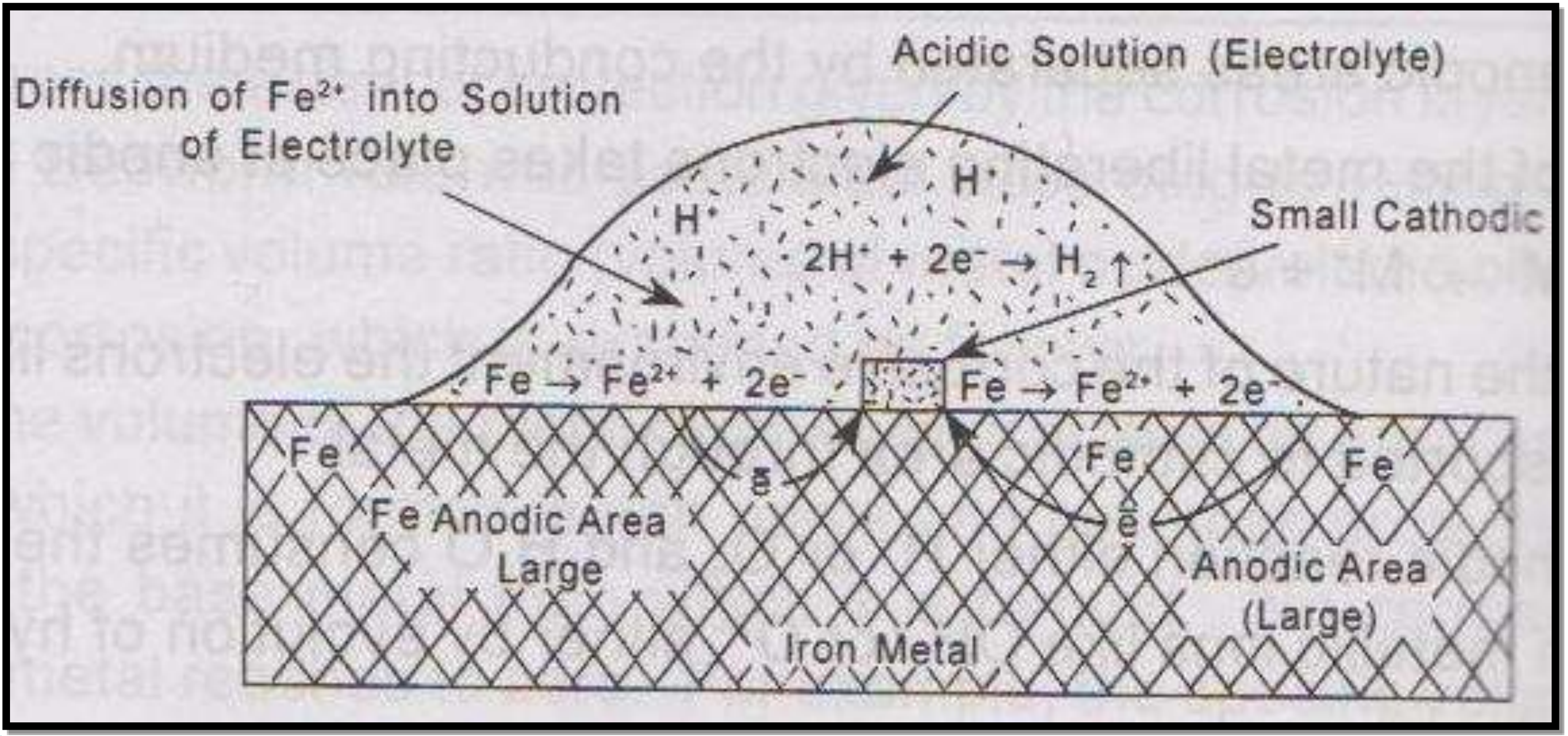
E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.
Anode: $Fe \text{----}\rightarrow Fe_2^+ + 2e^-$ (Oxidation)

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

  Cathode: $2H^+ + 2e^- \text{----}\rightarrow H_2$ (Reduction)
- The overall reaction is: $Fe + 2H^+ \text{-----}\rightarrow Fe_2^+ + H_2$

- All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas.

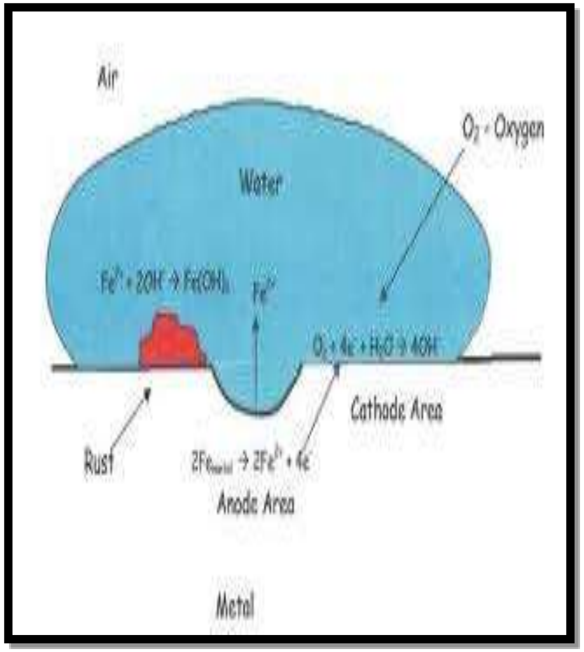
Mechanism of wet corrosion by hydrogen evolution



Absorption of oxygen

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.

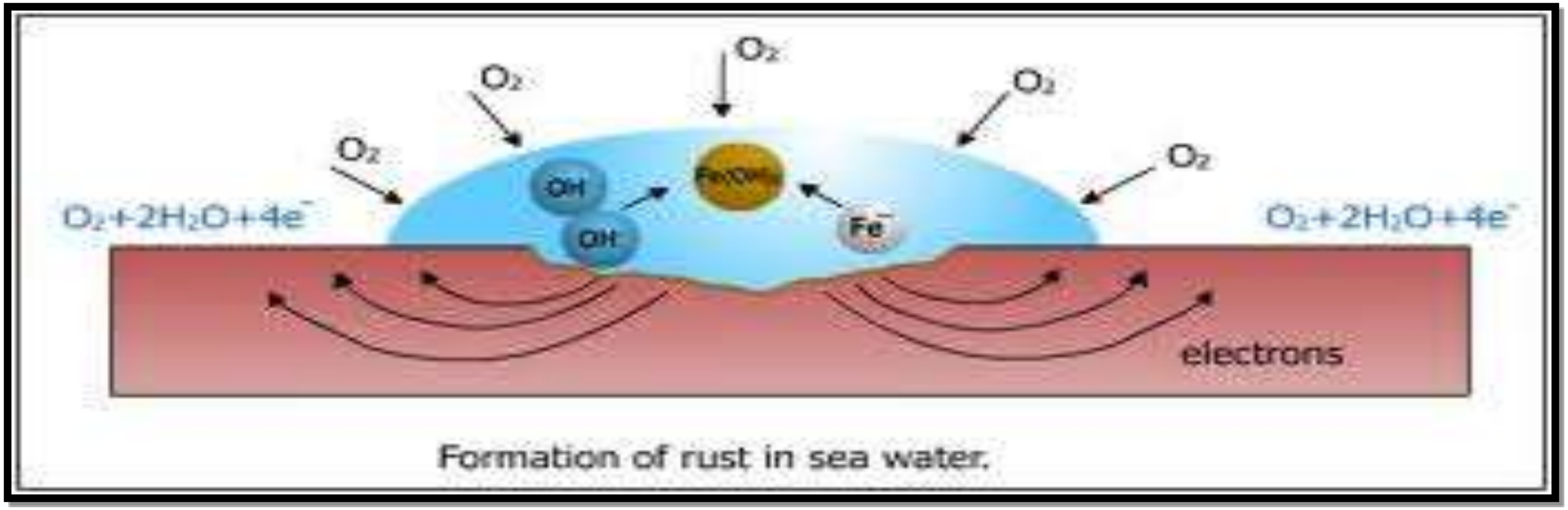


The released electrons flow from anode to cathode through iron metal.

.

At anode: Fe ----→$Fe_2^+ + 2e^-$ (Oxidation)
At cathode: ½ $O_2 + H_2O + 2e^-$ ---→$2OH^-$ (Reduction)
Overall reaction: $Fe_2^+ + 2OH^-$ -----→ Fe $(OH)_2$

The product called yellow rust corresponds to
$Fe_2O_3 . 3H_2O$



Formation of rust in sea water.

FACTORS EFFECTING THE CORROSION

- The factors that effect corrosion are

  i) Nature of the metal

  ii) Nature of the environment

Nature of the metal

- The rate and the extent of corrosion depends on the following factors

A) Purity of a metal

B) Position in galvanic series

C) Over voltage

D) Nature of oxide film

E) Nature of corrosion product

Nature of the 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 (e.g.. 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.

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.

***4.Relative areas of anodic and cathodic cells**:* When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. *i.e*, the relative areas o of corrosion is influenced by cathodic to anodic cells.

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

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

Nature of the 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. pH 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.

6.Velocity of ions which flow in the medium: As the velocity of the diffusion of the ions in the medium increases, the rate of corrosion increases .

CORROSION CONTROL METHODS

The various measures taken for corrosion protection are

I) CATHODIC PROTECTION

II) SURFACE COATINGS

CATHODIC PROTECTION

- The method of protecting metals and alloys from corrosion making them completely cathode.

- To achieve this auxilary anode is provided in the corroding medium which is connected to the structure.

- Cathodic protection is of two types

i) Sacrificial anodic method

ii) Impressed current cathodic method

Cathodic Protection

Force the metal to be protected to behave like cathode.

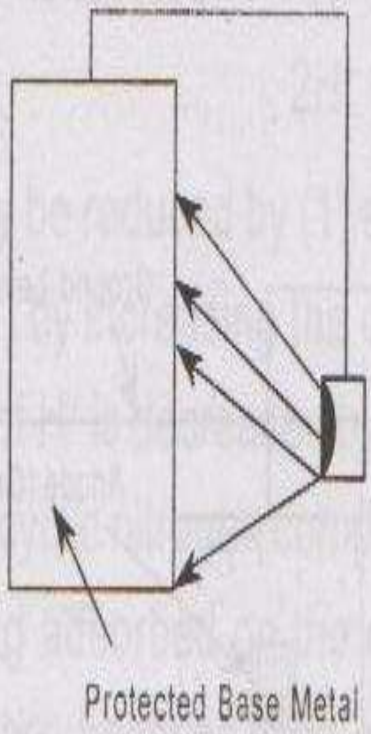
(i) **Sacrificial anodic protection**:

- Metal to be protected from corrosion connected to more anodic metal
- Commonly used metals Mg, Zn, Al and their alloys

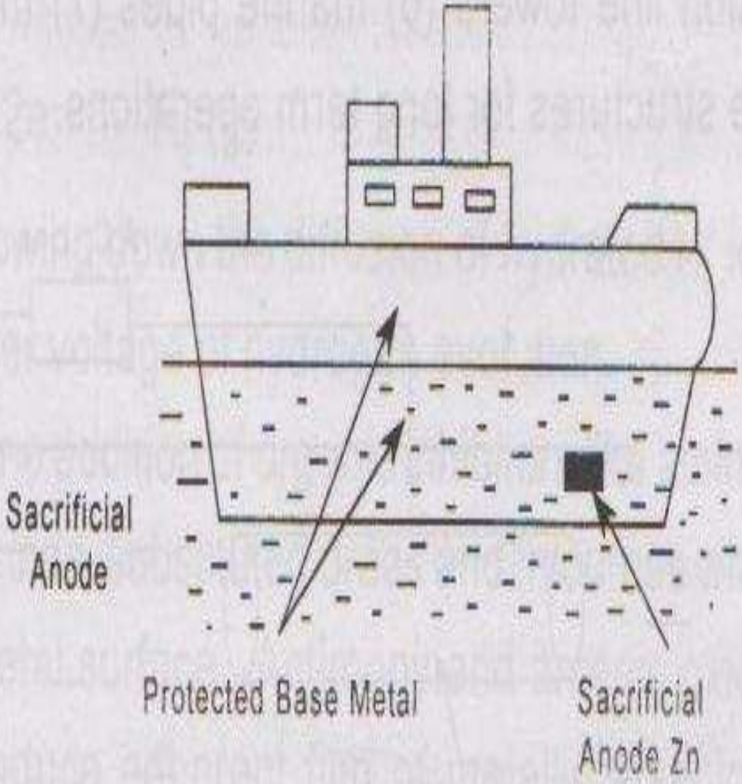
Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

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



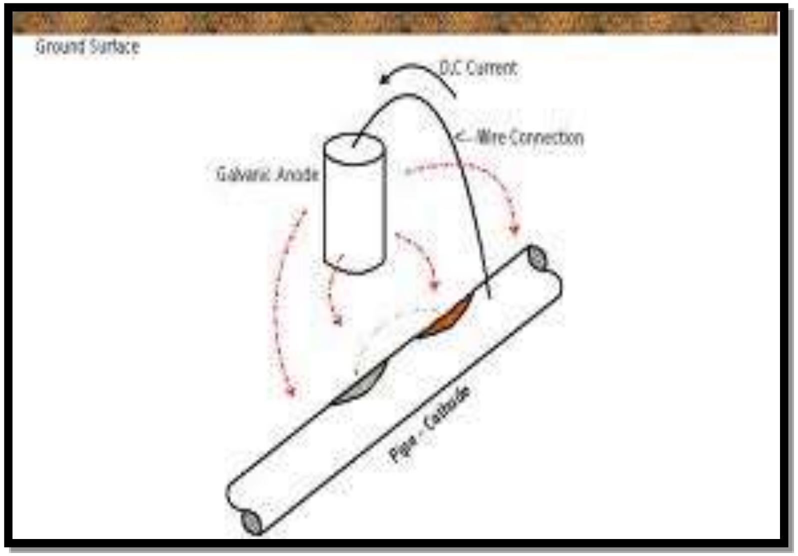
(b) Sacrificial anodic
protection

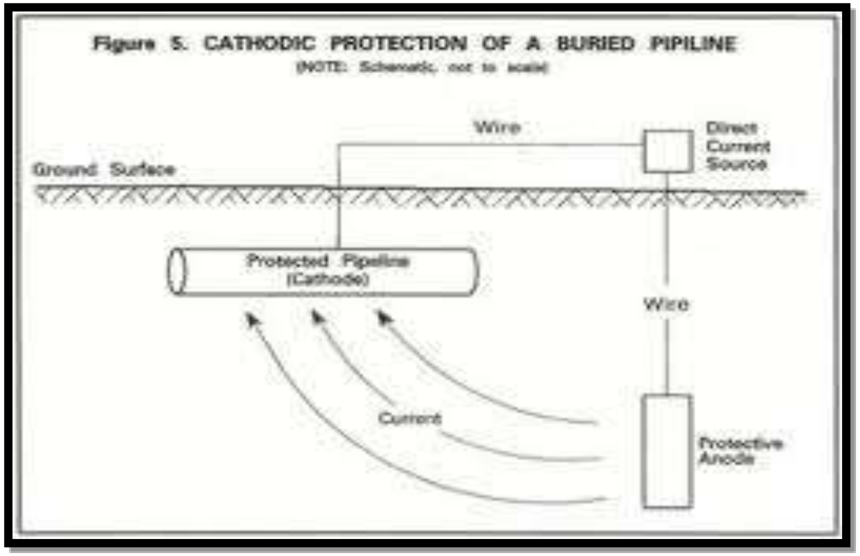


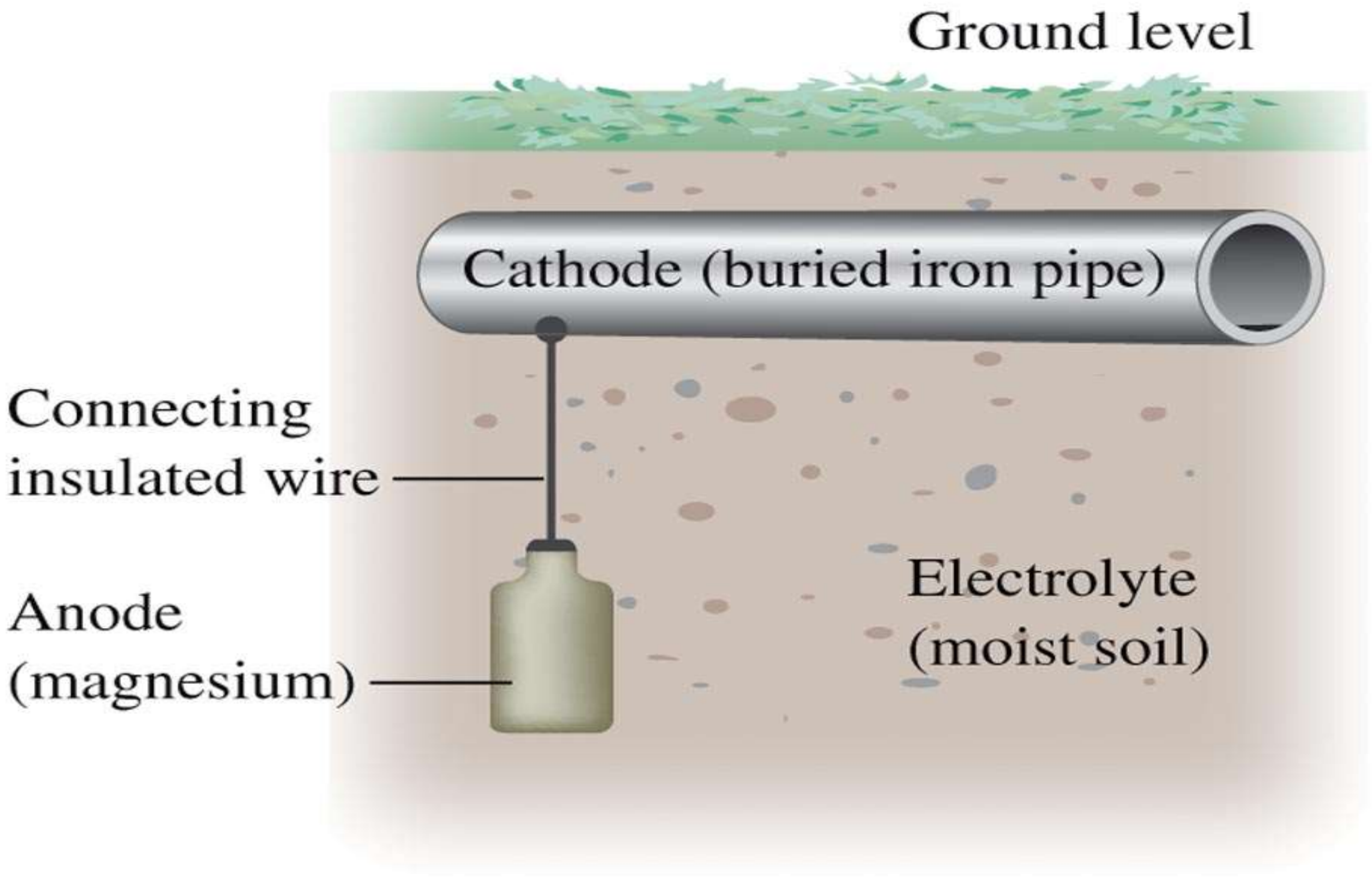
(c) Protection of ship-hull
below water line by

Impressed current method:

- Direct current is applied in opposite direction to nullify the corrosion current
- Converts the corroding metal from anode to cathode.






Ground level
Cathode (buried iron pipe)
Connecting insulated wire
Anode (magnesium)
Electrolyte (moist soil)

SURFACE COATINGS

- The metal surface is covered with a coating to protect it from corrosion.
- These may be

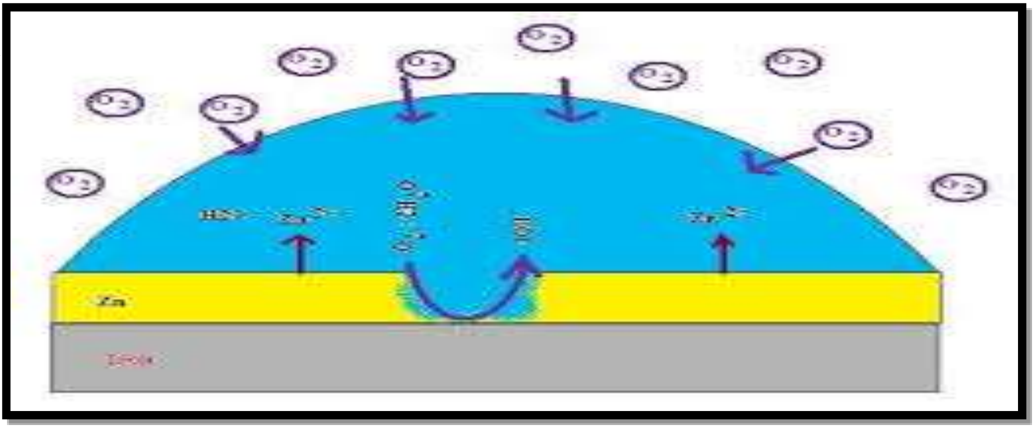
  i) Metallic

  ii) Organic

METALLIC COATINGS

The metals used for coatings may be placed under two categories

i) metals which are anodic to the metal i.e., metals above it in galvanic series.



ii) metals which are cathodic to the metal i.e., metals below it in galvanic series.

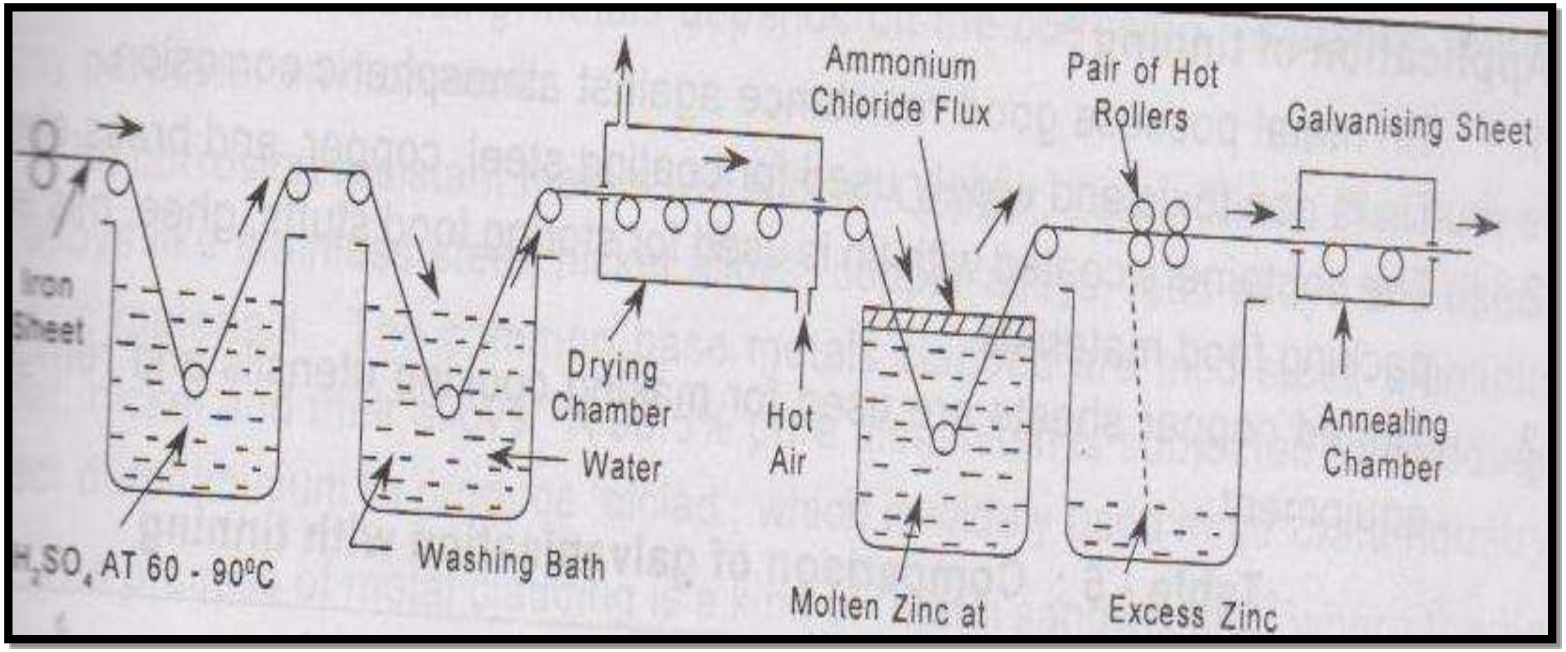
Methods of applications of metal coatings:

- Hot dipping: This technique is most widely used to control corrosion. Hot dipping is used for producing a coating for low melting metals such as Zn, Sn, pb ,Al.
- on Iron, steel, copper which are having high melting point usually underwent into corrosion due to their oxidising property.
- The process in general consisting of immersed a metal in a bath of its molten coating& covered by a molten layer.
- The flux cleans the base metal& prevent oxidation of metal coating with molten solution.
- Hot dipping is widely applied either by (1)GALVANIZING (2)TINNING

Galvanizing

- It is the process in which iron or steel is protected from corrosion by coating with a thin layer of zinc.
- Iron or steel is first cleaned by pickling with dil. H_2SO_4 solution for 15-20 mts at 60^0-90^0c. The steel is then washed well and dried .
- Then the metal sheet is dipped in bath of molten Zinc maintained at 425^0-430^0c.
  The surface of bath is kept covered with a $Zncl_2$ flux to prevent oxide formation.
- Then the metal sheet is passed through a pair of hot rollers which removes excess of Zinc and maintain uniform thickness of Zinc on metal sheet.

- The sheet is subjected to annealing process at 65^{0}c and cooled slowly.



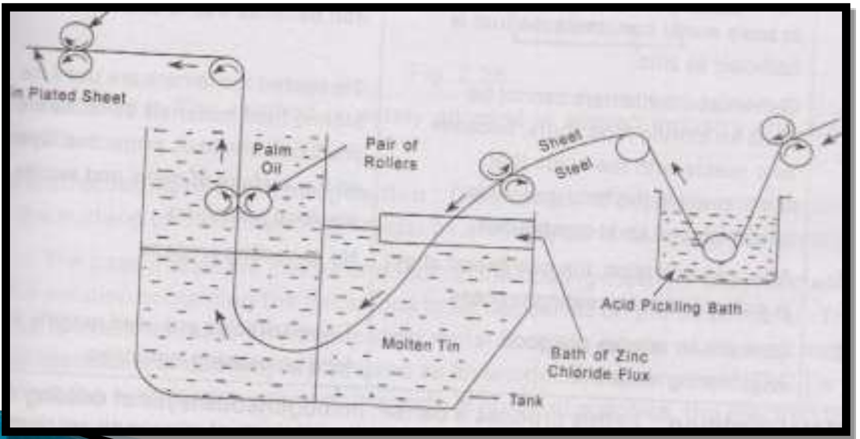
Uses of Galvanization: It is used to protect Iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets, and tubes.

Defects :Galvanised utensils are not used for cooking because of solubility of Zn.

TINNING

- Tinning is the process of coating of tin over the Iron sheet or steel articles
- A cleaned iron sheet is passed through a bath of molten flux, then passes through a tank of molten tin and finally through a layer of palm oil which protect hot tin coated surface against oxidation.

Uses: (1)It is widely used for coating of steel, copper, brass & bronze etc . It is used to store food stuff, ghee oils, kerosene& pickels and used for refrigerators equipment.



ELECTROPLATING

- Deposition of coating metal on the base metal by passing direct current through an electrolytic solution which contain the soluble salts of the coating material.

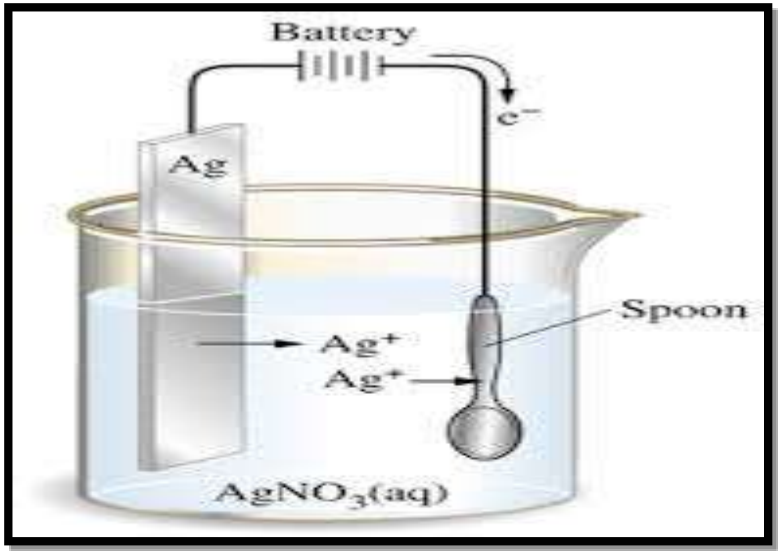
- Pure metal is made as cathode and base metal as anode.
- Electrochemically coat metal is deposited on base metal.
- This metal gives smooth, fine and uniform coating
- It depends on

(i) Temperature

(ii) Current density

(iii) Electrolyte Concentration

(iv) Nature of base metal (v) Time



Applications of Electroplating

- It is most important & frequently used technique in industries to produce metallic coating
- Both metals & non metals can be electroplated.
- In metals the electroplating increases resistance to corrosion, chemical attack, hardness, wear resistance and surface properties.
- In non metals electroplating increases strength and decorates the surface of non metal like plastics, wood, glass.

Electroless Ni plating:

- Pre treatment of surface:
- (1) CO, Ni, steel and Al can be directly plated.
- (2)Pb, Cd and Sn are first electroplated with Ni prior to electroless plating.
- (3)Non conductors are activated in $Sncl_2$ & HCl followed by dipping in $Pdcl_2$,Hcl.on drying thin pd layer is formed.

Organic paints

ORGANIC COATINGS

- Organic coatings protect the surface as they act as physical barriers between the metal to be protected and the corroding environment and are decorative.

- The extent of protection given by the organic coatings depends on

A) Impermeability to gases ,salts and water

B) Chemical inertness to the corrosive environment

C) Good surface adhesion

The Organic & Natural paint co.

PAINTS

- Paints form a protective layer over the surface of the metal to prevent corrosion.

The main constituents of the paints are

- Pigment
- Vehicle
- Thinner
- Driers
- Fillers
- Plasticizers
- Anti skinning agents

Pigment

- It is a solid constituent that obscures the surface and provides a decorative color.
- A liquid binds the pigment to the surface and protects it from decay.
- It usually comprises of 60 to 80% of the weight of the paint film.
- Increases the life of paint film since it prevents the entry of ultra violet rays.
- E.g.; lead oxide, red lead, lead chromate etc.,

Vehicle

- Film forming constituent of the paint.
- They hold the pigment on the metal surface.
- They give metal adhesion to the metal surface.
- They impart durability and toughness to the film.
- They isomerize , polymerize and condense to form characteristic tough, elastic ,coherent, highly cross linked structured macromolecular film.
- E.g.: mustard and sunflower oil etc.,

Thinners

- Viscosity is reduced by the addition of thinners.
- It is a volatile solvent helps to adjust the consistency of the paint.
- Thinner being volatile evaporates.
- They remain permanently in paints and varnishes.
- They improve elasticity of the film.
- They suspend the pigments in the paints.

E.g. Turpentine, mineral spirits, xylol, kerosene.

Fillers

- They are inert materials.
- They are used to improve the properties of the paints.
- They reduce the cost of paints.
- They serve to fill the voids in the film.
- Increases the random arrangement of pigment particles.
- Improves the durability of the film.
- E.g.: talc, chalk, silica etc.,

Driers

- Drying of the oil film is accelerated or catalyzed by driers.
- To reduce the drying time a drier is added.
- They are oxygen carrier catalyst.
- To improve the drying quality of oil film.
- This is done by condensation , oxidation and polymerization.

E.g. linoleates , borates, resinates etc.,

Plasticizers & Anti skinning agents

- They remain permanently in paints and varnishes.
- They improve elasticity of the film.
- To prevent cracking of the film.
- Anti skinning agents prevent the gelling and skinning of the paint film.

E.g.: tricresyl phosphate, tri phenyl phosphate,
di butyl tartarate etc.,

UNIT III

POLYMERIC MATERIALS

POLYMER

A word polymer is a combination of two greek words, “poly” means many and “mer” means parts of units.

DEFINITION: Polymers are macromolecules which are formed by linking together of a large number of small molecules called monomers.

Example: polythene is a polymer formed by linking together of a large number of ethene molecules.

Polymerisation: A process of forming polymer is called polymerisation.

Ethylene Monomer

Poly(ethylene)

POLYMERS

- **Based on Source**
  - **Natural Polymers**
    - Starch
    - Cellulose
  - **Semisynthetic Polymers**
    - rayon
  - **Synthetic Polymers**
    - Nylon
    - Polyester
- **Based on Structures**
  - **Linear Polymers**
    - Nylon
    - Polyester
  - **Branched chain Polymers**
    - PVC, - teflon
  - **Cross linked Polymers**
    - Bakelite, Melamine
- **Based on Reaction mode of Polymerisation**
  - **Addition Polymers**
    - **Homopolymers**
      - Polythene
      - Polupropene
    - **Copolymers**
      - Buna - S
  - **Condensation Polymers**
    - Nylon 6,6
    - Polyester
- **Based on Molecular forces**
  - **Elastomers**
    - Neoprene
    - Isoprene
  - **Fibres**
    - Nylon, Polyester
  - **Thermoplastic Polymers**
    - PVC, Polstyrene
  - **Thermosetting Polymers**
    - Bakelite, Melamine

Classification of polymers

Polymers can be classified in a number of ways.

Classification based on the source:
Natural polymers: Which are found in nature in animals and plants.. For example starch, cellulose, proteins, natural rubber etc.

Synthetic polymers: Man made polymers are known as synthetic polymer. eg. PVC, polyethylene, polystyrene, nylon-6, nylon-6,6; nylon-6,10; terylene, synthetic rubbers etc.

Classification based upon structure:
Linear polymers: Monomers are joined together to form long straight chains. The various linear polymeric chains are stacked over one another to give a well packed structure close packed in nature, having high densities, high melting point and high tensile (pulling) strength.
Example: polythene, nylons, polyester, etc.

Branched chain polymers: Polymers in which the monomeric units constitute a branched chain. Branched chain polymers have lower melting point low densities and tensile strength as compared to linear polymers.
Examples are amylopectin, glycogen, low density polyethylene and all vulcanized rubbers

Cross linked or Three-Dimensional network polymers:

When linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross linked polymers are always condensation polymers.
Examples: Bakelite urea-formaldehyde, etc.

Classification based upon molecular force:

Elastomers: Polymers in which the intermolecular forces of attraction between the polymer chains are the weakest (weak van der Waals forces of attraction) these polymers consist of randomly coiled molecular chains of irregular shape having a few cross links.
Examples are natural rubber, Buna-S, Buna-N etc.

Fibers: Those polymers in which the intermolecular forces of attraction are the strongest are called fibers. These polymers held together by H-bonding or dipole-dipole interaction. Fibres have high tensile strength, least elasticity having high melting point and low solubility.
Examples: Nylon 6:6, polyester, rayon, etc.

Thermoplastics: In thermoplastics intermolecular forces of attraction are in between those of elastomers and fibres. Thermoplastics become soft and viscous on heating and rigid on cooling. Examples are polythene, nylon-6, nylon-6:6, etc.

Thermosetting polymers: These polymers have low molecular masses and are semi-fluid substances. These polymers are hard and infusible.
Examples are melamine-formaldehyde, bakelite (phenol-formaldehyde) etc.

Classification based upon polymerisation:

Addition polymerization: A polymer formed by direct addition of repeated monomer possessing double or triple bond, without elimination of small molecule is called addition polymerisation.
Examples: polythene, PVC, etc.

Condensation polymerisation: A polymer formed by a reaction occurring between monomers containing polar groups, with the elimination of small groups like water, HCl, ammonia, etc. is called condensation polymerisation.
Examples: Nylon 6:6, terylene

Classification based upon monomers:

Homopolymers: If a polymer consists of one kind of monomers then it is called a homopolymer.
Examples: polythene, teflon, PVC, etc.

Copolymer: If a polymer consists of more than one kind of monomers is called a copolymer.
Examples: Nylon 6:6, polyester, Bakelite, Buna-S, etc.

Plastics/ Plastic Material

Definition: Organic materials which can be moulded into any desired form, when subjected to heat and pressure in presence of a catalyst.

Terms resin and plastics are now-a-day considered synonyms. However, both are different.

Resins: are the basic binding material which form a major part of th plastics and which has undergone polymerisation reaction during preparation.

Unique properties of plastics

- Lightness in weight
- Good thermal and electrical insulation
- Corrosion resistance
- Easy workability
- Adhesiveness
- Low fabrication cost
- Decorative surface effect
- Easy moulding
- Insect resistant
- Capable to being made to order
- Absorbent of vibrations and sound

- Low thermal expansion coefficient
- Chemical inertness
- Transparency
- Low maintenance cost
- Low softening points
- Ability to take variety of colours, shades, etc.
- Good shock absorption capacity
- High resistance to abrasion
- Impermeable to water
- Good strength and toughness
- Excellent in finish

Uses of Plastics

- Making electrical goods and appliances
- Aeronautical engineering
- Making furniture
- Making floor and wall linings
- Making special types of paints
- Heat and sound insulation
- Making windscreens, laminated glasses, table tops
- Preparing decorative laminates and mouldings

- Making overhead tanks, water pipes
- Making household articles
- Making synthetic fibres
- Making adhesives
- As water softening agents
- Making films for waterproofing, damp proofing and curing of concrete

Preparation of plastics

Prepared using- Polymerisation reaction it is of 2 types:

1. Addition Polymerisation: involves repeated addition of monomers to yield long chains of polymer.
2. Condensation Polymerisation: involves condensation/combination of 2 monomers resulting in loss of small molecules like H_2O, HCl, NH_3 etc. to yield a polymer.

POLY VINYL CHLORIDE (PVC)

Properties of PVC:

- Colourless
- Odourless
- Chemically inert,
- resistant to light, atmospheric oxygen,
- Acids and alkalis
- Pure resin possesses high softening point(148 ^oC)
- Greater stiffness, high rigidity
- It is brittle

Engineering applications of PVC

Unplasticized PVC

Used for making sheets employed for

- tank-linings
- light fittings
- safety helmets
- refrigerated components
- tyres
- cycle and motorcycle mudguards

Plasticized PVC(adding plasticizers)

Used for making sheets employed

- Rain coats
- Table cloths
- Curtains
- Covering of electrical cables
- Toys, tool handles, toiled good
- Plastic coated cloth
- Thermal insulating foam

TEFLON (Poly Tetra Fluoro Ethane)

Properties of Teflon:

- Extreme tough
- High softening point(350 ^{o}C)
- High chemical resistance to chemicals(except hot alkali metal and hot fluorine)
- Waxy touch, very low coefficient of friction
- Good electrical & mechanical properties
- It can be machined, punched & drilled

Engineering Applications of Teflon

Used for:

- Insulating material(motors, transformers,cables, wires, fittings etc)
- For making gaskets, packings, pump parts, tank linings, chemical carrying pipes, tanks, tubings
- For coating & impregnating glass fibres, cloths
- In non lubricating bearings
- Non sticking stopcocks for burettes

BAKELITE

Properties of Bakelite:

- ➢ Hard
- ➢ Rigid
- ➢ Scratch resistant
- ➢ Infusible
- ➢ Water resistant
- ➢ Resistant to acids, salts, organic solvents
- ➢ Attacked by alkalis
- ➢ Excellent electrical insulator

Engineering Applications of Bakelite

Used for making

Electrical insulator parts like

- Switches
- Plugs
- Switch boards
- Heater Handles

Moulded articles like

- Telephone parts
- Cabinets for radio and television

Also used in:

- Paints and varnishes
- As adhesives(binder) for grinding wheels
- As ion-exchange resins in water softening
- For making bearings, used in propeller shafts for paper industry and rolling mills

FIBRES

- Fibres are thread like structures that are thin, long and flexible strands

- There are two types of fibres:

1) Natural fibre- obtained from natural sources
   Examples- Silk, cotton,wool, jute etc

2) Synthetic fibre- Which are man made
   Examples- Rayon, Nylon, acrylic etc

Properties of Nylon Fibres

- Translucent
- Whitish, horn
- High melting point(160-264 °C)
- High tensile strength
- High temperature stability
- High abrasion resistance
- Insoluble in organic solvents
- Soluble in phenol and formic acid
- Have good strength

- Light, high melting
- Absorb little moisture(drip-dry in nature)
- Very flexible
- Regain original shape after use
- Resistant to abrasion
- On blending with wool, the strength & abrasion resistance increases
- Good physical strength and self lubricating properties

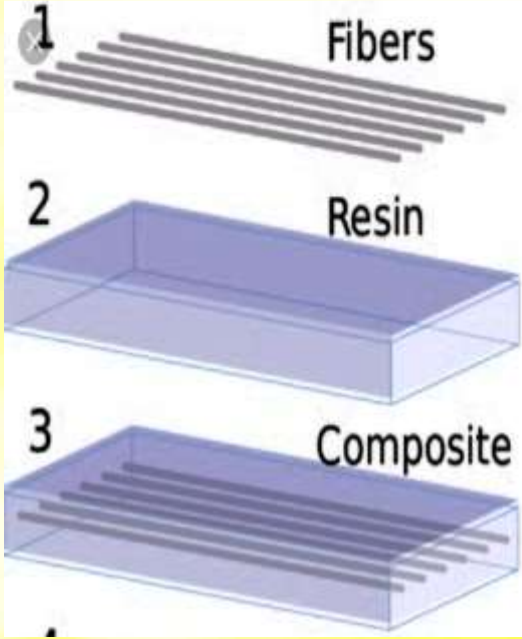
Engineering applications of Nylon

Used as:

- Thread in bristles for toothbrushes
- As gears, fittings & bearings, automotive industry
- Threads, ropes, filaments, nets
- Gun frames
- Surgical sutures
- Strings for musical instruments
- In hosiery and knitted garments
- Used to make ropes for rock climbing & parachutes

Fibre-reinforced plastic(FRP)

It is a composite material made of a polymer matrix reinforced with fibres



Fibres- They provide strength & stiffness.

- ➢ Common fibres used are glass, carbon, aramid, basalt
- ➢ Other fibres are paper, wood, asbestos

Matrix- Protects & transfers load between fibres & also supports them under compression loading.

- ➢ Common matrices are epoxy, vinyl ester, polyester, Polylactide etc.
- ➢ The original plastic without fibre reinforcement is known as matrix or binding agent

Properties of FRPs

- Light weight
- Corrosion resistance
- High tensile strength
- Non magnetic properties
- Specific stiffness
- High specific strength
- Easily constructed
- Ease of handling
- UV radiation stability
- Resistant to chemicals

Examples of FRPs

- GFRP (Glass Fiber Reinforced Polymer)
- CFRP (Carbon Fiber Reinforced Polymer)
- AFRP (Aramid Fiber Reinforced Polymer)

Glass Fibre Reinforced Plastic (GFRP):

- Commonly known as fiberglass
- Is synthetic material made by plastic (forms matrix) & extremely fine fibres of a glass.
  - Fibre: Glass fibre (E- glass, S- glass, R-glass)
  - Matrix: poly ester, epoxy, vinyl ester, poly styrene, polycarbonate etc.
- Glass fibres are made by mixing sand, limestone, folic acid and the mixture is heated about 1260 ^{o}C

Glass Fibre Reinforced Plastic (GFRP):

Advantages:

- High tensile strength
- light weight, strong, less brittle
- Heat resistant, weather resistant, insect resistant
- Corrosion resistant, chemical resistant (except HF, H_3PO_4)
- Dimensional stability: will not stretch or shrink
- Low moisture absorption
- Good electrical insulator
- Easy processing: ability to get molded into various complex shapes
- Incombustibility: doesn't support flame or emit smoke or toxic waste when exposed to heat

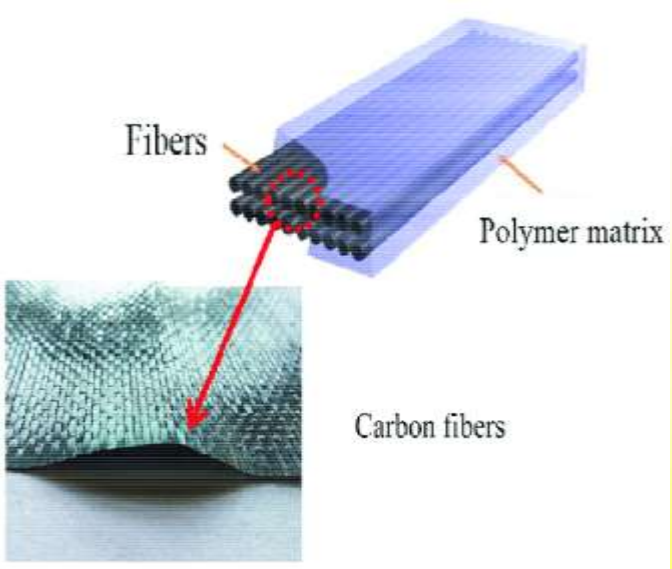
Applications:

- Manufacturing of automotive bodies: due to its lightweight
- Roofs, domes, pipes
- Boats
- Aquariums, fountains, waterslides, hot tubs, bath tubs, Surf boards, Gliders : due to anti-slip property
- Pump castings
- Storage containers
- for electromagnetic windows
- Screening for cooling towers
- Making aviation equipment and ducts (engine cowlings, bulkheads, storage bins and ground handling equipment)


APPLICATION
SURF BOARD
COMPOUND MATERIAL
WELDING
HEAT PRESERVATION

Carbon Fiber Reinforced Polymer

- CFRP the reinforcement material is carbon fibre
- Carbon fibre: is a long thin strand of carbon atoms which are bonded together in microscopic crystals that are woven together into a fabric
- Carbon fibers are microscopically small and about eight times thinner than a human hair.
- Carbon fibre can be combined with matrix to make almost any shape.
- Matrix: polymer resin such as epoxy, polyester, vinyl ester, nylon
- CFRP is five times lighter than steel and has only about 60% of the weight of aluminium.
- Thus CFRP's replaces steel and aluminium in a variety of industries.



Carbon Fiber Reinforced Polymers

Properties:

- ➢ Extremely strong
- ➢ Light weight
- ➢ High tensile strength
- ➢ High chemical inertness
- ➢ Good corrosion resistance
- ➢ Low thermal expansion
- ➢ X- ray transparency
- ➢ Low density
- ➢ Vibration resistance
- ➢ Low thermal conductivity
- ➢ Good rigidity
- ➢ Non magnetic
- ➢ Bad conductor of electricity

Applications:

Used in manufacturing of

Automotive field:

- ➢Racing car bodies
- ➢Vehicle parts such as body components

Marine field: Boats, submarines, yacht

Spacecraft & aerospace :

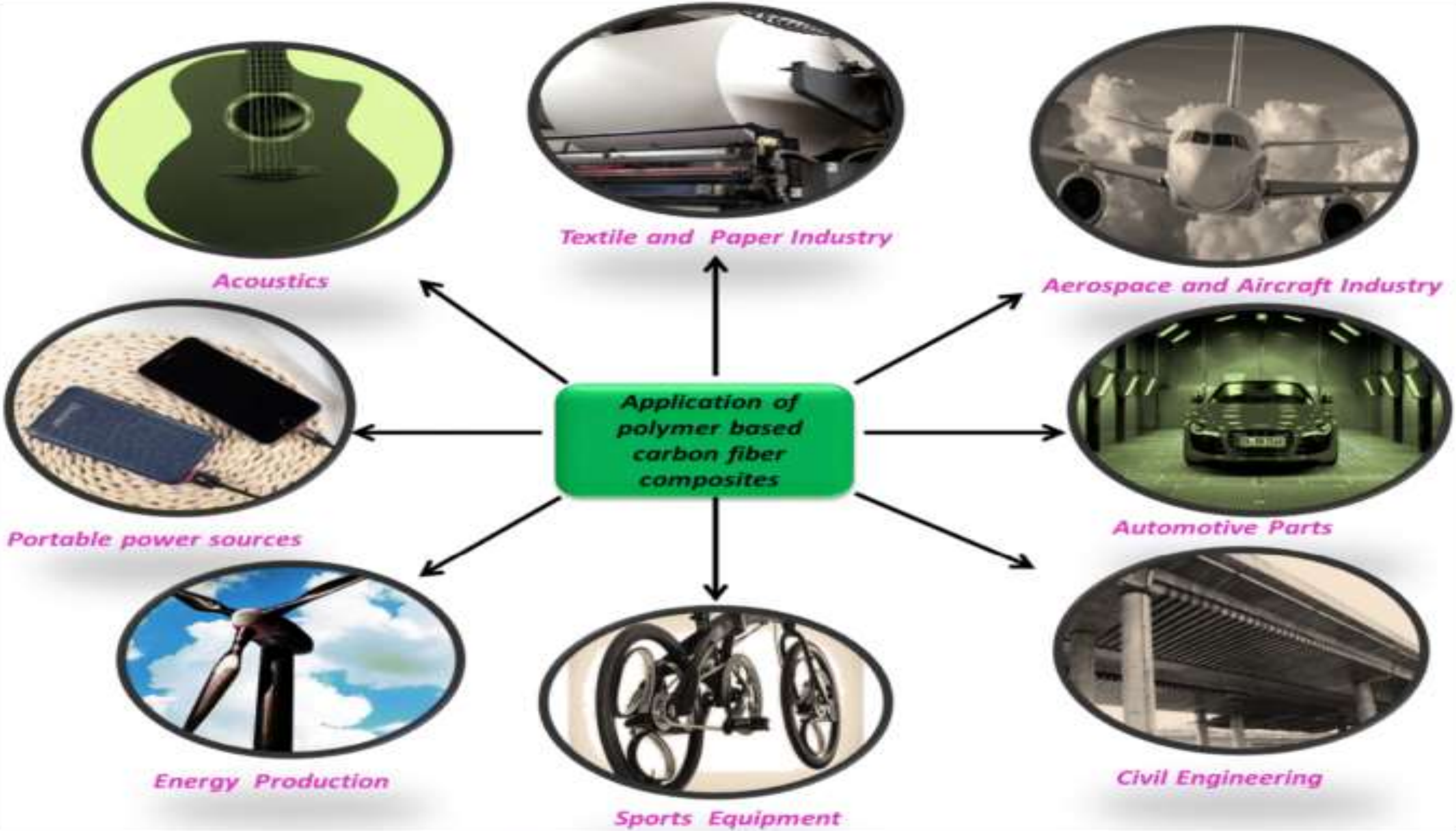
- ➢Main body of the plane, parts of the wings & tail parts

Sports goods:

- ➢Golf club shafts
- ➢Tennis racquets

Others:

- ➢Fishing rods
- ➢Bicycle frames
- ➢Racing car bodies
- ➢Robotic arms



Application of polymer based carbon fiber composites

Textile and Paper Industry

Acoustics

Aerospace and Aircraft Industry

Portable power sources

Automotive Parts

Energy Production

Sports Equipment

Civil Engineering

Aramid fibres

In AFRP the reinforcement material is aramid fibre

Aramid fibres are high strength fibres which are made by aromatic polyamide

Matrix: epoxy, polyester, vinyl ester

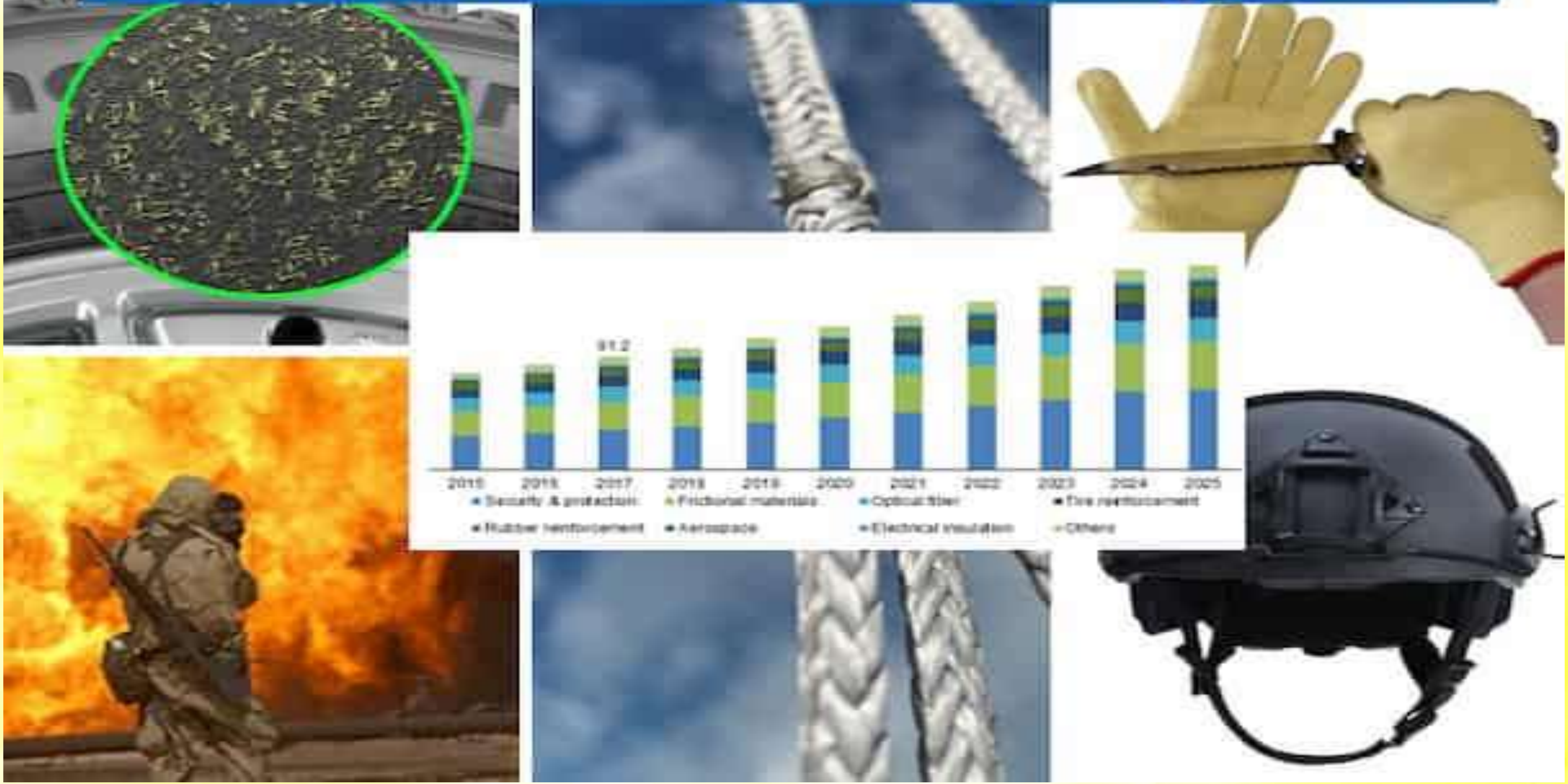
Properties:

- High tensile strength
- Flame resistance
- High chemical resistance
- High compression strength
- High elasticity
- High abrasion resistance
- Low weight

Applications:

- Bullet proof vests
- Fire protection cloths
- Protective gloves, helmets, body armor
- Sports goods
- Aircraft & military vehicles
- Ropes and cables

Aramid- The Ideal Shield for Defence Applications



BULLET / STAB
PROOF VESTS

DIVING GLOVES

WALKING BOOTS

MILITARY HELMET

CUT RESISTANT
GLOVES

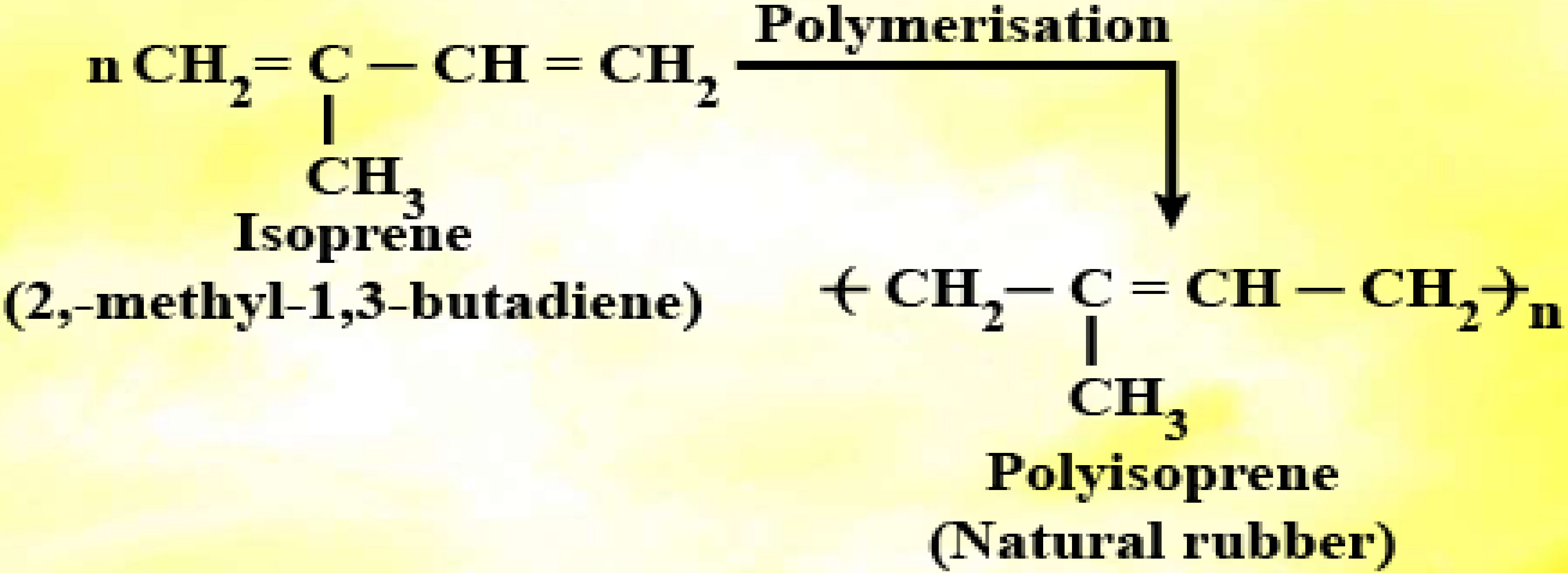
BICYCLE TYRES

CAR TYRES

FIRE PROOF
CLOTHING

Natural Rubber

Natural rubber is a natural polymer of organic compound isoprene obtained from the bark of the rubber trees.



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

Isoprene
(2,-methyl-1,3-butadiene)

Polyisoprene
(Natural rubber)

Preparation of natural rubber

- Natural rubber is made up of a solid particles suspended in a milky white liquid called latex obtained from the cuts of the bark of a rubber tree.
- Latex is diluted and filtered to eliminate any dirt present in it.
- Acetic acid or formic acid is added to coagulate rubber into a white mass
- The coagulated white mass is washed
- It is allowed to pass through rollers to make it soft and flexible

Properties of natural rubber:

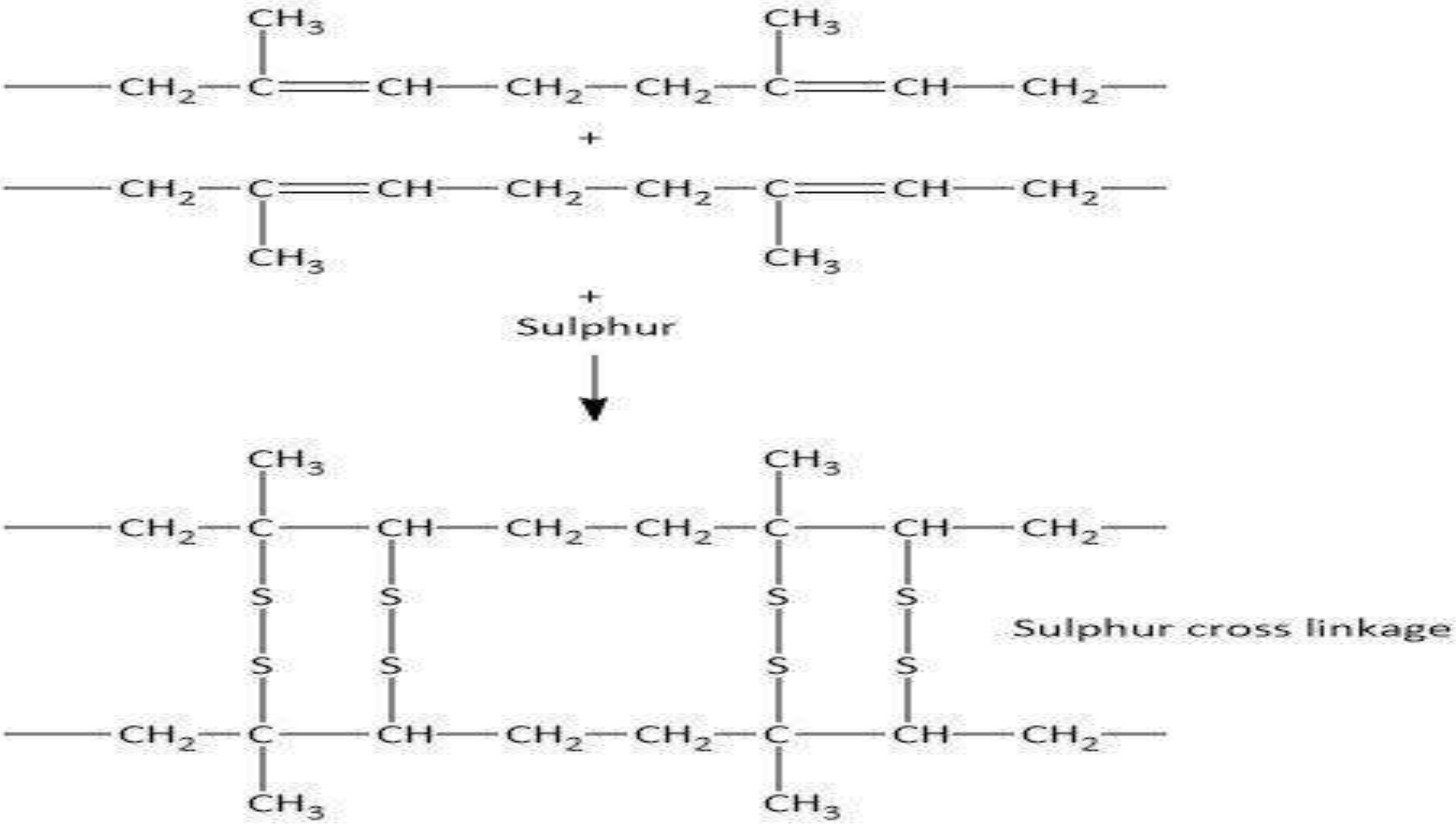
- Soft & sticky
- Flexible
- Low tensile strength
- Plastic in nature
- Sensitive to heat, light
- Low water absorption capacity
- Chemical resistant
- Less resistance to oil, non polar solvents, fats, greases

Vulcanisation of Natural rubber

- Natural rubber is too soft and cannot be used in most of the applications.

  To improve the properties of rubber :

- Natural rubber is heated with sulphur to 140 C
- Sulphur atoms react with the double bonds in the rubber molecule chain to form C-S-S-C cross link between rubber molecules


+
+
Sulphur
Sulphur cross linkage

Advantages of Vulcanised rubber

- High tensile strength
- Excellent resilience
- Low water absorption
- High resistance to oxidation
- High resistance to abrasion
- High resistance to wear and tear
- Better electrical insulator
- Resistant to organic solvents
- Low elasticity

Applications of vulcanised rubber

- Rubber hoses
- Shoe soles
- Toys
- Erasers
- Tires
- Insulating materials
- Rubber lined tanks
- Conveyor belts
- Suction cups
- Rubber seals
- Hockey pucks

Elastomers

Elastomer is a rubbery material composed of long chain molecules that possess the ability to return to its original shape after being stretched.

The molecules of elastomers held together by weak intermolecular forces.

Elastomers have viscosity as well as elasticity therefore they are known as viscoelasticity.

Following are the examples of the elastomers

- ➢ Natural rubber: They are used in automotive industry and in the manufacture of medical tubes, balloons, adhesives etc
- ➢ Polyurethanes: They are used in the textile industry for manufacturing elastic clothing like lycra.
- ➢ Styrene-butadiene rubber(Buna-S): Used as an adhesive, in footwear industry, in electrical insulation.
- ➢ Neoprene: These are used in manufacture of wet suits and in industrial belts.
- ➢ Silicone rubber: They are used in automotive, electrical, medical, cookware etc

Applications of elastomers

- **Motor vehicles**: Elastomers doesn’t melt easily and offers excellent wear resistance making it efficient in building seals, tyres, interior & exterior parts, engine components.
- **Consumer products**: Elastomers has widest range of products starting from shoe soles to baby pacifiers and many more.
- **Construction**: They are used as adhesives and sealants especially for filling the gaps
- **Industrial products**: Elastomers are hugely used in making industrial tools, appliances, belts, molds, lubricants, etc.
- **Wire & cables**: Elastomers provide good insulation, high resistance to heat & easily reshaped therefore they are used to build wires, telecommunication cables.

Conducting polymers

Polymers which conduct electricity are called conducting polymers.

Reason of conduction in the polymer:

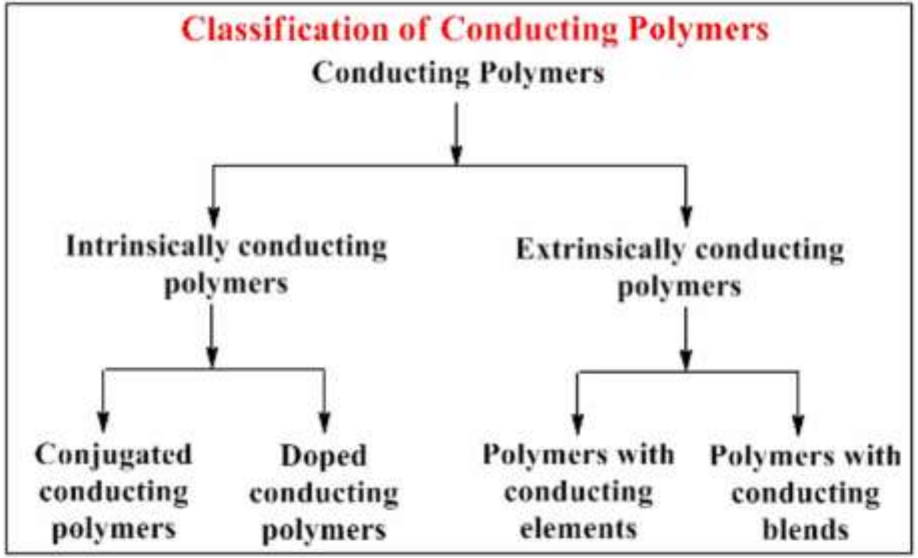
- Presence of unsaturated conjugated double bonds in the polymer
- Addition or removal of electrons (doping) into the polymer

Characteristics:

- Good electrical conductivity
- Easy of preparation
- Light in weight
- Easy to process

Types of Conducting Polymers

- Linear-backbone polymers (polyacetylene, polypyrrole, polyaniline, etc.) **and their copolymers are the main class of conductive polymers.** The different conducting polymers are classified according to their composition. **Table 1** presents some organic conductive polymers according to their composition.



Classification of Conducting Polymers

Conducting Polymers

Intrinsically conducting polymers

Extrinsically conducting polymers

Conjugated conducting polymers

Doped conducting polymers

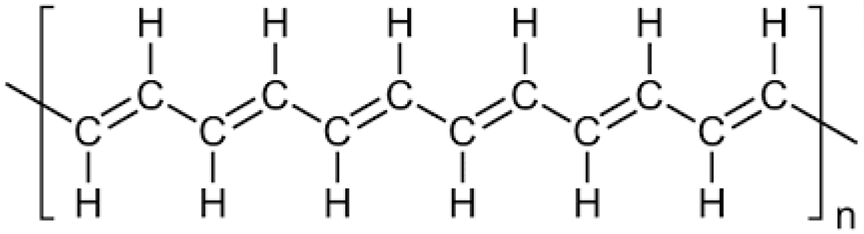
Polymers with conducting elements

Polymers with conducting blends

How can a polymer become conducting?

For a polymer to become electrically conductive, it has to imitate a metal, that is, its electrons need to be free to move and not bound to the atoms.

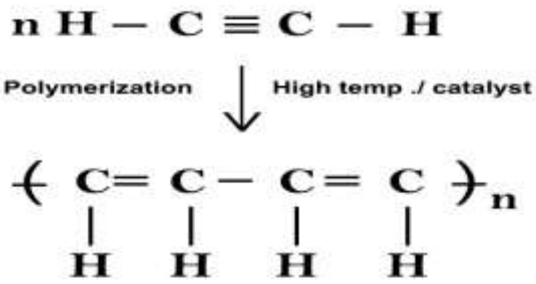
Polyacetylene is the simplest possible conjugated polymer. It is obtained by polymerisation of acetylene. The polymer consists of alternating single and double bonds, called conjugated double bonds.



(In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised "sigma" (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localised "pi" (π) bond which is weaker)

Mechanism of conduction in polyacetylene

Preparation of polyacetylene: Polyacetylene is prepared by passing acetylene gas over Ziegler-Natta catalyst to get polyacetylene.



$$n\,H-C\equiv C-H \xrightarrow[\text{High temp ./ catalyst}]{\text{Polymerization}} \left(\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}\right)_n$$

The conductance can be improved by either p-doping or n-doping

Types of doping

p- doping:

- Lewis acids or halogens are added to the polymers having conjugated double bonds
- Oxidation takes place
- Creates positively charged sites on polymer backbone, which are current carriers for conduction.
- Examples for p-dopants:

I_2, Br_2, $AlCl_3$, AsF_5, etc.

n-doping :

- Lewis bases or alkali metals are added to the polymers having conjugated double bonds
- Reduction takes place
- Creates negative charged sites on polymer backbone, which are responsible for the conduction
- Examples for n-dopants:

Li, Na, K, tetrabutyl ammonium, etc.

p-doping

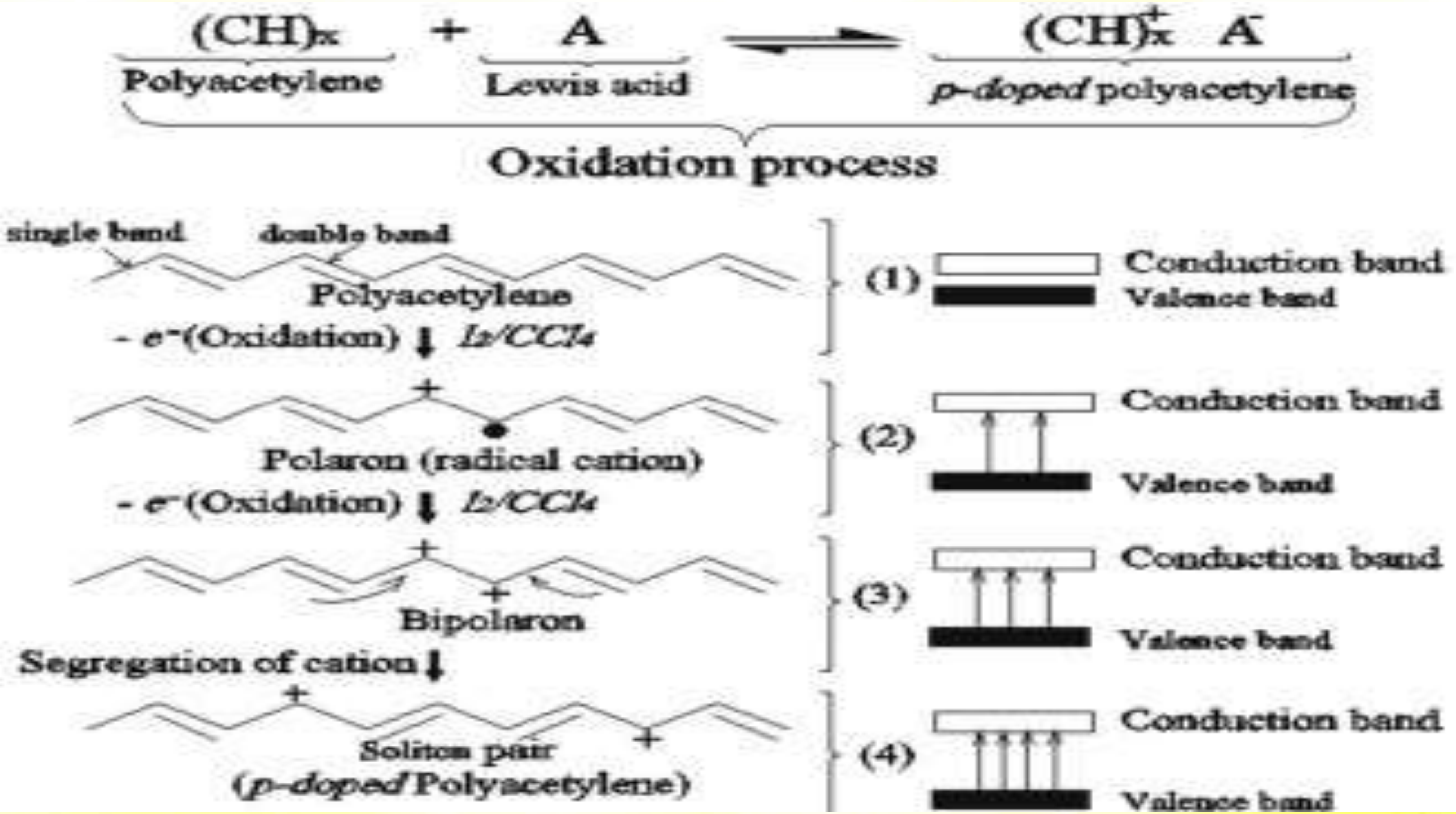
It involves two steps

Step I: It involves the oxidation of a polyacetylene with iodine vapour(Lewis acid)

During oxidation the iodine molecule remove an electron from polyacetylene chain creates positive charge called polaron.

Step II: The second oxidation of polaron produces two positive charges on the chain called bipolaron.

This positive charges are mobile due to delocalisation and responsible for conduction.



$$\underbrace{\underbrace{(CH)_x}_{\text{Polyacetylene}} + \underbrace{A}_{\text{Lewis acid}} \rightleftharpoons \underbrace{(CH)_x^{+}\ A^{-}}_{p\text{-doped polyacetylene}}}_{\text{Oxidation process}}$$

n-doping

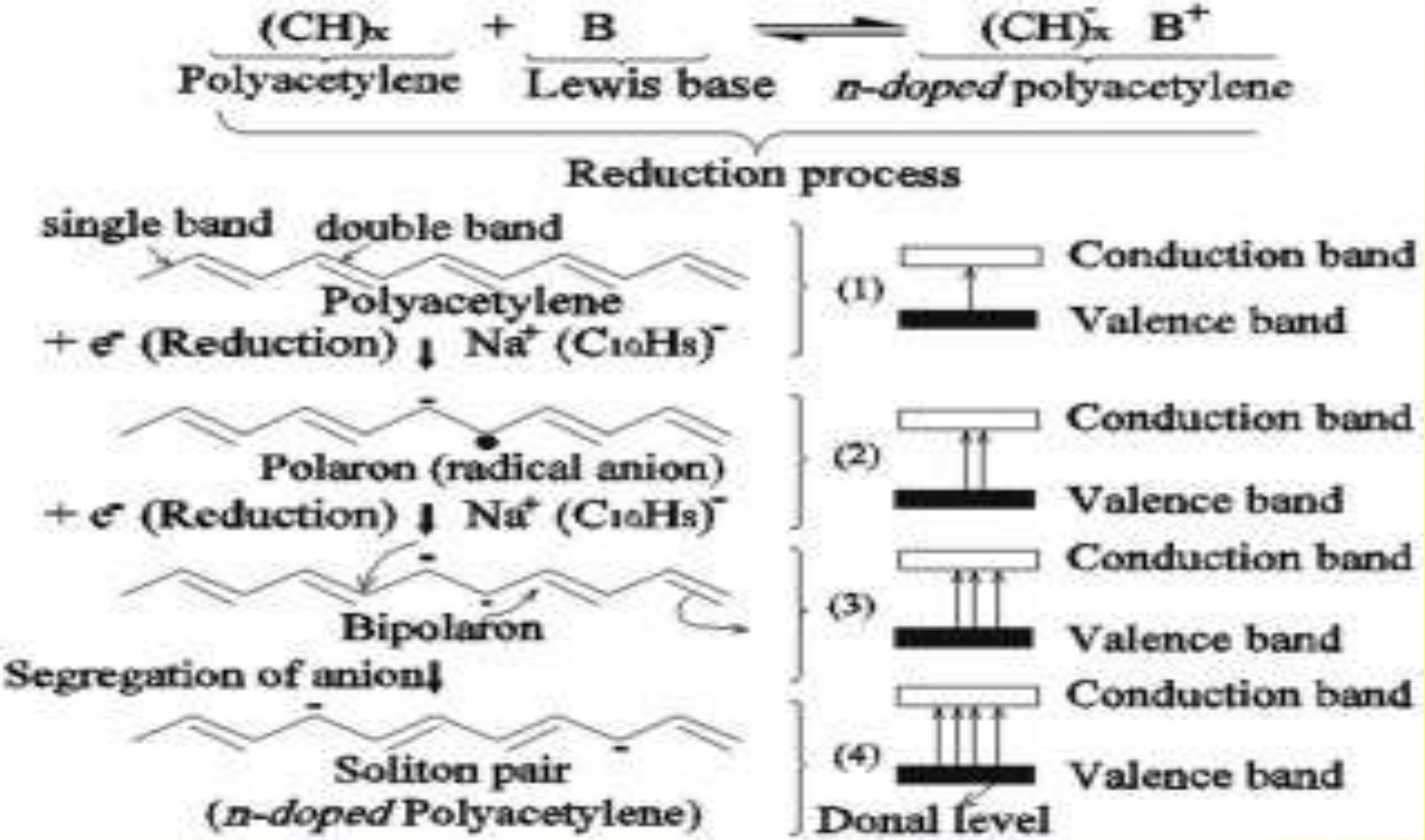
It involves two steps

Step I: It involves the reduction of polyacetylene of with sodium naphthalide

During reduction sodium naphthalide donates an electron to polyacetylene chain creates negative charge on the chain called polaron.

Step II: The second reduction of polaron two produce two negative charges on the chain called bipolaron.

This negative charges are mobile due to delocalisation and responsible for conductance.



(CH)x + B ⇌ (CH)x⁻ B⁺
Polyacetylene
Lewis base
n-doped polyacetylene
Reduction process
single band
double band
Polyacetylene
+ e⁻ (Reduction) ↓ Na⁺ (C₁₀H₈)⁻
Polaron (radical anion)
+ e⁻ (Reduction) ↓ Na⁺ (C₁₀H₈)⁻
Bipolaron
Segregation of anion↓
Soliton pair
(*n-doped* Polyacetylene)
(1)
Conduction band
Valence band
(2)
Conduction band
Valence band
(3)
Conduction band
Valence band
(4)
Conduction band
Valence band
Donal level

Applications of conducting polymers

- ➢ Incorporated into commercial displays and batteries
- ➢ Printed electronic circuits
- ➢ Organic light emitting diodes
- ➢ Supercapacitors
- ➢ Chemical sensors
- ➢ Used in solar cells
- ➢ Electromagnetic shielding
- ➢ Flexible transparent displays
- ➢ Microwave absorbing coating
- ➢ Radar-absorptive coating on stealth aircraft

Biodegradable polymers

Polymer that can be decomposed by the action of microorganisms are called biodegradable polymers

These polymers broken into small segments by enzyme catalysed reactions, and microorganisms produce this enzymes.

Examples of biodegradable polymers are polylactic acid, polyvinyl alcohol

Poly lactic acid

Advantages:

- Easy to process
- Bio compatible
- Biodegradable plastic
- Good plasticity
- Low cost
- Rigidity

Applications:

- Medical implants like stents
- Implantable drug dispenser
- Food packaging
- Disposable tableware
- Compost bags

Poly vinyl alcohol

Advantages:

- High chemical stability
- High thermal stability
- Low manufacturing cost
- Excellent water resistant
- High strength

Applications:

- Paper making
- Contact lenses
- Absorbable sutures
- Drug delivery systems
- Artificial heart surgery
- Cartilage replacements

Properties biodegradable polymers

- Biodegradable polymers can retain good mechanical integrity until degraded.
- Since biodegradable polymers have extremely strong carbon backbones that are difficult to crack, degradation begins at the end-groups.
- Biodegradable polymers are non toxic
- Degradation rates can be regulated
- Biodegradable polymers are hydrophilic

Uses of biodegradable polymers

Used in

- Controlled drug release systems
- Plasma replacements
- Agricultural materials such as films & seed coatings
- Fast food wrappers & personal hygiene products
- Drug delivery
- Post operative stitches

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UNIT-IV

ENERGY SOURCES

Introduction

A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives a large amount of heat that can be used economically.

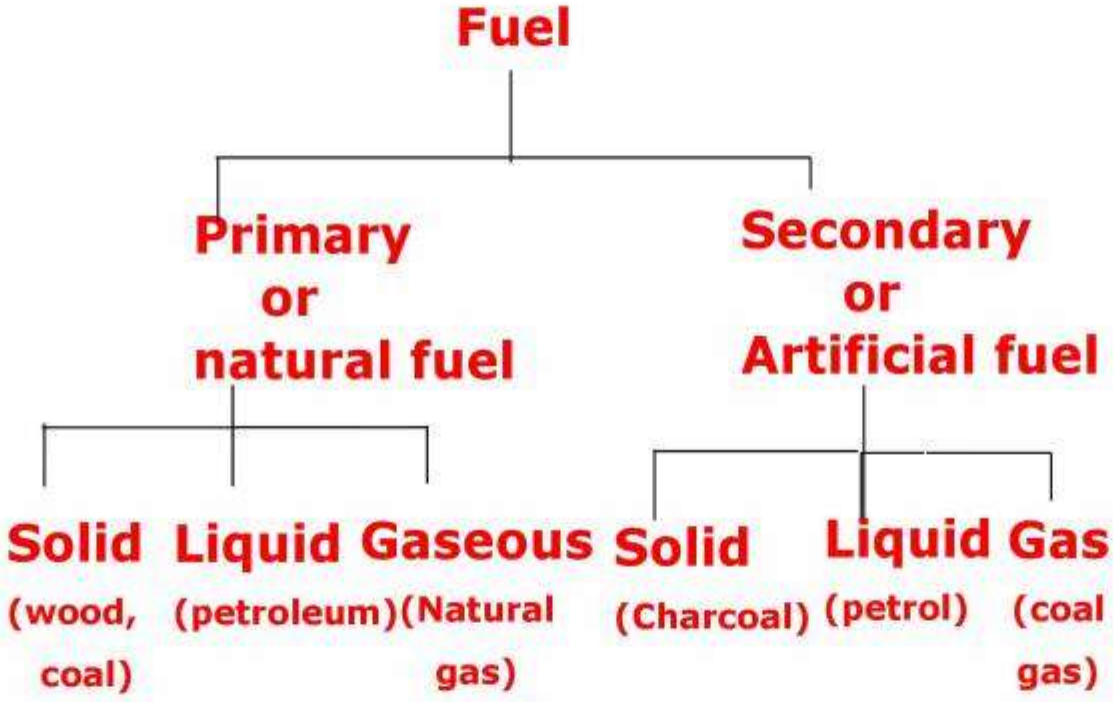
For example, wood, coal, kerosene, petrol, diesel and water gas.

Combustion is a chemical reaction in which a substance combines with oxygen producing heat, light and flame.

Combustion reaction of a fuel can be represented as follows

$$C_nH_{2n+2} \rightarrow CO_2(g) + H_2O\,(g) + \text{heat}$$

Classification of fuel



Fuel

Primary or natural fuel

Solid (wood, coal)

Liquid (petroleum)

Gaseous (Natural gas)

Secondary or Artificial fuel

Solid (Charcoal)

Liquid (petrol)

Gas (coal gas)

Primary fuels are found in nature whereas

Secondary fuel are prepared from primary fuel by processing them in a number of ways.

Calorific value

Calorific value of a fuel is the total quantity of heat liberated when one unit of fuel is burnt completely.

Gross or Higher calorific value (G.C.V or H.C.V): It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been cooled to room temperature.

Net or Lower calorific value (N.C.V or L.C.V)): It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been permitted to escape.

L.C.V= H.C.V – Latent heat of water vapour formed

Latent heat of steam= 537 cal/gm

Characteristic of good fuel

A good fuel should have

- high calorific value
- moderate ignition temperature
- low moisture content
- low non combustible matter content
- low cost and easy availability
- easy to transport and storage cost should be low
- products of combustion should not be harmful.
- burn in air without much smoke
- combustion should be easily controllable.

Theoretical calculation of calorific value using Dulongs formula

H.C.V= $[8080C + 34500(H-O/8)+ 2240 S]/100$ kcal/kg

Where,

C= % of carbon in the fuel

H= % of hydrogen in the fuel

O= % of oxygen in the fuel

S= % of sulphur in the fuel

And

Calorific value of carbon= 8080 kcal/kg

Calorific value of hydrogen= 34500 kcal/kg

Calorific value of sulphur= 2240 kcal/kg

L.C.V= H.C.V – Latent heat of water vapour formed

$=[H.C.V-9H \times 537/100]$kcal/kg

$=[H.C.V-0.09H \times 537]$kcal/kg

Gaseous fuel

1. **Natural gas:** It occurs in nature (mostly found under earth crust along with crude oil) is a mixture of hydrocarbons (80-95% methane and 5-20% ethane and other hydrocarbons.

Calorific value: 12000-14000 kcal/m3
Use: largely used as domestic fuel

A. CNG (Compressed natural gas): It is the natural gas compressed under high pressure.
Use: largely used as alternative fuel for motor vehicles.

B. LNG (Liquefied natural gas): It is the liquefied natural gas by refrigerating natural gas to -260°F.
Use: Since it is more dense than CNG, so is good for large trucks that need to go on long distance.

2.LPG (Liquefied petroleum gas): It is a mixture of hydrocarbons (80-95% proane and 5-20% ethane and other hydrocarbons.
Calorific value: 27800 kcal/m3Use: used as domestic and industrial fuel

Bio fuel

3. Gobar gas or bio gas: Animal dung converted to Bio gas which is a clean fuel. It is a mixture of hydrocarbons (50-60% methane and 30-40% carbon dioxide) and little N_2 and H_2 and traces of H_2S.

Process: A slurry of cow dung and water (1: 1) is put into the plant. Gobar gas is produced by anaerobic bacterial decomposition of the mixture which is drawn through pipes. The residue left is rich in nutrient which can be used as manure.

Calorific value: 1200 kcal/m3

Use: mostly used as domestic fuel (cooking and lighting)

Bio gas can also be generated from animal and plant wastes.

Gaseous fuel

4. Water gas: It is mainly a mixture of CO and hydrogen and it is produced by passing alternatively steam and little air through a bed of red hot coke maintained at about 900-1000°C.

At first steam reacts with red hot coke at 900-1000°C to produce CO and H_2.

$$C + H_2O \longrightarrow CO + H_2 \;\; -29 \text{ kcal (endothermic reaction)}$$

This reaction is endothermic and temerature of the bed of coke falls. In order to raise the coke bed temperature to 1000°C, the supply of steam is temporarily cut off and air is blown when the following exothermic reactions took place.

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal (exothermic reaction)}$$

$$2C + O_2 \longrightarrow 2CO + 59 \text{ kcal (exothermic reaction)}$$

Composition: H_2 =50% ; CO= 40%, N_2 and CO_2 = 4% each

Calorific value: 2800 kcal/m3

Use: used as industrial fuel

Gaseous fuel

5. Producer gas: It is mainly a mixture of CO and nitrogen and it is produced by passing air over white hot coke bed maintained at about 1000-1400°C.

$2C + O_2 \longrightarrow 2CO + 59$ kcal (exothermic reaction)

$C + O_2 \longrightarrow CO_2 + 97$ kcal (exothermic reaction)

Carbon dioxide formed is reduced to CO by heated coke.

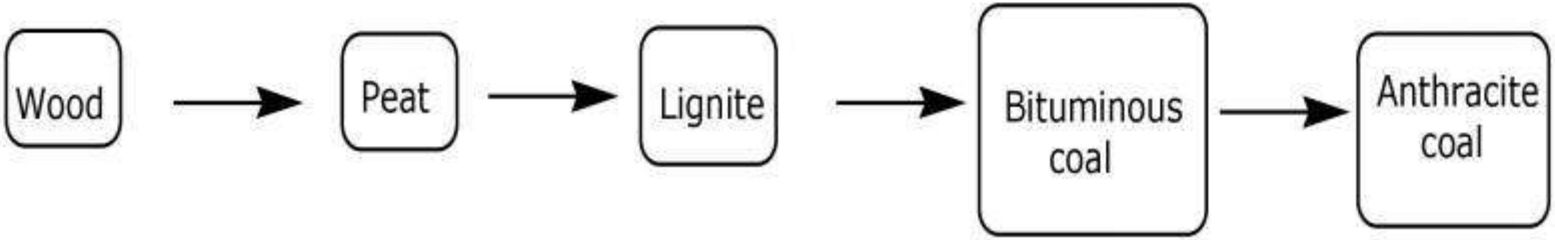
$CO_2 + C \longrightarrow 2CO - 39$ kcal (endothermic reaction)
This reaction is endothermic and temperature of the coke bed is maintained at 1000-1400°C.

Composition: $N_2 = 50\%$; $CO = 30\%$, $H_2 = 4\%$, and rest CO_2, CH4 etc.
Calorific value: 1300 kcal/m3
Use: used as industrial fuel (for heating of open hearth furnaces in steel and metallurgy).

Classification of coal

Coal is a primary solid fuel which occurs in nature in very impure form of carbon. It is a fossil fuel.

Wood, peat, lignite, bituminous and anthracite are the different stages in the conversion of wood to coal. Carbon content is highest in anthracite coal.



Wood → Peat → Lignite → Bituminous coal → Anthracite coal

Analysis of coal

Analysis of coal sample is required to access the quality of coal.

(A) Proximate analysis (PA): It is the process of determination of moisture, volatile matter, ash and fixed carbon content.

(B) Ultimate analysis (UA): It is the process of determination of composition of various components of coal which includes the determination of % of C, H, S, N, O and ash content. It is necessary for utilization of coal for industrial purpose.

Proximate Analysis

(1) **Moisture content:** 1 g of finely powdered coal, taken in a crucible, is heated in an electric oven at 105-107oC for 1h. Percentage moisture content can be calculated from the loss of weight.

(2) **Volatile matter content:** 1 g of finely powdered moisture free coal, taken in a covered crucible, is heated in a muffle furnace at 950°C for 7 min. Percentage volatile content can be calculated from the loss of weight.

(3) **Ash content:** It is the residue obtained after burning of the coal in a muffle furnace under current of air at 700-750°C till a constant weight is obtained.

(2) **Fixed carbon content:** It is determined indirectly by deducting the sum of total moisture, volatile matter and ash content from 100.

Proximate analysis

- (1) **Moisture**: About 1 g of finely powered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105° - 110°C. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture (on percentage-basis).
- $$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$
- (2) **Volatile matter**: The dried sample of coal left in the crucible in (1) is then covered with a lid and placed in an electric furnace (muffle furnace), maintained at 925°± 20°C. The crucible is taken out of the oven after 7 *minutes* of heating. The crucible is cooled first in air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

Percentage of volatile matter=

$$\frac{\text{Loss in weight due to removal of volatile matter}}{\text{Wt. of coal sample taken}} \times 100$$

- (3) **Ash:** The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at 700 ± 50° C for 1/2 *hour.* The crucible is then taken out, cooled first in air, then in desiccator and weighed.

- Heating, cooling and weighing is repeated, till a *constant weight* is obtained. The residue is reported as ash on percentage-basis.

$$\text{Percentage of ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100$$

(4) **Fixed carbon**: Percentage of fixed carbon = 100 - % of (moisture + volatile matter + ash)

- high percentage of rued carbon is desirable.

Importance of proximate analysis

- Proximate analysis provides following valuable informations in assessing the *quality of coal:*

- **(1) Moisture:** Moisture lowers the effective calorific value of coal. Moreover, 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 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. Higher volatile content in coal is undesirable.

- A high volatile matter content means that high-proportion of fuel will be distilled and burned as a gas or vapour. The volatile matter present in the coal may be combustible gases (such as methane, hydrogen, carbon monoxide and other hydrocarbons) or non-combustible gases (like CO2 and N2). Volatile matter content is of special significance in coal gas manufacture and in carbonization plants, particularly when by-product recovery is the main object. Thus, high-volatile matter containing coals do not cake well; whereas medium-volatile matter content coals are capable of yielding hard and strong coke on carbonization.

- **(3) 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 clinker), which block the inters paces of the grate. 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. 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 its calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel.

Ultimate Analysis

(1) Determination of % of C & H: This is usually done through a single experiment based on combustion in excess of pure oxygen.

(2) Determination of % of Nitrogen: This is done by Kjeldhal's method where a known weight of the given sample is heatedb with conc. H_2SO_4 in presence of catalytic amount of K_2SO_4 and $HgSO_4$.

(2) Determination of % of S: This is done by heating known weight of the given sample with fuming HNO_3.

Ultimate analysis

Carbon and hydrogen: About 1-2 g 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.

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

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

Significance of ultimate analysis

- (1) **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 matter and hence, it affects the use to which the coal is put. Also higher percentage of carbon in coal reduces the size of combustion chamber required. The amount of carbon, the major combustible consti1fent of coal, depends on the type of coal and its percentage increases with rank from lignite to anthracite. Thus, percentage of carbon forms the basis of classification of coal.

- (2) **Nitrogen** has no calorific value and hence, its presence in coal is undesirable; thus, a good quality coal should have very little nitrogen content.

Nitrogen: About 1 g of accurately weighed powdered 'coal is heated with concentrated H_2SO_4 along-with K_2S0_4(catalyst) in a long-necked flask(called *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:

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

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

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

Ash determination is carried out as in proximate analysis.

Oxygen: It is obtained by difference.

- **(3) Sulphur**, although contributes to the heating value of coal, yet on combustion produces acids (S02 and S03), which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 3.0% 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 (formed as combustion products) pollute the atmosphere and leads to corrosion.

- **(4) 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 in 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

Mining and Refining of Petroleum

- The crude oil obtained from the earth crust contains water, sulphur and some unwanted impurities. After removal of water, sulphur and these impurities, the crude oil is separated into various useful fractions by fractional distillation and finally convel1ed into desired specific products having different boiling points. The process is called "Refining of Petroleum" and the refining plants are called "Oil refineries". The process of refining involves the following steps.

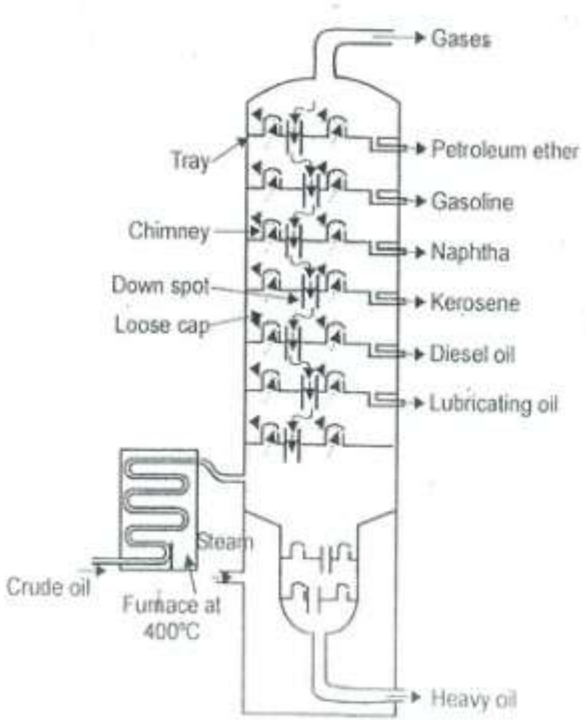
- **Step -I: Separation of water (Cottrell's process)**
- The crude oil from the oil well is an extremely stable emulsion 0 f oil and salt water. The crude oil is allowed to flow between two highly charged electrodes, where colloidal water droplets coalesce to form large drops, which is then separated out from the oil.

- **Step - II: Removal of harmful impurities**
- a) The presence of NaCI and MgCI in the crude oil can corrode the refining equipment, hence these salts are removed by electrical desalting and dehydration methods.
- b) The sulphur compounds present in the crude oil is removed by treating oil with copper oxide, which results in the formation of copper sulphide (solid), which is then removed by filtration.

Fractional distillation

- **Step - III: Fractional distillation**
- The crude oil is then heated to about 400°C in an iron retort, whereby all volatile substances (except asphalt or coke) are evaporated. The hot vapors are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. (Figure)
- When the vapours of the oil go up in the fractionating column, they become gradually cooler and get condensed at different heights of column. The fractions having higher boiling points condense at lower trays whereas the fractions having lower boiling points condense at higher trays. The gasoline obtained by the fractional distillation is called straight --run gasoline. Various fractions obtained at different trays are given in table.

Fractional distillation of Crude oil



Various fractions of crude oil and their composition and uses

S n.	Name of the fractions	Boiling range (°C)	Composition of Hydrocarbons.	Uses
1.	Uncondensed gases	Below 30°C	C_1 to C_4	As domestic and industrial fuel under the name LPG
2.	Petroleum ether	30 70 °C	C_5 to C_7	As a solvent.
3.	Gasoline (or) petrol.	40 - 120 °C	C_5 to C_9	As motor fuel, solvent and in dry cleaning.
4.	Naphtha (or) solvent spirit .	120. - 180 °C	C_9 to C_{10}	As solvent and in dry cleaning.
5.	Kerosene oil.	180 - 250 °C	C_{10} to C_{16}	As fuel for jet engines and an illuminant.
6.	Diesel oil (or) gas oil	250 320 °C	C_{10} to C_{18}	As Diesel engine fuel.
7.	Heavy oil.	320 - 400 °C	C_{17} to C_{30}	Production of gasoline by cracking process.

Various fractions recovered from Heavy Oil

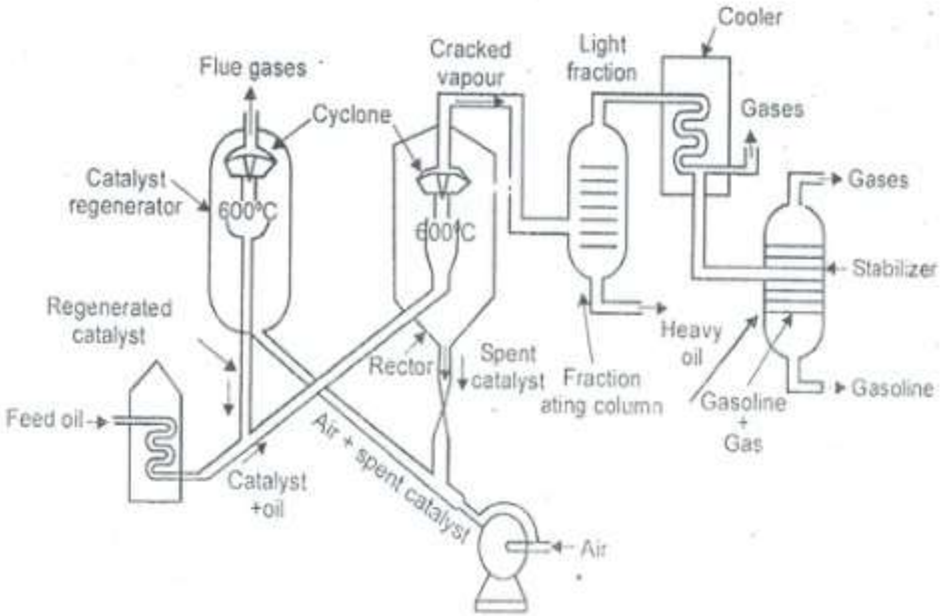
Sn.	Name of the fractions	Boiling range (^{O}C)	Composition of Hydrocarbons.	Uses
1.	Lubricating oil	-	C_{17} to C_{20}	Used as lubricants
2.	Petroleum jelly (Vaseline)	-	-	Used in medicines and cosmetics
3.	Paraffin wax	-	C_{20} to C_{28}	Used in candles, wax paper, boot polish, etc
4.	Grease	-	-	Used as lubricants.
				Used for making

Cracking

- The decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight is called cracking.
- The gasoline obtained from the fractional distillation of petroleum, has the highest demand as a motor fuel, but the yield of this fractions is only 20-30% (Crude oil) and also quality as straight-run gasoline which is not good an_ hence is used only after proper blending. To overcome these difficulties, the higher boiling fractions (e.g. fuel oil and gas oil) are converted into lower boiling fractions gasoline (petrol) by cracking process.
- The cracked gasoline gives better engine performance i.e., they are suitable for spark -ignition engines of automobiles. In cracking process, higher saturated hydrocarbon molecules are converted into simpler molecules such as paraffinic and olefinic hydrocarbons,
- There are two methods of cracking in use
- 1. Thermal cracking 2. Catalytic cracking

- **ii) Fluid (Moving)-bed catalytic cracking**
- In this process, solid catalyst is finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock (gas oil, heavy oil, etc.,) mixed with fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier molecules into lighter molecules occurs at a temperature of 530°C and pressure of about 3' to 5 kg/cm2. The top of the reactor, there is a centrifugal separator, which, allows the low boiling lighter molecules move up to the top of the reactor and enter into the fractionating column but retains all the catalyst powder in the reactor itself. The carbon deposited on the catalyst powder are burnt off in the regenerator and the temperature rises to about 590°C or more. The cracked gases and gasoline are removed from the top of the fractionating column and sent to a cooler, where gasoline is condensed. It is then sent to a stabilizer to recover pure gasoline. The product contains a higher proportion of aromatics and iso-paraffins.

Fluid (Moving)-bed catalytic cracking

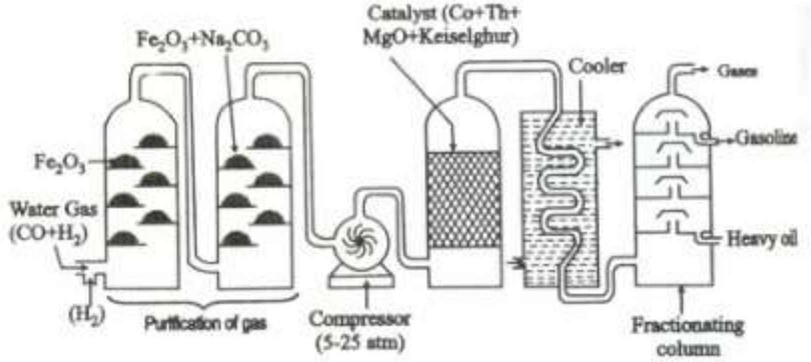


- **Synthesis of Gasoline**
- The gasoline obtained from the fractional distillation of crude petroleum oil is not enough to meet the requirement of the present community due to vast increase of automobiles. Hence an alternate source need of finding out to manufacture synthetic petrol.
- Synthetic petrol can be manufactured by the process of hydrogenation of coal. The preparation of liquid fuels from solid coal is called hydrogenation of coal.
- Gasoline is synthesised by the following methods.
- 1. Fischer- Tropsch process.
- 2. Bergius process.

1. Fischer- Tropsch process

- In this process, coal is first converted into coke. Then water gas is produced by the action of steam over red hot coke. It is mixed with hydrogen and the mixture is compressed to 5-25 atmospheres. The compressed gases are then led through a converter which is maintained at a temperature of 200-300°C. The converter is provided with a suitable catalyst consisting of a mixture of 100 parts cobalt, 5 parts thoria, 8 parts magnesia and 200 parts kieselguhr. A mixture of saturated and unsaturated hydrocarbons occurs as a result of polymerisation.

- $n\,\mathrm{CO} + 2\,n\,\mathrm{H2} \longrightarrow \mathrm{CnH2n} + n\,\mathrm{H2O}$
-
- $n\,\mathrm{CO} + (2\,n + 1)\,\mathrm{H2} \longrightarrow CnH2n{+}2 + n\,\mathrm{H2O}$
- The reactions are strongly exothermic. Hence, the hot out coming gaseous mixture is led to a cooler where a liquid resembling crude oil is obtained. The crude oil thus obtained is then fractionated to yield gasoline and high boiling heavy oil. The heavy oil is used for cracking to get more gasoline



Knocking

- Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine.

- In a petrol engine, a mixture of gasoline vapour and air at 1: 17 ratio is used as fuel. This mixture is compressed and ignited by an electric spark. The products of oxidation reaction (combustion) increases the pressure and pushes the piston down the cylinder. If the combustion proceeds in a regular way, there is no problem in knocking. But in some cases, the rate of combustion (oxidation) will not be uniform due to unwanted chemical constituents of gasoline. The rate of ignition of the fuel gradually increases and the final portion of the fuel-air mixture gets ignited instantaneously producing an explosive sound known as "Knocking". Knocking property of the fuel reduces the efficiency of engine. So a good gasoline should resist knocking.

- **Chemical structure and knocking**
- The knocking tendency of fuel hydrocarbons mainly depends on their chemical structures. The knocking tendency decreases in the following order.
- Straight chain paraffins> Branched chain paraffins> Cycloparaffins > Olefins > Aromatics.

- **Improvement of antiknock characteristics**
- The octane number of fuel can be improved by
- (i) blending petrol of high octane number with petrol of low octane number, so that the octane number of the latter can be improved.

  (ii) the addition of anti-knock agents like Tetra-Ethyl Lead (TEL).

Anti-Knocking agent

- **LEADED PETROL (ANTI-KNOCK AGENT)**

- The anti-knock properties of a gasoline can be improved by the addition of suitable additives. Tetraethyl lead (TEL) or $(C_2H_5)_4$ Pb is an important additive added to petrol. Thus the petrol containing tetra ethyl lead is called leaded petrol.

- TEL reduces the knocking tendency of hydrocarbon. Knocking follows a free radical mechanism, leading to a chain growth which results in an explosion. If the chains are terminated before their growth, knocking will cease. TEL decomposes thermally to form ethyl free radicals which combine with the growing free radicals of knocking process and thus the chain growth is stopped.

- **Disadvantages of using TEL**
- When the leaded petrol is used as a fuel, the TEL is converted to lead oxide and metallic lead. This lead deposits on the spark plug and on cylinder walls which is harmful to engine life. To avoid this, small amount of ethylene dibromide is added along with TEL. This ethylene dibromide reacts with Pb and PbO to give volatile lead bromide, which goes out along with exhaust gases.
- But this creates atmospheric pollution. So nowadays aromatic phosphates are used instead of TEL
- (iii) Nowadays aromatic phosphates are used as antiknock agent because it avoids lead pollution.

OCTANE NUMBER (or) OCTANE RATING

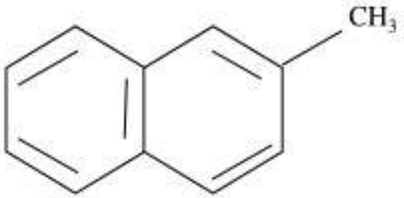
- Octane number is introduced to express the knocking characteristics of petrol. It has been found that n-heptane knocks very badly and hence, its anti-knock value has been given zero. On the other hand, iso-octane gives very little knocking and so, its anti-knock value has been given 100.

- *Thus octane number is defined as 'the percentage of iso-octane present in a mixture of iso-octane and n-heptane.‘*

- **Iso-octane (Octane number = 100)**
- CH3 – CH2 – CH2 – CH2 – CH2 – CH2 - CH3
- **n - heptane (Octane number = 0)**

CETANE NUMBER (or) CETANE RATING

- Cetane number is introduced to express the knocking characteristics of diesel. Cetane has a very short ignition lag and hence its cetane number is taken as 100. On the other hand 2-methyl naphthalene has a long ignition lag and hence its cetane number is taken as zero.
- CH3 – (CH2)14 – CH3
- n-cetane (hexa decane)
- cetane number = 100



- **2-methyl naphthalene (cetane number = 0)**
- Thus the cetane number is defined as "the percentage of hexa decane present in a mixture of hexa decane and 2-methyl napthalene, which has the same ignition lag as the fuel under test".
- The cetane number decreases in the following order.
- n-alkanes > Cycloalkanes > alkenes >branched alkanes >aromatics
- The cetane number of a diesel oil can be increased by adding additives called dopes.
- **Important** dopes: *Ethyl nitrate, Iso-amyl nitrate.*

Biodiesel

- A fuel derived from organic oils, such as vegetable oil, rather than petroleum. Biodiesel's use and production are increasing. It's typically used for aircraft, vehicles and as heating oil.
- **Transesterification**
- Animal and plant fats and oils are composed of triglycerides, which are esters containing three free fatty acids and the trihydric alcohol, glycerol. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol are used. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol. Under normal conditions, this reaction will proceed either exceedingly slowly or not at all, so heat, as well as catalysts (acid and/or base) are used to speed the reaction. It is important to note that the acid or base are not consumed by the transesterification reaction, thus they are not reactants, but catalysts. Common catalysts for transesterification include sodium hydroxide, potassium hydroxide, and sodium methoxide.

- Almost all biodiesel is produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids). However, biodiesel produced from other sources or by other methods may require acid catalysis, which is much slower.

UNIT-V

ENGINEERING MATERIALS

Lubrication

- ***Friction*** is the resistance to relative motion between two surfaces in contact.
- Any substance placed between the rubbing surfaces, which reduces friction is called ***lubricant.***

The important functions of lubricant in bearings are;

1. To reduce friction & wear between the sliding surfaces by separating them by a thin film of oil.
2. To remove the heat generated by friction.
3. To provide a protective film against corrosion.
4. In machine tools, it flushes out the metal chips.
5. In automobile engines, a detergent added to lubricant removes sludge deposits.

Types of Lubricants

Lubricants are classified as;

(i) Liquid lubricants

(ii) Semi-liquid lubricants

(iii) Solid lubricants.

Liquid lubricants may be

mineral oils (produced from refining of petroleum products)

synthetic oils (produced from sand, coal, etc.)

Animal & vegetable oils (fish oils, lard oil, Castor oil, cotton seed oil, Olive oil, etc.)

Liquid Lubricants

Semi Liquid Lubricants

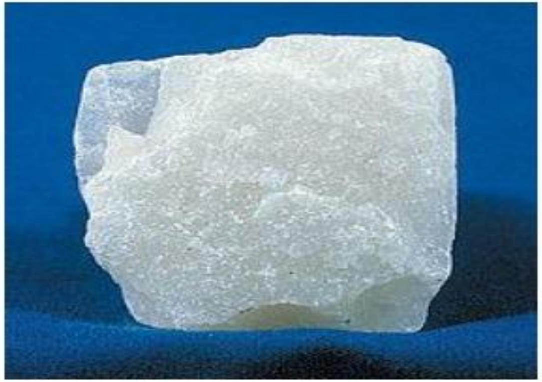
- ***Semi liquid lubricant or Grease*** is obtained by compounding the petroleum products with soap mixtures.
- They are highly viscous. They can withstand high pressure, temperature and also they resist corrosion.
- They are used in gear drives, chain drives, flexible cables, etc.
- They may be of Aluminium base, Calcium base, sodium base or mixed base types.

Greases

Solid Lubricants

Graphite

Soap Stone



Talc

French Chalk

Properties of Lubricants

The following are the important properties of a lubricant.

Viscosity:

- It is the property of a fluid by virtue of which it offers resistance to shear (flow).
- If the viscosity is too low, a liquid film can not be maintained between the moving surfaces.
- On the other hand, a high viscosity oil will offer greater resistance to moving parts.
- The viscosity decreases with increase in operating temperature.
- ***A good lubricant, the change of viscosity with temperature must be a minimum.***

Types of viscosity

Viscosity of a lubricant may be defined by

(i) Absolute (or Dynamic) Viscosity (m)

- It is the force required to move a surface of unit area at unit velocity when separated by an oil film of unit thickness.
- In SI system, unit of absolute viscosity is N-sec/m^2 (Pascal-sec)

(ii) Kinematic Viscosity (n)

- It is the ratio of absolute viscosity to mass density of the fluid. Its SI unit is m^2/sec.

Flash Point:

- Flash point is the minimum temperature at which an oil gives off sufficient vapour to ignite momentarily on introduction of flame.
- A good lubricant must have its flash point ***above the operating temperature.***

Fire Point:

- Fire point is the lowest temperature at which an oil gives off sufficient vapour to burn continuously when bought in contact with a flame.
- A good lubricant must have ***a high fire point.***

Pour Point & Cloud Point:

- Pour point is the lowest temperature at which an oil ceases to flow when cooled.
- Cloud point is the lowest temperature at which wax and other substances crystallize and separate out when cooled.
- A good lubricant must have ***a low pour & cloud points.***

Carbon residue:

- Lubricating oils contain higher percentage of carbon in the combined form. At high temperatures, they decompose resulting in carbon deposits on bearing surfaces which is undesirable.
- ***A good lubricant should not decompose even at high temperatures.***

Mechanisms of Lubrication

1. Fluid-film (or) Thick-film (or) Hydrodynamic lubrication
2. Boundary lubrication (or) Thin-film lubrication
3. Extreme pressure lubrication

1. Fluid Film/Thick-Film/Hydrodynamic Lubrication (~ 1000 Å)

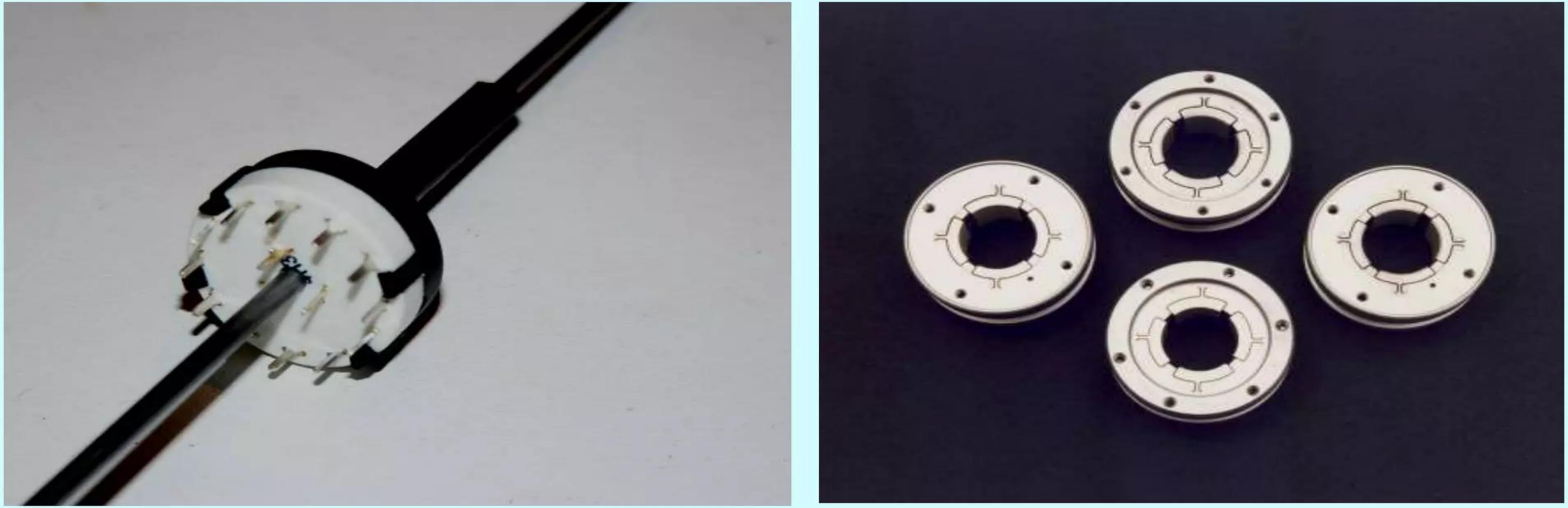
Characteristics:

- The surfaces are separated by a thick-film (at least 1000 Å thick) and hence there is no direct surface to surface contact.
- No welding of junctions.
- Since thick film lubricant covers/fills the irregularities on the both surfaces, there is no direct contact between material surfaces and so the wear is reduced.

In Fluid Film Lubrication, the Lubricating properties depend on:

- Viscosity of lubricant (Lubricant should be of low viscosity).
- Thickness of lubricant layer.
- Relative velocity and area of moving/sliding surfaces.

Example: Shaft running (Journal bearings)



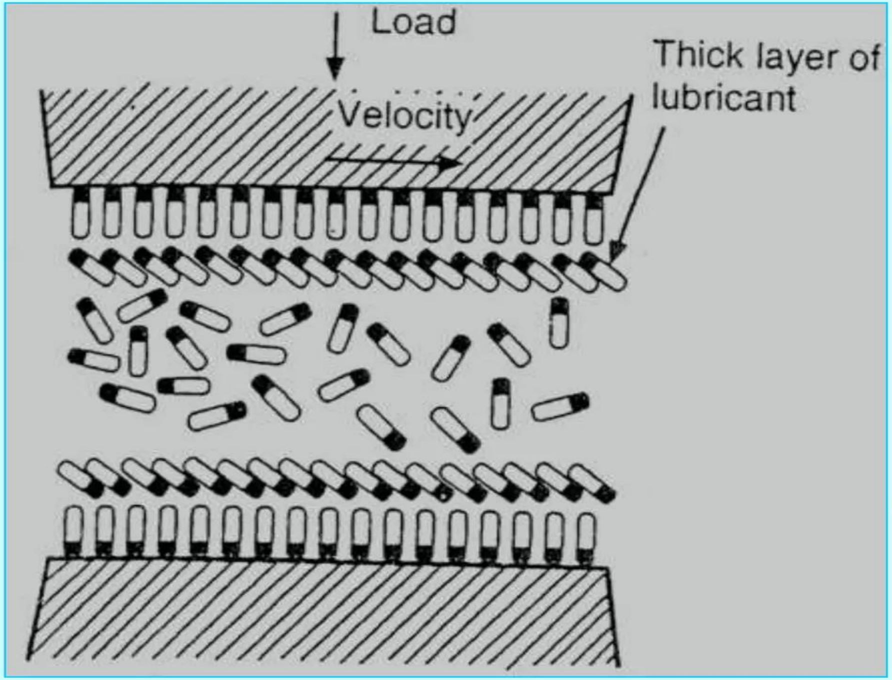
Lubricant oil covers the irregularities of the shaft as well as the bearing surfaces.

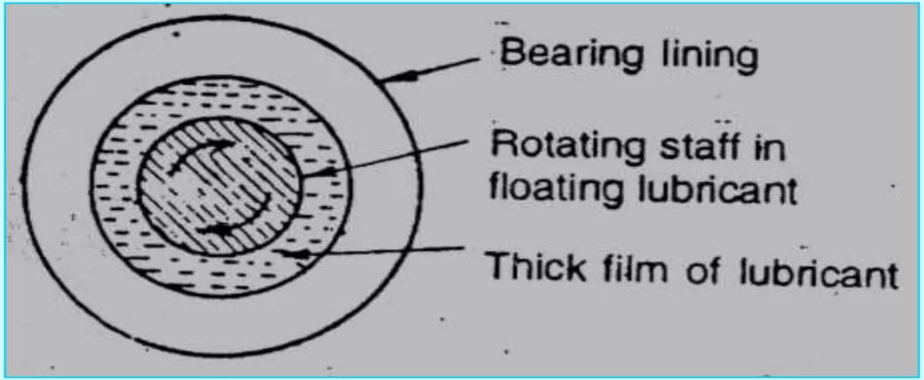
- **Examples where fluid film lubrication is used are :**
  - i) Sophisticated instruments
  - ii) Light machines like watches, guns, sewing machines etc.
- **Examples for fluid-film lubricants are:**

Hydrocarbon oils **are considered to be satisfactory lubricants.**

- ➢ To maintain viscosity throughout lifecycles long chain polymers are used as blenders with normal hydrocarbons oils.
- ➢ Small amount of unsaturated hydrocarbons present in hydrocarbon oils produced from petroleum fractions, which causes oxidation and produce gummy like products. Hence, anti-oxidant like aminophenol are used in journal bearings with lubricant

Mechanism of fluid film lubrication





2. Boundary Lubrication/Thin-film Lubrication

Characteristics of thin film lubrication are:

- High viscosity-index.
- Resistance to heat and oxidation.
- Good Oiliness.
- Low pour-point.

Mechanism of Boundary Lubrication/Thin-film Lubrication

This Lubrication takes place due to:

- Adsorption of lubricating oils to both surfaces by physical/chemical means.
- The adsorbed layers on the both metal surfaces carry the applied load.
- Co-efficient of friction, f = 0.05 - 0.15 and distance between surfaces is to be the order of the distance of the asperities.

For boundary lubrication, the lubricant molecule should have:

(i) Long hydrocarbon chain with polar groups.

(ii) Polar groups promote spreading and orientation over the metallic surfaces at high pressure.

(iii) Lateral attraction between the chains.

(iv) Active groups or atoms, which can form chemical linkages metal or other surfaces.

Examples of Boundary lubrication

- **Vegetable and animal oils (glycerides of higher fatty acids & their soaps).**
  - These oils either physically adsorbed to metal surfaces or react chemically at the metal surfaces.
  - Although these oils posses greater adhesion property, yet they tend to breakdown at high temperatures. Hence, fatty acids are added to improve the oiliness.
- **Graphite and Molybdenum disulphide alone or oil suspension may be used because:**
  - They have Low internal friction
  - They can bear/withstand compression
  - They are thermally stable

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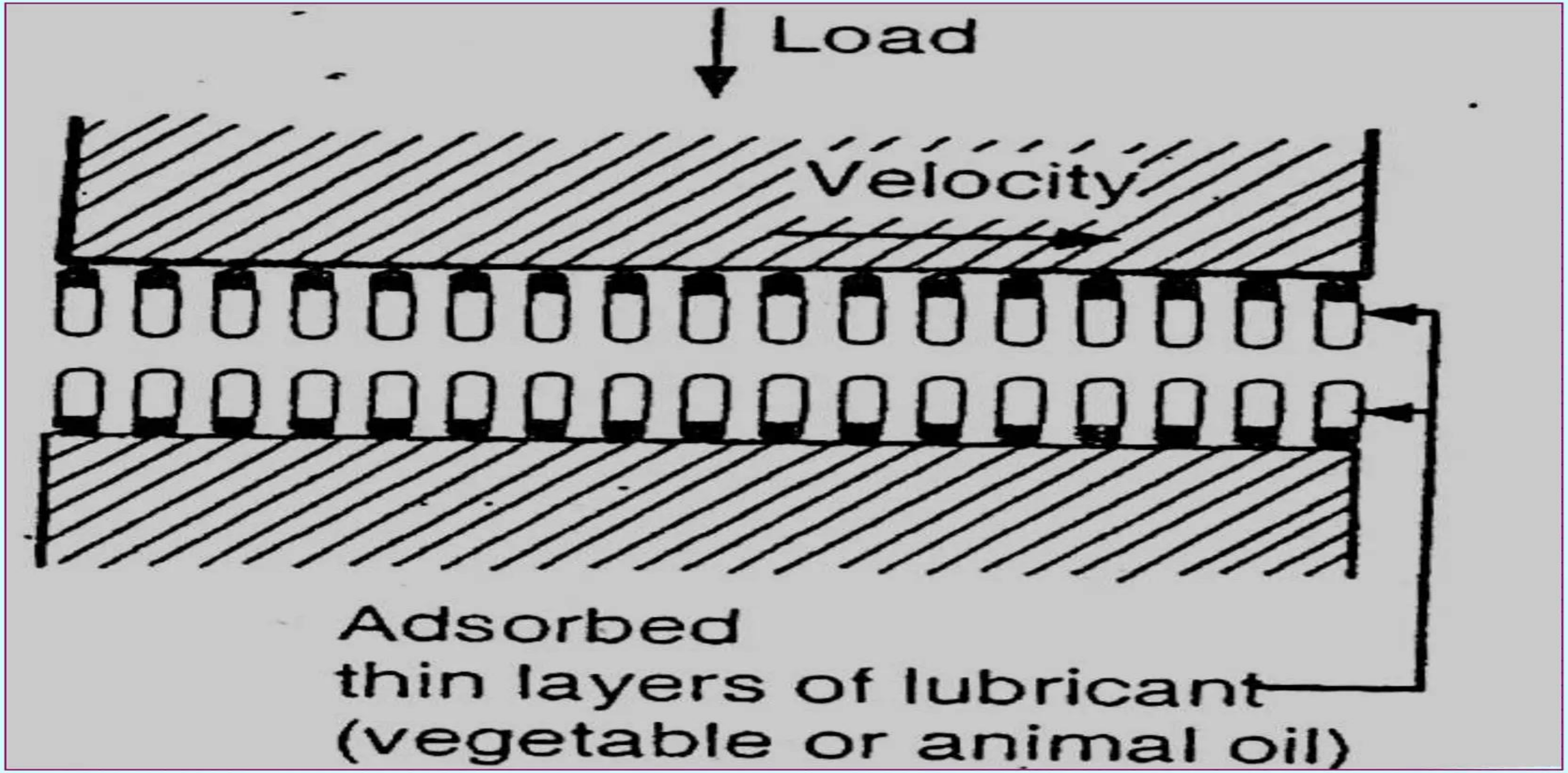
Mechanism of Boundary Lubrication



3. Extreme-pressure Lubrication

- When moving/sliding surfaces are under very high pressure and speed, a high local temperature is attained.
- In such conditions, liquid lubricants fail to stick and may decompose and even vaporize.
- To avoid this, special additives are added to mineral oils. These are called "extreme-pressure additives".

Mechanism

- The "extreme-pressure additives" form on metal surfaces more durable films, capable of withstanding very high loads and high temperatures.

Examples:

- Organic compounds containing chlorine, sulphur and phosphorus.

- These compounds react with metallic surfaces, at prevailing high temperatures, to form metallic chlorides, sulphide or phosphides.

Types of Liquid Lubricants

a) Animal and Vegetable oils:

- Usable under very high temperature and heavy load.

❖ Disadvantages of its usages are

1. Costly
2. Undergo oxidation easily in contact with air and forms gummy and acidic products, and get thickened.
3. Tendency to hydrolyze in contact with moist-air or aqueous medium.

So, they are used as "*blending agents*" with other mineral oils.

b) Mineral oils or petroleum oils:

- They are obtained by distillation of petroleum.

- Length of hydrocarbon chain varies between 12 to 50 carbon atoms.
- Shorter- chain oils have lower viscosity than the longer- chain hydrocarbons.

- **Liquid lubricants are most widely used lubricants because they are**
  1. Cheap
  2. Available in abundance
  3. Quite stable under service conditions.

- But they have *poor oiliness character* compared to animal and vegetable oils.

- So, high molecular weight compounds like oleic acid, stearic acid are used to over come this problem.

c) Blended oils:

- No single oil serves as the most satisfactory lubricant for many of the modern machines. Hence, additives are used to improve the properties. These blended oils give desired lubricating property required for a machinery.

CLASSIFICATION OF LUBRICANT

- Based on Physical state, lubricants are classified as:

a) Lubricating oils or liquid lubricants

b) Semi solid lubricants or greases

c) Solid lubricants

Additives used are:

a) Oiliness- carriers:

- Coconut oil, caster oil, and palmitic, stearic and oleic acids.

b) Extreme-Pressure additives such as:

- Fatty esters or acids which form oxide film with metal surface.
- Organic materials containing sulphur.
- Organic chlorine compounds.
- Organic phosphorous compounds.
- Sometimes lead (Pb) compounds could be used as high pressure lubricants.

c) Pour-point depressing additives:

- Phenol, condensation product of chlorinated wax with naphthalene.

d) *Viscosity index improvers* : hexanol

e) *Thickeners* : Polystyrene or polystyers

f) *Antioxidants or inhibitors* : Aromatic phenolic or amino compounds

g) *Corrosion preventers* : Phosphorous or Antimony organic compounds

h) *Abrasion inhibitors* : tricresyl phosphate

i) *Antifoaming agents* : glycols and glycerol

j) *Emulsifiers* : sodium salts of sulphonic acid

k) *Deposit inhibitors* : detergents such as salts of phenol and carboxylic acids

2. Semi-Solid Lubricants or Greases

- Semi solid consisting of a soap dispersed throughout a liquid lubricating oil.

- May be Petroleum oil or synthetic oil with a specific additive.

Preparation:

Saponification of fat (such as tallow or fatty acid) with alkali (like lime, caustic soda etc.,)

↓

Addition to hot lubricating oil under agitation

- To increase the heat resistance of grease, inorganic solid thickening agents (like finely divided clay, bentonite, colloidal silica, carbon block etc.,) are added.
- Have higher <u>shear or frictional resistance</u> than oils and hence support much heavier load at lower speeds.

Applications of Greases:

- When oil cannot remain in place due to high load, low speed, intermittent operation, sudden jerks etc.
- Work at high temperature
- When external contamination may create problem
- When dripping or spurting of oil is undesirable

Types of greases:

- Calcium based greases or cup-greases
- Soda-based greases
- Lithium-based greases
- Axle- greases → lime with resin and fatty acids
- Graphite greases
- Soap stone

3. SOLID LUBRICANTS

Solid lubricants are used when:

- Other lubricants can not be used
- Contamination undesirable
- Too high temperature or load are involved
- Combustible lubricants not acceptable

Examples of solid lubricants used are:

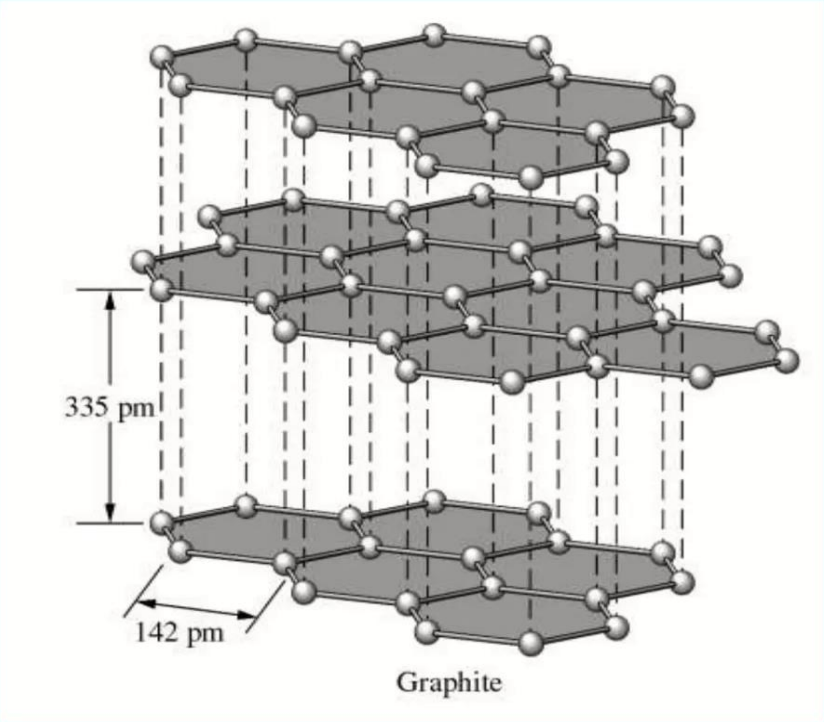
a) Graphite (or)

b) Molybdenum disulphide

Examples of Solid Lubricants

1.Graphite:

- Very soapy in touch
- Non inflammable
- Not oxidized in air below 375°C
- Oil + graphite → oildag
- Water + Graphite → aquadag
  - Emulsifying agent (tannin)
- Grease + graphite → graphite -greases

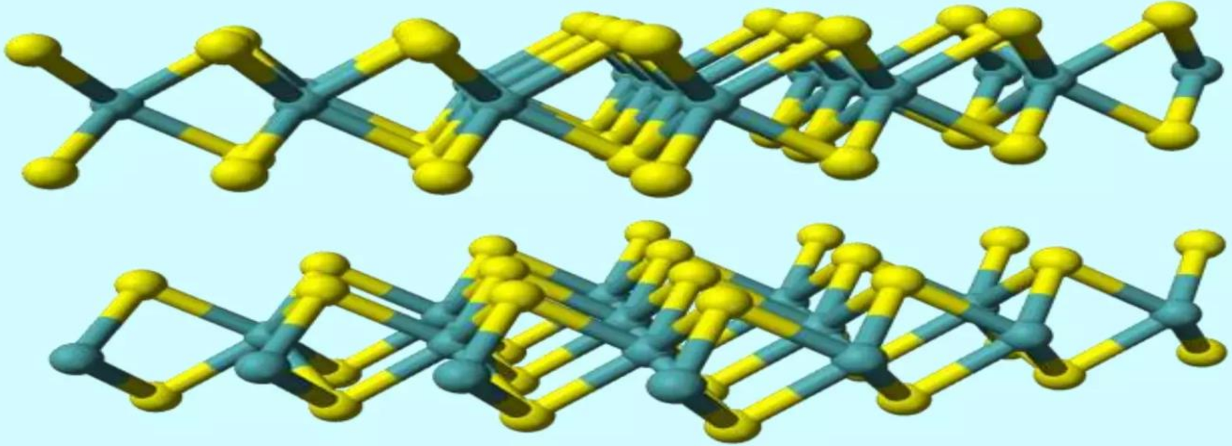


Graphite

Examples of Solid Lubricants

2. Molybdenum disulphide:

- Low coefficient of friction
- Stable in air up to 400 ° C



- Soapstone, talc or mica are also used as solid lubricants.