UNIT II
CORROSION

Corrosion: Destruction or deterioration of metals by surrounding environment through electrochemical process.

Eg: rusting of iron, Green scales formed on copper plates.

Electrochemical theory of corrosion:

Corrosion can be best explained by taking rusting of iron as an Eg:

When a metal like iron is expose to the environment, according to electro chemical theory the following changes occur.

- Formation of minute galvanic cells on the same metal(anodic and cathodic)
- Anodic and cathodic areas are formed due to the impurities in the metal.
- Oxidation takes place at anode Reduction takes place at cathode.
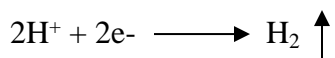- Anode corrodes but cathode is unaffected.
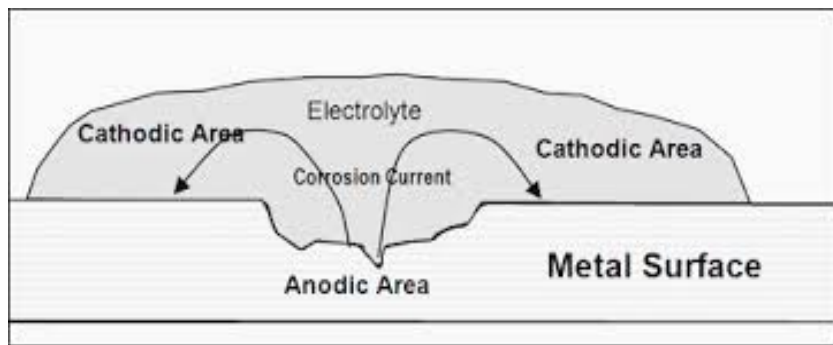
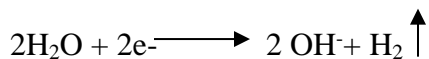**At Anode:** At anode metal undergoes oxidation where metals are converted to metal ions.

$$Fe \longrightarrow Fe^{2+} + 2e-$$
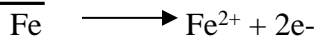
At cathode: undergoes reduction in the presence and absence of oxygen

Case i) In the acidic medium and absence of oxygen.

$$2H^+ + 2e- \longrightarrow H_2 \uparrow$$
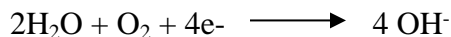
Case ii) In the neutral and alkaline medium and absence of oxygen.

$$2H_2O + 2e- \longrightarrow 2 OH^- + H_2 \uparrow$$

Case iii) In the acidic medium and presence of oxygen.

$$4H^+ + O_2 + 4e- \longrightarrow 2H_2O$$
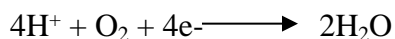
Case iv) In the neutral and alkaline medium and presence of oxygen.

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

Overall reaction: It is understood from the above reaction that Fe^{2+} and OH^- ions are formed at the anode and cathode sites respectively.

$$2Fe^{2+} + 4 OH^- \longrightarrow 2Fe (OH)_2$$
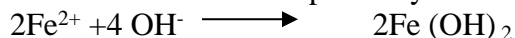
2Fe (OH) $_2$ in the presence of excess and limited oxygen and moisture forms yellow rust and black rust.

$$2Fe (OH)_2 + O_2 + 2H_2O \longrightarrow Fe_2 O_3.nH_2O \text{ (yellow rust)}$$

$$2Fe(OH)_2 + O_2 + 2H_2O \longrightarrow Fe_3O_4.nH_2O \text{ (black rust)}$$
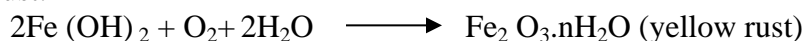
Differential Metal Corrosion:

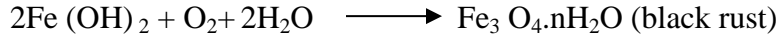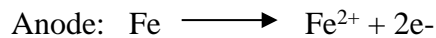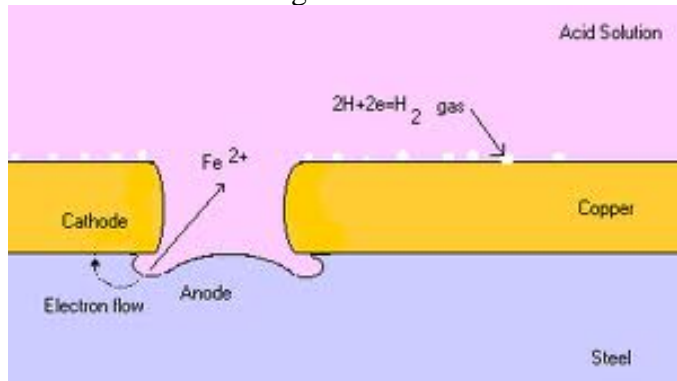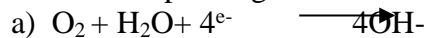This type of corrosion occurs when two dissimilar metals are in contact with each other in a corrosive conducting medium . The two metals differ in their tendencies to undergo corrosion The one with the lower electrode potential (-ve potential) act as anode thereby undergoes corrosion and the one with the higher electrode potential (+ve potential)act as cathode which is safe. The potential difference b/w the two electrodes is the driving force for corrosion.
The reactions occurring are

Anode: $Fe \longrightarrow Fe^{2+} + 2e-$
Cathode: depending on the nature of corrosion environment
a) $O_2 + H_2O + 4e- \longrightarrow 4OH-$
b) $2H^+ + 2e- \longrightarrow H_2 \uparrow$

Differential aeration Corrosion:
This type of corrosion occurs when a metal is exposed to differential air or oxygen concentration .The part of the metal exposed to higher concentration of O_2 acts as cathode and the part of the metal exposed to lower concentration acts as anode consequently poorly oxygenated anode undergoes corrosion.

The reactions occurring are
Anode: $M \longrightarrow M^{n+} + ne-$
Cathode: depending on the nature of corrosion environment
a) $O_2 + H_2O + 4e- \longrightarrow 4OH-$
b) $2H^+ + 2e- \longrightarrow H_2 \uparrow$

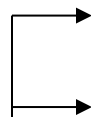**Hence** $M^{n+} + 4OH- \longrightarrow M(OH)_2$
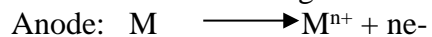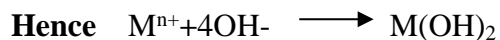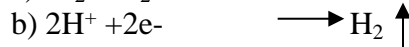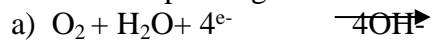
Water Line Corrosion
Differential aeration Corrosion
Pitting corrosion
Water Line Corrosion:

Water storage steel Tank   Ship in sea
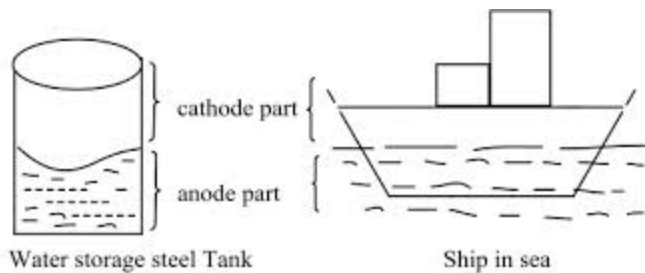
Water Line Corrosion is observed in the cases of ocean ships, water storage steel tanks where in apportion of the metal is always under water. The part of the metal below water acts as anode and undergoes corrosion the part of the metal exposed to atmospheric oxygen n acts as cathode which is safe. A distinct brown line is formed just below the water level due to the deposition of rust
Eg ocean ships, water storage steel tanks

Pitting corrosion-

This is one of the destructive forms of corrosion leading to the formation of pits or holes. Pitting corrosion results when small particles of dust / impurities/water drop gets deposited on the metal surface. The metal surface covered by he dust will be less aerated when compared to exposed surface. Thus the covered portion becomes anode w.r.t the surface exposed .In the presence of electrolytes and moisture, corrosion starts beneath the dust forming a pit. Corrosion rate increases as there exists small anodic area when compared to cathodic area resulting the enlargement of pit.

Eg: Pin stapled to paper
    Nail inside the wall

Cathode: $O_2 + H_2O + 4e^- \longrightarrow 4OH^-$

Anode:Fe $\longrightarrow$ Fe^{2+} +2e-
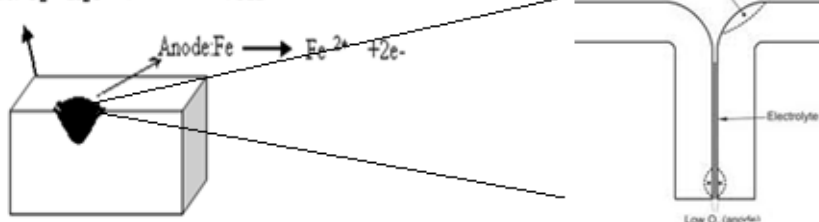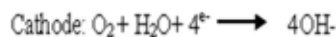
Stress corrosion: (stress cracking)

It can be an internal or external stress developed during the fabrication of articles, when subjected to mechanical operations like poor design, hammering, bending, riveting. The metal atoms under stress are always at higher energy levels and they are highly reactive. As a result corrosion cell formed with stressed part acting as anode and unstressed part acting as cathode. Corrosion takes place at the stressed regions

Stress corrosion is best explained by taking caustic embrittlement of steel

Caustic embrittlement of steel occurs in the case of boilers operating at high temperatures and pr. at the stressed regions such as Cracks, rivets, bends and joints.
The water fed into the boilers contains caustic soda (NaOH) left behind during the softening process. At high temperatures and pr. Na_2CO_3 undergoes hydrolysis to produce NaOH and CO_2.

36

$$Na_2CO_3 \longrightarrow NaOH + CO_2$$
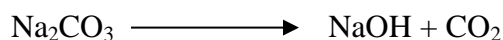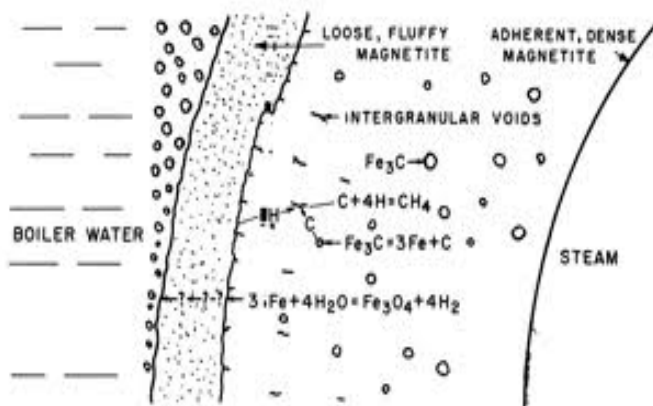
The NaOH seeps to the cracks, rivets, as there is a poor circulation of water in these regions the NaOH gets deposited when the concentration of NaOH reaches 10% it reacts with Fe giving Na_2FeO_2 sodium ferroate. This again under goes hydrolysis depositing magnetite Fe_3O_4.

$$Na_2FeO_2 \longrightarrow NaOH + Fe_3O_4$$

The NaOH regenerates thus forming a corrosive environment. Thus at extreme cases the metal becomes brittle due to the deposition of magnetite. The corrosion cell is represented as
Metal under stress / Conc NaOH / Dil NaOH /Metal without stress
ANODE –oxidation /corrodes
CATHODE-Reduction / unaffected

Factors affecting the rate of corrosion

	Primary Factors(Related to metal)	Secondary factors(Relate to Environment)
Factors are:	Position in the galvanic series	pH
	Physical state of the metal	Temperature
	Hydrogen over voltage	Conductance of the medium
	Nature of the protective layer	Humidity
	Polarisation	Presence of impurities in Environment
	Anodic and cathodic areas	
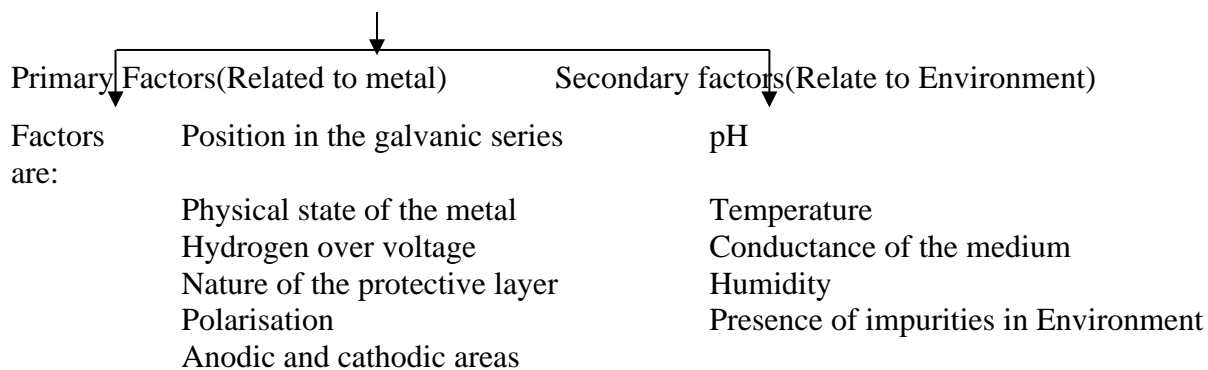
Position in the galvanic series:
• Extent of corrosion depends on the position of metal in emf or galvanic series
• Zn ($E_0 =-0.76$) corrodes faster than Ni($E_0=-0.23$)
• Metals above H_2 in emf series get corroded vigorously

• The more active metal(or higher up in the series) suffers corrosion when two metals or alloys are in electrical contact. (**galvanic corrosion**).
• The greater is the difference in their position, the faster is the corrosion of anodic metal/alloy.
• The potential diff. between the anode and cathode is the driving force of an electrochemical reactions.
• The greater is the difference in their position, the faster is the corrosion of anodic metal/alloy.

Physical state of the metal
- The rate of corrosion is influenced by the physical state of the metal such as, grain size, stress, etc.
- The smaller the grain size, it is easily soluble and greater the rate of corrosion and vice versa.
- The areas under stress, tend to be anodic and susceptible for corrosion.

Hydrogen overvoltage
- A metal with low hydrogen over voltage (OV) is more susceptible to corrosion, when the cathodic reaction involves hydrogen evolution.
- The reduction in the over voltage of the corroding metal/alloy, accelerates the corrosion rate.
- Example: when Zn metal in contact with 1N H_2SO_4, it undergoes corrosion by the evolution of hydrogen gas. The rate of the reaction is very slow, because its O.V. is high (~0.7V). If a few drops of Cu solution is added the rate of corrosion increases since, Cu gets deposited on Zn forming minute cathodes, where the hydrogen OV value is only 0.33V.

Nature of the protective layer
- In aerated atmosphere almost all metals get covered with a thin surface film of metal oxide.
- The thickness of the oxide layer varies with respect to the nature of the metal and the environment.
- The ratio of the volumes of the metal oxide to the metal is called specific volume ratio.
- If the specific volume ratio is higher, the oxide film is nonporous, protective in nature, prevents the further corrosion and vice-versa.

Polarization
- The anodic and cathodic reactions take place simultaneously during corrosion, and causes polarization of the electrodes.
- The polarization of anode or cathode decreases the corrosion rate substantially.
- The presence of depolarizers reduces the polarization effect and thereby increases the rate of corrosion.
- The addition of complexing agents around anode and/or the presence of oxidizing agents around cathode, acts as depolarizers.

Area effect
- The rate of corrosion (x) is directly proportional to the ratio of area of cathode to the area of anode. i.e., x = area of cathode/ area of anode
- Higher the value of x, greater is the rate of corrosion..

When anode is small and cathode is large all the electrons liberated at anode, are consumed at the cathodic region. Therefore, the rate of anodic reaction is greater and increases the extent of corrosion.

pH of the medium
- Acidic media are generally more corrosive than alkaline/neutral media. The pH of the solutions decides the type of cathodic reaction.
- The corrosion of iron in oxygen free water is slow, until the pH<5, the corresponding corrosion rate is much higher in presence of oxygen.
- The metals which are amphoteric in nature viz. Al, Zn, etc., dissolve in alkaline solutions as complex ions.
- Corrosion of metals readily attacked by acid can be reduced by increasing the pH of the environment. Example: Zn suffers from severe corrosion even in the presence of mild acidic medium, whereas corrosion is minimum at pH=11.

Temperature:
- The velocity of a chemical reaction increases with increase in temperature.
- If the medium is acidic, hydrogen evolution takes place at cathode. The rate of diffusion of H^+ towards cathode increases with increase in temperature and enhances the rate of corrosion.
- If the medium is alkaline / neutral, oxygen absorption takes place at cathode. Since the solubilities of the dissolved gases decreases with increase in temperature, the rate of corrosion also decreases.
- Passive metals becomes active at high temperature and increases the rate of corrosion with increasing temperature. Ex. Caustic embrittlement in high pressure boilers.

Impurities present in the Environment
• Atm vicinity of industrial areas contains corrosive gases like CO2. H_2S,SO_2, fumes of HCl, H_2SO_4 etc.
• These gases increase the acidity of the liquid, electrical conductivity and corrosion current.
• In marine atm the presence of Na and other chlorides increase the conductivity of the sea water and thereby corrosion is speeded up.

Conductiance of the medium
• Conductance of the medium is very important for the underground and submerged structure.
• Conductivity of dry dandy soil is lower than those of clay or mineralized soil. Stray current (Power from leakage) will cause more severe damage to the metallic structure under clay and mineralized soil.
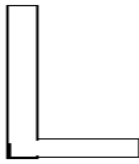
Corrosion Control
1. Proper design and selection of materials:
2. Metal coatings
3. Cathodic protection

1. Proper design and selection of materials:
   a. Avoid using 2 dissimilar metals
   b. Use an insulator at the contact points
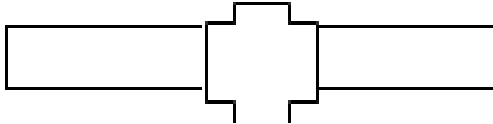   c. Select 2 metals having closer electrode potentials

d. Select a large anodic area with a small cathodic area

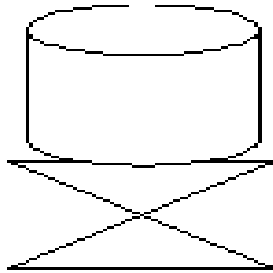Metals having sharp edges will undergo
stress corrosion- Bad design

Metals having smooth edges-
-good design

Metal pieces joined with metal connecter
Undergoes Differential metal corrosion
– Bad design

Metal pieces joined by welding
–Good design

Steel tank on wood block under goes
Differential aeration corrosion
– Bad design
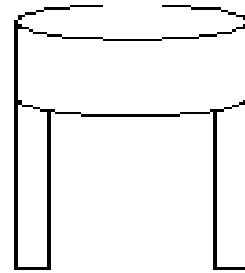
Steel tank supported on leg
with free circulation of air
–Good design

Galvanization
2. Metal coatings:
Tinning

Galvanization:

The process application of zinc coating on iron or steel to prevent from corrosion is called
Galvanization.

40

The process involves

- The article is cleaned with solvent to remove oil and grease this process is called as degreasing.
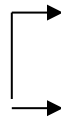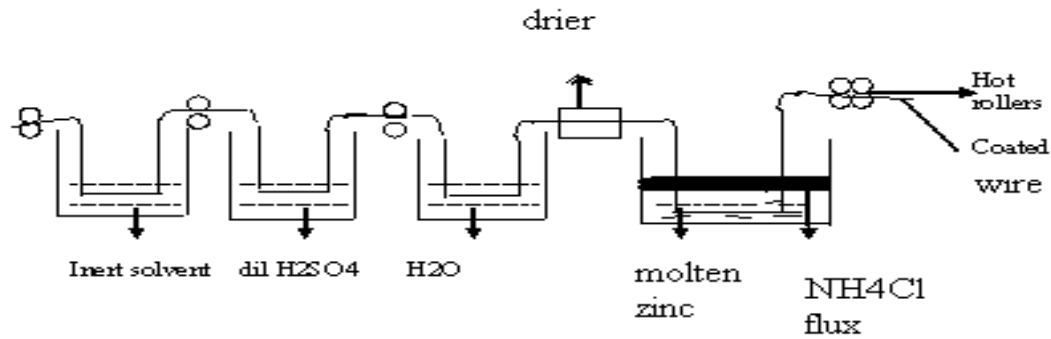- The article is then dipped in dil. H_2SO_4 for 10-15 min at 60-70^{0}C to remove scales or any rust impurities this process is called pickling.
- The article is washed well with water and dried using drier.
- It is then dipped in a bath of molten zinc maintained at 425-430 0c the surface is covered with NH4Cl flux to prevent the oxidation.
- The article taken out is found have a coating of zinc
- It is then passed through a pair of hot rollers to squeeze out the excess zinc adhered to the article.

Uses: pipes, nails, bolts, buckets etc.,

Tinning:

The process of application tin coating on iron or steel to prevent from corrosion is called tinning.
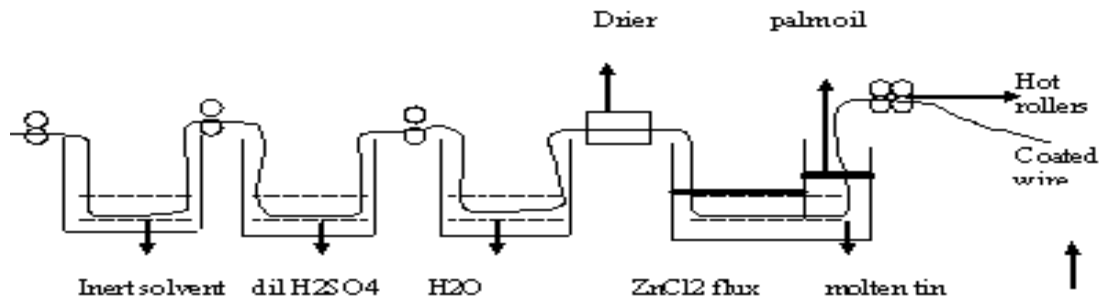

The process involves

- The article is cleaned with solvent to remove oil and grease this process is called as degreasing.

- The article is then dipped in dil. H_2SO_4 for 10-15 min at 60-70^{0}C to remove scales or any rust impurities this process is called pickling.
- The article is washed well with water and dried using drier.
- It is then dipped in a bath of $ZnCl_2$ flux to help the molten tin to adhere to the article.
- Then the article is dipped in a bath of molten tin, where the surface is covered with palm oil. The palm oil prevents the oxidation.
- The article taken out is found have a coating of tin
- It is then passed through a pair of hot rollers to squeeze out the excess tin
- adhered to the article.

Uses: food stuffs containers, ghee, oil, packing materials Etc.
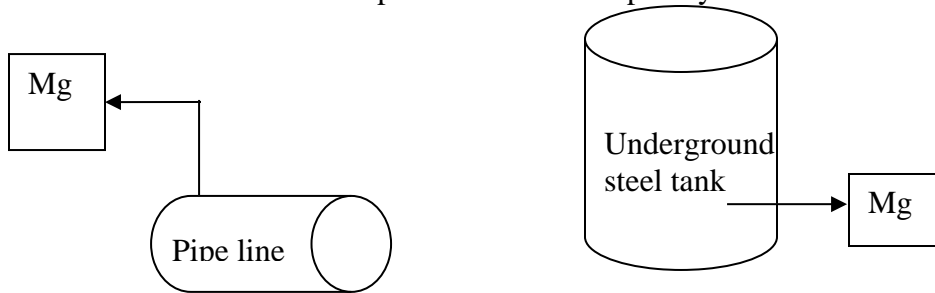
4. Cathodic protection:

During corrosion, anode undergoes corrosion and cathode is unaffected. The principle of cathode protection is to reverse the flow of electrons. The technique of offering protection to the metal by making it as cathode (by providing electrons) is called cathodic protection. They are of 2 types
a) Sacrificial anode method
b) Impressed current method

a)Sacrificial anode method:

In this method the metal to be protected is connected to a more anodic metal, as a result anodic metal under goes corrosion and original structure becomes cathode hence, protected.
Here, the more active anode sacrifices to protect the original metal are called as Sacrificial anode method. The active anode is replaced when it completely corrodes.

b) Impressed current method:

In this method, an impressed current is applied in opposite direction to nullify the corrosion current. The corroding metal is thus converted from anode to cathode and is hence protected. The impressed current is derived from a D.C source with an anode like graphite.

Corrosion
Current

Impressed
Current

Metal to be protected

i
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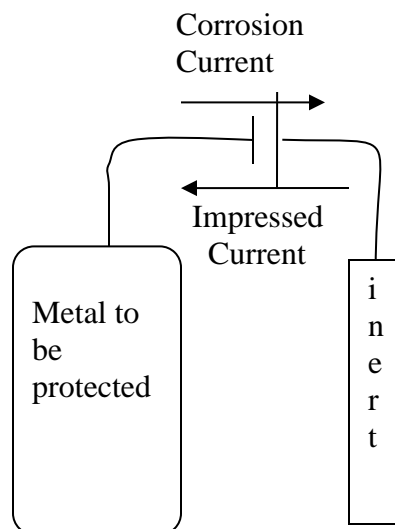
WATER TECHNOLOGY

CHEMICAL ANALYSIS OF WATER:

1. DETERMINATION OF DISSOLVED OXYGEN (Winkler's method)

Procedure:

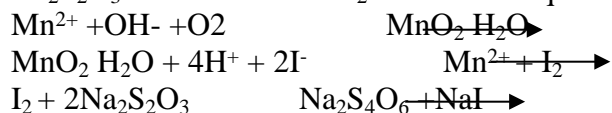Principle: In this method, the given sample of water is treated with Manganese sulphate and alk.KI solution. In alk. Medium dissolved oxygen oxidizes Mn^{2+} to Mn^{4+} and precipitates as$MnO_2.H_2O$. On acidification Mn^{4+} oxidizes KI to I_2 this liberated iodine is estimated against $Na_2S_2O_3$. Here amount of I_2 liberated is equal to the amount of dissolved oxygen.

$Mn^{2+} + OH^- + O2 \longrightarrow MnO_2 H_2O$

$MnO_2 H_2O + 4H^+ + 2I^- \longrightarrow Mn^{2+} + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + NaI$

Burette: $Na_2S_2O_3$

Conical flask: Take 10 ml of the waste water and dilute to 500ml divide to 2 equal parts

Part 1 at 0 times: Pipette out known volume of the water into the in a glass stoppered bottle+ 2 ml $MnSO_4$ + 5 ml of alk. KI. Shake it well allow the ppt to settle.+ Con. H_2SO_4 dissolve the ppt. Titrate against $Na_2S_2O_3$ using starch as the indicator till the blue colour disappears. Note the reading (V1 ml)

Part 2 after 5 days: at 20^0C similarly as above. Note the volume. (V2 ml)

Observations and calculations

Volume of water sample taken =V ml

Normality of $Na_2S_2O_3$ =N

Volume of 0 time reading = V1 ml

Normality of DO= N x V1 for 0 time
                    V

Amount of DO for zero time=D1= N x V₁x 8x 1000   mg/l of O_2
   V

43

Amount of DO on 5 day $=D2= \dfrac{N \times V_2 \times 8 \times 1000}{V}$ mg/l of O_2

Therefore, BOD $= \dfrac{(D1-D2) \times 500}{10}$ mg/l of O2

2. DETERMINATION OF COD OF WASTE WATER

Principle: In this method, the given samples of water containing organic and inorganic impurities are oxidized by $K_2Cr_2O_7$ and the un reacted $K_2Cr_2O_7$ is titrated against the burette solution in the presence of a redox indicator, which shows its colour change in the oxidized (bluish green) and reduced states (reddish brown).

$K_2Cr_2O_7 + H_2SO_4 \xrightarrow{\quad K_2SO_4 \quad} Cr_2(SO_4)_3 + H_2O + 3(O)$

$3(O) + {}_§ CHO \xrightarrow{\qquad} CO_2 + H_2O$
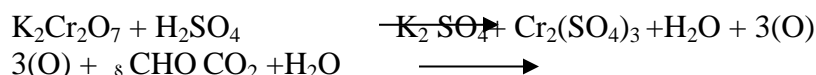
Procedure:
Burette: Std. FAS (redusing agent) + H_2SO_4 and diluted up to the mark.
Conical flask:
Back titration: Pipette out V ml of the waste water + 25 ml of $K_2Cr_2O_7$ + 2-3 drops of Ferroin indicator and titrate it against FAS.
Blank titration: Similar to back titration but using V2 ml of distilled water
Observations and calculations
Normality of FAS =N
Volume of Back titration =V1 ml
Volume of Blank titration = V2 ml
Volume of $K_2Cr_2O_7$ in terms of FAS= (V2- V1) ml

Normality of V ml of waste water $= \dfrac{N \times (V2-V1)}{V}$

COD of waste water $= \dfrac{N \times (V2-V1) \times 8 \times 1000}{V}$ mg/l of O_2

<u>**SOURCES OF WATER:**</u> River water, lake water, rain water, Sea water etc.

IMPURITIES IN WATER:
- **Dissolved Gases:** The water mainly CO_2 and O_2. Some water may contain NH_3 and H_2S which impart foul smell to water.
- **Dissolved solids:** The soluble salts impurities in water Ca, Mg, Na in various salts forms.
- **Suspended impurities:** like wood pieces, dead leaves, dead animals, fishes, algae, protozoa etc.
- **Microorganism:** Many pathogenic bacteria, microorganisms etc.

SOURCES OF WATER POLLUTION:
- Radio active waste from radioactive plants, laboratories.
- Domestic wastes like house hold waste, excretes etc

- Oil spillage from ships and oil industries.
- Gases like NH_3, H_2S etc.
- Pesticides and insecticides from industries.
- Industrial waste containing toxic chemicals.

Sewage: Water containing any one of these waste is called as **effluent or sewage**.

SEWAGE TREATMENT: The water containing heavy load of BOD, pathogenic bacteria, colour and annoying smell can't be directly discharged into the rivers as they mainly affect the aquatic life and causes many water borne diseases
The domestic sewage, therefore needs proper treatment which is carried out in 3 stages
- Primary treatment
- Secondary treatment
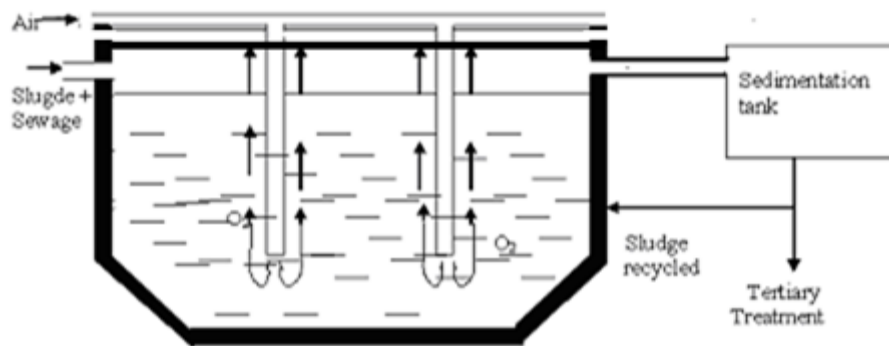- Tertiary treatment

Primary treatment: involves
- **Screening**: Removal of large suspended or floating water in sewage using mesh screens.
- **Slit and Grit removal**: Removal of heavy particles like sand, glass pieces etc. using grit chambers.
- **Removal of oil and grease**: is mainly done using skimming tanks by blowing air through the sewage and oils are lifted to the surface as foams (soapy mixture)which is then skimmed off.
- **Sedimentation process**: involves addition of coagulants like alum, ferrous salts etc. and there by ppt. out the suspended particles by sedimentation process.

Secondary treatment
Involves aerobic biochemical oxidation of sewage water. The sewage water after sedimentation is subjected to aerobic oxidation, during which the organic matter is converted N_2 to NH3 and nitrates and nitrites
    Activated Sludge Method (Biological treatment) this process involves extensive aeration of the sewage water and the process of aerobic is enhanced by addition of a part of the sludge from the previous oxidation process, into the fresh sewage water. Sludge mainly contains aerobic bacteria and other micro organisms. to H_2O and CO_2
    The sediment sewage water is mixed with proper quantity of activated sludge is sent to the aeration tank and agitated for several hours, during this organic matter are oxidized after this the effluent is sent into the sedimentation tank where sludge is deposited and water free from organic matter is drawn off. A part of the sludge is recycled for the next process.

Tertiary treatment involves

- Removal of phosphate using lime
  $PO_4{}^{3-} + Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2$

- Removal of heavy metals by sulphides.
  $Hg + S \longrightarrow HgS$

- Degasification of NH_3, H_2S, CO_2 by stripping hot water through water

- Disinfection of microorganisms by chlorine. Acid kills microorganisms
  $Cl2 + H2O \longrightarrow HOCl$ (hypochlorous acid)

POTABLE WATER-Water that is fit for human consumption and free from pathogenic bacteria and toxic chemicals is called potable water.

DESALINATION-The process of removal of dissolved salts from sea water to the extent that water becomes usable is described as desalination.
The important methods of desalination are:-

a. Reverse Osmosis.
b. Electrodialysis.

REVERSE OSMOSIS:-
Principle:-The principle of osmosis is that when fresh water and salt solution are separated by a semi permeable membrane, it has been observed that the fresh water will move through semi permeable membrane into the solution side. And this tendency of fresh water moving over to salt solution side is known as osmosis.
        In reverse osmosis if a hydraulic pressure in excess of osmotic pressure is applied on the salt solution side then fresh water tends to flow from salt solution to fresh water.

salt water

fresh water

Pressure

Pure water

Semi Permeable Membrane
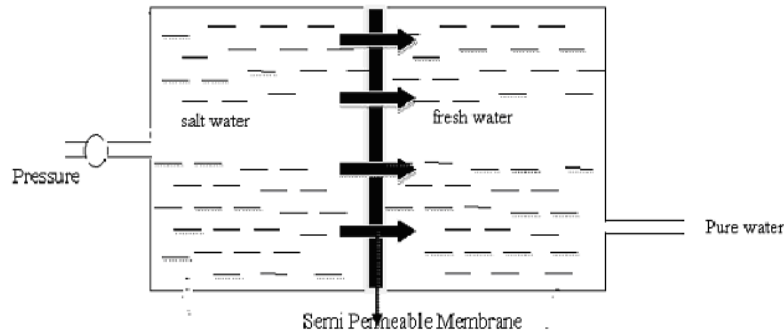
It is studied that sea water exerts an osmotic pressure of about 4500-5500 KPa Therefore in this method a pressure, which is more than 5500 KPa is applied on sea water side hence reverse osmosis takes place that means pure water moves from sea water to pure water side. This water can be used for human consumption.

ELECTRODIALYSIS
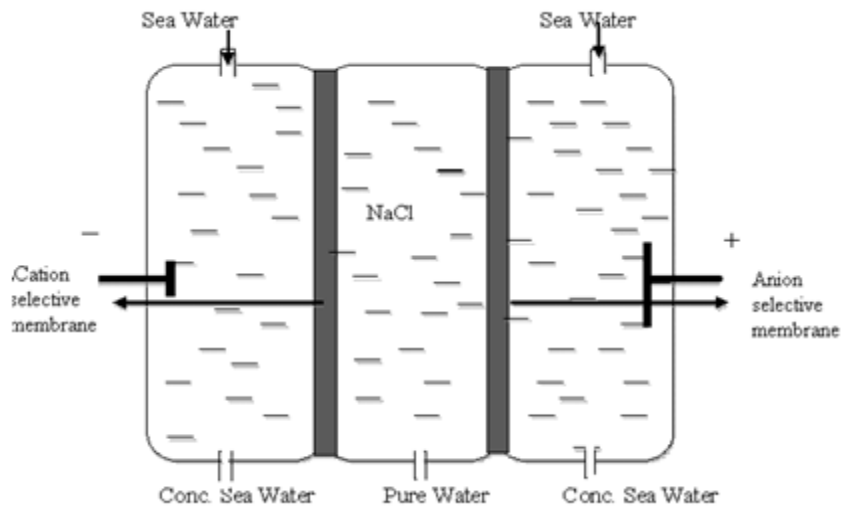
It is based on the migration of ions, under the influence of an applied EMF, towards oppositely charged electrons. In actual process Na+ and Cl- ions present in sea water attracted towards cathode and anode respectively, and the ions are not allowed to pass through anion and cation selective membrane respectively. Therefore only pure water is allowed to move towards middle compartment, thus pure water gets separated.

Problems

1. Calculate the COD of the effluent sample when 25 ml of an effluent requires 8.3 ml of 0.001M $K_2Cr_2O_7$ for oxidation. [Given molecular mass of $K_2Cr_2O_7$ =294 eqwt 49).
   Solution: Given Concentration of $K_2Cr_2O_7$ =0.001M

Molecular mass of $K_2Cr_2O_7$ =294