Q.1 Define corrosion

CORROSION- "Destruction, deterioration and loss of solid metallic material, starting at its surface by chemical or electrochemical attack."

E.g.:- Rusting of iron, green deposits on copper surface etc.

Ore (Combined state of Metal) Corrosion Metal

Q.2 Write a note on theories of corrosion

Theories of corrosion (or) mechanism of corrosion

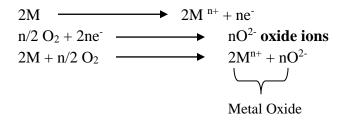
- 1. Dry or Chemical corrosion.
- 2. Wet or Electrochemical corrosion.
- **1.** Dry or Chemical corrosion- It is due to direct chemical action of environment/ atmospheric gases[Electronegative] (O₂, Cl₂, H₂S, N₂) and anhydrous inorganic liquids on the metal surface[Electropositive].

Chemical corrosion is best explained by oxidation corrosion

Oxidation corrosion

It occurs due to direct action of oxygen at low or high temperatures on metals in the absence of moisture.

Mechanism



Oxidation occurs at the surface of metal and the resulting metal oxide scale that acts as a barrier for further oxidation.

For further oxidation to continue a) the metal ion must diffuse outwards or

b) oxide ion must diffuse inwards.

Former occurs more readily as because of the smaller size of the metal ion.

In oxidation corrosion, the nature of the oxide film plays an important role. It may be-

- a) Stable A stable layer of metal oxide is formed which is impervious and this protects the metal from further corrosion. Eg :- Al, Sn.
- b) Unstable- The oxide layer decomposes back to metal and oxygen.

MO \longrightarrow M + Oxygen

Eg :- Au, Ag, Pt

- c) Volatile- Oxide layer evaporates as soon as it is formed. Then by the metal surface is exposed for further attack. Eg :- MoO₃.
- d) Porous- Oxide layer has porous or cracks, so oxygen has access to the underlying metal. Hence, corrosion continues.

<u> Pilling – Bed worth rule-</u>

It tells about the nature of the oxide layer- protective or non - protective.

"If the volume of the oxide film is greater than the volume of the meta surfacel, then the oxide layer is protective and non-porou''s.

On the other hand," if the volume of the metal oxide is less than the volume of the metal, then the layer is non-protective and porous".

Eg :- Alkali and alkaline earth metals form non-protective oxide film.

Al forms protective oxide film.

2. Wet or Electrochemical corrosion-

This Corrosion occurs when the environment favors the formation of anodic and cathodic areas on the metal,

i) A metal is exposed to two different concentrations of environment.

ii) Two different metals are in contact in a medium.

At anode:- Oxidation (Corrosion) takes place ie M \longrightarrow Mⁿ⁺ + ne⁻

At cathode:- Reduction takes place, Where electrons are consumed.

Corrosion of an anode is based on how electrons are consumed at cathode

At cathode consumption of electron takes place either by

a) Liberation / evolution of hydrogen -occurs in acidic medium

Eg: - Fe \longrightarrow Fe²⁺ + 2e⁻ (oxidation at anode) $2H^+ + 2e^- \longrightarrow$ H₂ (reduction at cathode) Fe + 2H⁺ \longrightarrow Fe²⁺ + H₂

b) **Absorption of oxygen-** Occurs in neutral aqueous solution (NaCl solution) in the presence of atmospheric oxygen.

Eg:- Rusting of iron in presence of NaCl solution.

Fe \longrightarrow Fe²⁺ + 2e⁻ (oxidation at anode)

 $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (reduction at cathode)

The Fe^{2+} combines with OH^{-} to form $Fe(OH)_2$ precipitate.

 $Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$

In presence of sufficient amount of Oxygen,

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

In presence of limited amount of oxygen, black anhydrous magnetite is formed.

Q.3 Explain various factors influencing corrosion

Factors affecting the corrosion : The rate of corrosion mainly depends on two factors.

- A. Nature of the metal
- B. Nature of corroding environment.

A. Nature of metal

1. Position in Galvanic series:-

When two different metals are in contact in presence of

Medium, the more active metal (top in galvanic series) undergoes

Corrosion. The rate of corrosion depends on difference in their positions

2. Over voltage:-

When Zn is placed in $1N-H_2SO_4$, it undergoes corrosion by evolution of H₂. The rate of corrosion is slow because of high overvoltage (0.77V) of Zn metal. If few drops of CuSO₄ is added, the corrosion of Zn is accelerated, because Cu deposited on Zn acts as minute cathode, where the evolution of H₂ is 0.33V.

Reduction in overvoltage accelerates the corrosion rate.

3. Relative areas of anodic and cathodic parts:-

Smaller the anodic area and larger the cathodic area severe will be the corrosion.

4. Purity of the metal:-

Impurities in a metal cause <u>heterogeneity</u> and forms minute electrochemical cells and anodic area gets corroded.

5. Physical state of metal:-

Rate of corrosion depends on grain size, orientation of crystals, stress etc. Smaller the grain size and area under stress, greater will be the corrosion.

6. Nature of surface film:-

The ratio of volume of metal oxide to metal is called "Specific volume ratio". Greater the specific volume ratio, lesser will be the oxidation corrosion.

Eg: Specific volume ratio of Ni, Cr, W are 1.6, 2.0. 3.6. Oxidation corrosion is least is W.

7. Passivity:-

Metals like Ti, Al, Ca, and Mg are passive and they have high corrosion resistance. This is due to formation of protective oxide film having salt-healing nature.

Mg Zn Al Cd Al alloys Mild steel Cast iron Pb Sn Brass Cu Ni Ag Au pt

Galvanic series

B. Nature of the corroding environment-

- 1. *Temperature-* The rate of corrosion increases with increase in temperature.
- 2. *Humidity of air:* Rate of corrosion increases with increase in humidity and the relative humidity above which the rate corrosion increases sharply is called critical humidity.
- 3. *Presence of impurities in atmosphere-* Presences of gases like CO₂, H₂S and fumes of HCl increases acidity of liquid surrounding metals and increases corrosion.
- 4. *Presence of suspended particles-* Chemically active particles NaCl absorbs moisture and forms strong electrolyte enhances corrosion.
- 5. *Influence of pH :-* Corrosion is more in acidic medium than neutral or alkaline medium.
- 6. Eg :- Zn corroded rapidly in weakly acidic solution and suffers minimum corrosion at pH = 11.
- 7. *Nature of ions-* Presence of silicate leads to formation of insoluble corrosion products, which inhibits further corrosion.
- 8. *Conductance of the medium*: Dry sandy soils are less corrosive than clayey and mineralized soils.
- 9. Formation of oxygen concentration cell: with increase in supply of oxygen to metal surface, the corrosion is promoted. Less oxygenated parts acts as anode and more oxygenated parts acts as cathode. This results in formation of "oxygen concentration cell".

Q.4 write a note on the following types of Corrosion-

1. *Galvanic corrosion or Bimetallic corrosion*- When two dissimilar metals are connected in an electrolyte, the metal higher in electrochemical series undergoes corrosion.

Eg:- Zn and Cu. Zn acts as anode and is protected & Cu acts as cathode.

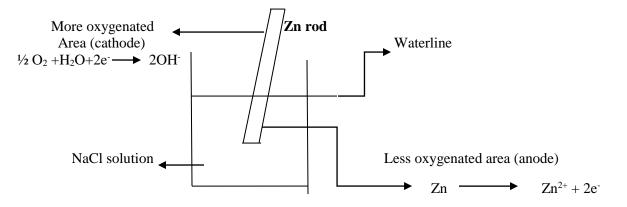
At anode:- Zn \rightarrow Zn²⁺ + 2e⁻

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At cathode:- 2H^+ H_2
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Eg:- Corrosion of

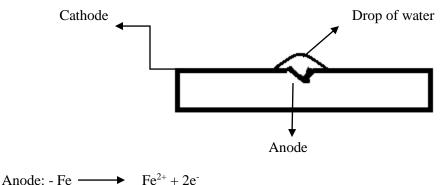
- 1) Steel screws in a brass marine hardware.
- 2) Lead- Antimony solder around copper.
- 2. *Concentration Cell corrosion* It is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration. This may be the result of local differences in metal ion concentrations.

<u>Differential aeration corrosion</u>. The most common type of concentration cell corrosion occurs when different parts of the metal are exposed to different O_2 or air concentration. Less oxygenated part acts as anode and undergoes corrosion, where as more oxygenated parts acts as cathode. A differential current flows from anode to cathode. E.g.: (1) - Zn rod in NaCl(aq)



When Zn is immersed partially in neutral NaCl solution, then the area below the waterline is less oxygenated acts as anode and undergoes corrosion. The area just above the waterline is more oxygenated acts as cathode.

Eg: (2) - Corrosion of iron under a drop of water (in salt solution)



Cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

Q.5 How to protect a metal from corrosion by cathodic protection?

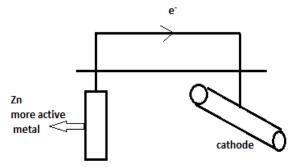
Cathodic protection-

Principle- The metal to be protected is forced to behave like cathode, there by corrosion does not occur.

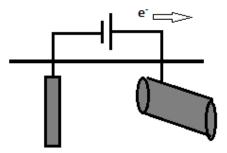
There are two types of cathodic protection

i) *Sacrificial anodic protection*- In this method, the metallic structure (to be protected) is connected to more anodic material. So, that the corrosion is concentrated at more active metal. The more active metal sacrifies itself by corrosion and protects the structure (cathode). The sacrificial anode are Zn, Mg, Al.

This method is mainly used for protection of underground pipeline, cables, and marine structures.



ii) *Impressed current cathodic protection*- In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. The impressed current is derived from a direct current source like a battery. Sufficient D.C current is applied to an insoluble anode, buried in the soil and connected to the metallic structure to be protected. This type of cathodic protection is applied to open water-box coolers, water-tanks, buried oil or water pipes etc.



Q 6. Write a brief note on corrosion inhibitors

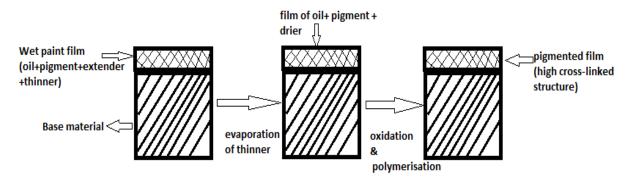
Corrosion inhibitors- A corrosion inhibitor is a substance which when added in small quantities to the aqueous corrosive environment and effectively decreases the corrosion of the metal. Inhibitors are-

- Anodic inhibitors- they control the corrosion reaction occurring at the anode, by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface, forming a protective film or barrier, thereby reducing the corrosion rate.
 E.g.:- Transition metal ions with chromates, phosphates, tungstates etc.
- ii) Cathodic inhibitors- In acidic medium, the corrosion rate can be reduced either by slowing down the diffusion of hydrated of hydrogen ions to cathode or by increasing the overvoltage of hydrogen evolution. In natural solutions, corrosion can be controlled by either by eliminating oxygen from the corroding medium or by retarding its diffusion to the cathode areas.

Q7. What is paint? Mention the constituents with examples

Paints:- It is a mechanical dispersion mixture of one or more pigments in a vehicle. Vehicle is a liquid, consisting of non-volatile, film-forming material, a drying oil and a highly volatile solvent, thinner.

Mechanism- when paint is applied, the thinner evaporates, while the drying oil slowly oxidizes forming a dry pigmented film.



Constituents of paints-

- 1. Pigment-
 - Provides capacity, strength & color.
 - Gives protection to the pain film by reflection harmful UV light.
 - Provides resistance to paint film against abrasion/water.
 - Pigments used whites (Titanium oxide, zinc oxide), black- carbon black, and green- chromium oxide.
- 2. Vehicle or drying oil-
 - Film forming constituent.
 - Glycerol esters of high molecular-weight fatty acids present in animal and vegetable oils. Mostly used drying oils are linseed oil, soyabean oil.

3. Thinners-

- Reduces viscosity.
- Dissolves vehicle, additives of vehicle.
- Increases the penetration power of vehicle.
- Increases the elasticity of paint film.
- Common thinners are turpentine, mineral spirits, benzene, dipentene etc.

4. Driers-

- Oxygen- carrier catalysts.
- Accelerates the drying of the oil-film through oxidation, polymerization and condensation.
- Improves the drying quality of oil-film.

- Common driers are tungstates, resonates etc.
- 5. Extenders-
 - Low refractive indices materials.
 - Increases durability of paint.
 - E.g:- barites, talc, gypsum, china-clay.
- 6. Plasticizers-
 - Provides elasticity.
 - Minimizes cracking.
 - Common plasticizers are triphenyl phosphate, tributyl phthalate etc.
- 7. Antiskinning agent-
 - Prevents gelling and skinning. Polyhydroxy phenols are used.

Q 8. What are Varnishes? Mention the constituents with examples

<u>Varnishes</u>-It is a homogenous colloidal dispersion solution of natural or synthetic resin in oil or thinner or both. It acts as a protective layer by evaporation, oxidation and polymerization of the constituents.

Types of varnishes-

- a) **Oil varnish** homogenous solution of one or more natural or synthetic resins in a drying oil and volatile solvent.
- b) Spirit varnish- contains resin dissolved in a volatile solvent.

Constituents of varnish-

- 1. Resin-
 - Natural resins (shellac, dammer etc)
 - Synthetic resins (phenol-aldehyde, urea-formaldehyde etc).
- 2. Drying oils-
 - Oils like linseed oil, soyabean oils are used.
 - They dry by oxidation and polymerisation.
- 3. Solvents or thinners-
 - Turpentine, petroleum spirits etc are used.
- 4. Driers-
 - Enhance the drying rate of oil constituents.
 - Pb, Co linoleates etc.
- 5. Antiskinning agents-
 - Tert-amyl alcohol, guiacol etc are used.