Corrosion

Topics:

Dry and wet corrosion - detrimental effects to buildings, machines, devices & decorative art forms, emphasizing Differential aeration, Pitting, Galvanic and Stress corrosion cracking; Factors that enhance corrosion and choice of parameters to mitigate corrosion.

Natural Abundance of Metals

- In the form of oxides, carbonates, chlorides, silicates etc.

Corrosion:

Any process of deterioration and consequent loss of solid metallic material, through an unwanted chemical or electrochemical attack by its environment.

Types

- Dry or Chemical Corrosion
- Electrochemical Corrosion

Dry or Chemical Corrosion

1. Oxidation Corrosion
2. Corrosion by other gases
3. Liquid Metal Corrosion

Oxidation Corrosion

Oxygen present in the atmosphere attacks the metal surface

– formation of oxide layers

$$2M \longrightarrow 2M^{n+} + 2n\ e^-$$

$$\frac{n}{2} O_2 + 2n\ e^- \longrightarrow n\ O^{2-}$$

$$2M + \frac{n}{2} O_2 \longrightarrow 2\ M^{n+} + n\ O^{2-} \text{ (or) } MO$$

Mechanism

Nature of the Oxide

When oxidation starts, a thin layer of oxide film will be formed on the surface and the nature of the film decides the further action!

i.e. Porous film or non-porous film

Pilling – Bedworth rule

$$R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{n \cdot M_{metal} \cdot \rho_{oxide}}$$

-If the volume of the metallic oxide is equal or greater in volume to the metal surface
- The metal surface is compact, non-porous
productive

Eg. Cu, In, Al, Ni, Cr forms oxides whose volume is greater than the volume of the metal

-If the volume of the metallic oxide is less than the volume of the metal surface
- the oxide layer is porous, non-protective

Eg. Alkali and alkaline earth metals – Li, Na, K, Mg

The oxide films are classified as

1. **Stable oxide layer**

A fine-grain of oxide which forms a compact surface adhered tightly to the parent metal surface; Eg. Oxides of Al, Sn, Cu, etc.

Impervious in nature (which cuts of the penetration of O_2)

Such a films behaves like a protective Coating

2. **Unstable oxide layer**

$$\text{Metallic Oxide} \rightleftharpoons \text{Metal} + \text{Oxygen}$$

Oxides of noble metals such as platinum, silver etc.

3. Volatile layer

Oxide layers volatilize as soon as they are formed

Excessive corrosion

Molybdenum oxide (MoO_3)

4. Porous Oxide layer

Oxide layers with minute pores

Volume of the oxide layer is …….. than metal

Corrosion ……..

Corrosion by other gases

SO_2, CO_2, Cl_2, H_2S, F_2 etc.

The extent of corrosive effect depends mainly on the chemical affinity between the metal and gas

It can form Protective layer (AgCl) and Non-protective layer ($SnCl_4$)

Liquid Metal Corrosion

Chemical action of flowing liquid metal at high temperatures on solid metal or alloy

a. dissolution of solid metal by liquid metal

b. internal penetration of the liquid metal in to the solid metal

Wet or Electrochemical Corrosion

- When a conducting liquid is in contact with the metal
- When two dissimilar metals or alloys either immersed or partially dipped in a solution

Existence of separate “anodic” and “cathodic” areas/parts, between which current flows through the conducting solution

At Anode

$M \longrightarrow M^{n+} + n\,e^-$

Dissolves in solution

Forms compounds like oxides

Corrosion Always occurs at anode

At Cathode

Reduction reaction- Gain of electrons

Cathodic reactions do not affect the cathode - Most of the metals can't be reduced

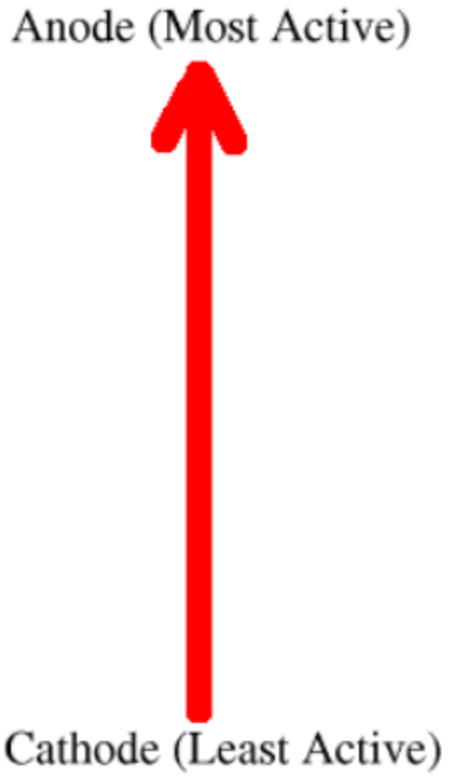
The principle of electrochemical corrosion is involved in the following types of corrosion:

1. Hydrogen Evolution Corrosion
2. Oxygen absorption corrosion
3. Galvanic Corrosion
4. Concentration Cell Corrosion

Electrochemical Series

Electrode		Electrode reaction	$E^{\ominus}$/V
Au	Gold	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.43
Ag	Silver	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
Cu	Copper	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
H	Hydrogen	$H^+ + e^- \rightleftharpoons H$	0
Pb	Lead	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13
Sn	Tin	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
Ni	Nickel	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.25
Cd	Cadmium	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.40
Fe	Iron	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
Zn	Zinc	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
Ti	Titanium	$Ti^{2+} + 2e^- \rightleftharpoons Ti$	−1.63
Al	Aluminium	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66
Mg	Magnesium	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.37
Na	Sodium	$Na^+ + e^- \rightleftharpoons Na$	−2.71
K	Potassium	$K^+ + e^- \rightleftharpoons K$	−2.93
Li	Lithium	$Li^+ + e^- \rightleftharpoons Li$	−3.05

Galvanic Series



Magnesium
Zinc
Aluminum (2S)
Cadmium
Aluminum (175T)
Steel or Iron
Cast Iron
Lead - Tin solder
Lead
Nickel
Brass
Copper
Bronze
Stainless Steel (304)
Monel Metal
Stainless Steel (316)
Silver
Graphite
Gold

Differences between dry and wet corrosion

Dry corrosion	Wet corrosion
• Corrosion occurs in the absence of moisture	• Corrosion occurs in presence of conducting medium.
. • It involves direct attack of chemicals on the metal surface.	• It involves formation of electrochemical cells.
• The process is slow.	• It is a rapid process.
• Corrosion products are produced at the site of corrosion.	• Corrosion occurs at anode but rust is deposited at cathode.
• The process of corrosion is uniform.	• It depends on the size of the anodic part of metal.

Factors Influencing Corrosion

Nature of the Metal

Position in galvanic series
Overvoltage

Relative areas of anode and cathode

Purity of the metal

Physical state of the metal

Nature of the surface film
Passive character of the metal

Solubility of corrosion products

Environment

Temperature

Humidity

Presence of impurities in atmosphere

Suspended particles

pH

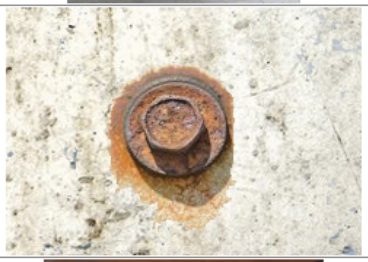
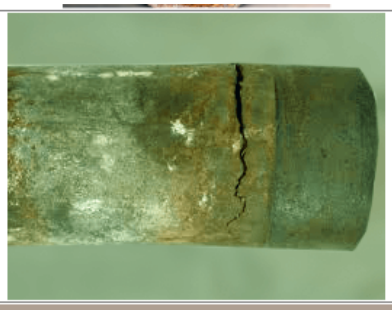
Silicates

Conductance

Formation of O_2 conc. cell

Flow velocity

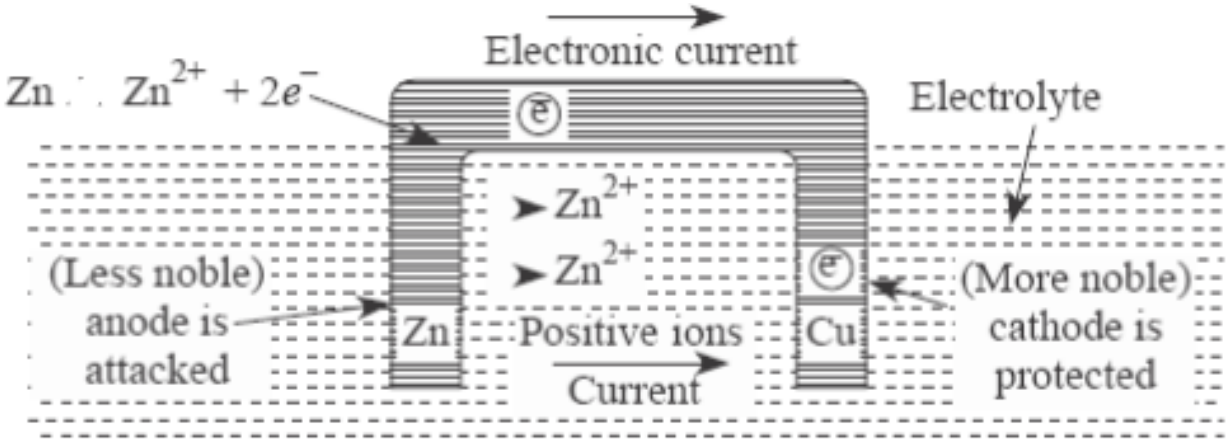
Forms of Corrosion

Example	Types of Corrosion
	**Uniform Corrosion** • Generally occurs due to direct chemical attacks
	**Galvanic Corrosion** • An electrochemical action that occurs between two dissimilar metals which are in contact with other.
	**Concentration Cell Corrosion** • It occurs when two metal surfaces are in contact with different concentrations of the same solution.
	**Pitting Corrosion** • A kind of localized corrosion that occurs with pits at underneath surface formed due to corrosion product accumulation.
	**Crevice Corrosion** • It occurs when metals are in contact with nonmetals.
	**Filiform Corrosion** • It occurs on painted surfaces due to penetration of coated surface by moisture in the form of filaments.
	**Intergranular Corrosion** • It occurs on grain boundaries of a metal or alloy.

	**Stress Corrosion Cracking** • It occurs due to applied loads, residual stresses or a combination of both.
	**Corrosion Fatigue** • A special case of stress corrosion that occurs due to combined effects of cyclic stress and corrosion.
	**Fretting Corrosion** • It is a rapid corrosion, occurs at the interface between highly loaded metal surfaces due to vibratory motions.
	**Erosion Corrosion** • It occurs due to combination of a chemical environment with high fluid-surface velocities.

Galvanic Corrosion and Its Prevention

1.



At anode: $Zn \longrightarrow Zn^{++} + 2e^-$ [Oxidation] corrosion

At cathode: $Cu^{++} + 2e^- \longrightarrow Cu$ [Reduction] unaffected

-This type of electrochemical corrosion is also called bimetallic corrosion. When two dissimilar metals are connected and exposed to an electrolyte, they will form a galvanic cell.
-The anodic metal will be oxidised and it will undergo corrosion. Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell.
-Zinc acts as anode and undergoes corrosion while cathode will be unaffected.

Examples of galvanic corrosion:

1. Steel screws in brass marine hardware,
2. Steel pipe connected to copper plumbing,
3. Steel propeller shaft in bronze bearing,
4. Zinc coating on mild steel,
5. Lead–tin solder around copper wires.

Prevention of galvanic corrosion:

1. Galvanic corrosion can be avoided by coupling metals close to the elec- trochemical series.
2. Fixing insulating material between two metals.
3. By using larger anodic metal and smaller cathodic metal.

Differential aeration corrosion

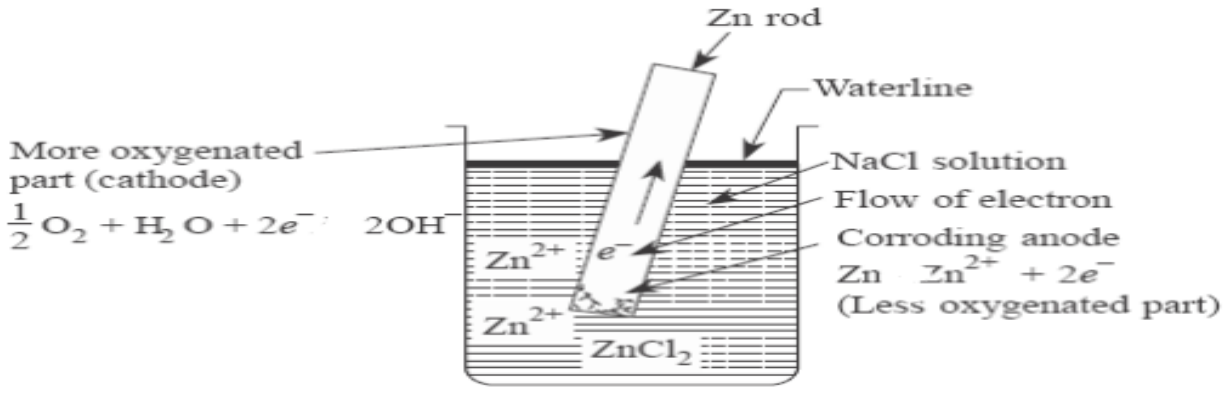
- If a metal rod is dipped in an electrolyte, the portion dipped in water is poor in oxygen concentration and works as anode which gets corroded and the portion above water acts as cathode which is protected.
- The system will act as a concentration cell and the chemical reactions for zinc dipped in water are given as:

$$Zn \longrightarrow Zn^{++} + 2e^-$$

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

$$Zn + H_2O + \frac{1}{2}O_2 \longrightarrow Zn(OH)_2$$

$Zn(OH)_2$ is the corrosion product here.



Harmful Effects of Corrosion

Definitely there are many harmful effects of corrosion. Some of them are listed below

- Lose of efficiency
- Contamination of product
- Damage of metallic equipment
- Inability to use metallic materials
- Lose of valuable materials such as blockage of pipes, mechanical damage of underground water pipes
- Accidents due to mechanical lose of metallic bridges, cars, aircrafts etc.
- Causes pollution due to escaping products from corrosion
- Depletion of natural resource (Metals)

Corrosion Resistance

Since corrosion deteriorate the physical and chemical properties of metals, therefore we always try to make corrosion resistance metal surfaces. There are various ways to make metals corrosion resistance. Few of corrosion control methods are listed below.

- Environmental Modifications
- Metal Selection
- Protective Coatings and plating
- Addition of inhibitors
- Corrosion Allowances
- Cathodic Protection

Corrosion resistance methods can be classified as:

- ***Active corrosion protection*****:** Development of corrosion-resistant alloys or addition of inhibitors
- ***Passive corrosion protection*****:** Coating by protective layer, film
- ***Permanent corrosion protection:*** Tin plating, Galvanization, Coating, Copper plating
- ***Temporary corrosion protection:*** Protective coating

MODULE 3