
8. Learning of Corrosion Chemistry

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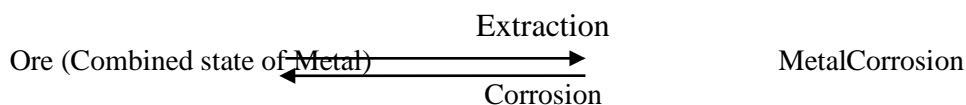
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Corrosion can be defined as **“Destruction, deterioration and loss of solid metallic material, starting at its surface by chemical or electrochemical attack.”**

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



The process of slowly deterioration of the metal due to attack of atmospheric gases on the surface of metal resulting into the formation of more stable compounds such as oxides, sulphide, carbonates etc. is known as Corrosion. The most common corrosion is rusting of Iron ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$).

8.1 Two Types of Corrosion:

- Dry or Chemical corrosion.
- Wet or Electrochemical corrosion.

8.1.1 Dry or Chemical Corrosion:

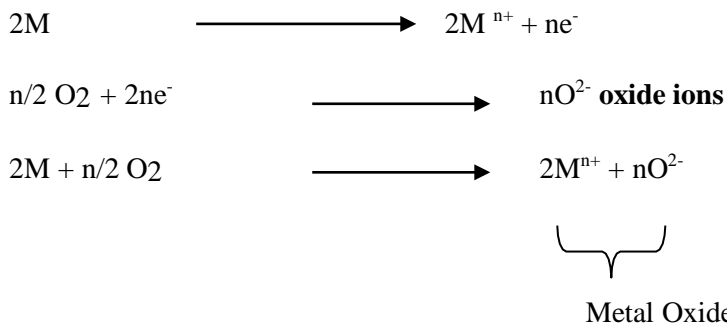
It is due to direct chemical action of atmospheric gases (O₂, Cl₂, H₂S, N₂) and anhydrous inorganic liquids on the metal surface.

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

- the metal ion must diffuse outwards or
- 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-

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



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.

Pilling – Bed worth rule-

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 metal surface, then the oxide layer is protective and non-porous".

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.

8.1.2 Wet or Electrochemical Corrosion:

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

- A metal is exposed to two different concentrations of environment.
- Two different metals are in contact in a medium.

At anode:- Oxidation (Corrosion) takes place ~~place~~ $\rightarrow M \rightarrow M^{n+} + ne^{-}$

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. Evolution of hydrogen –occurs in acidic medium

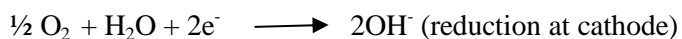
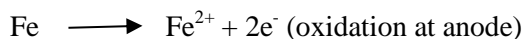
Eg: - Fe \longrightarrow Fe²⁺ + 2e⁻ (oxidation at anode)

2H⁺ + 2e⁻ \longrightarrow H₂ (reduction at cathode)

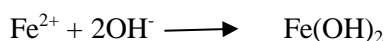


b. Absorption of oxygen- Occurs in neutral aqueous solution (NaCl solution) in the presence of atmospheric oxygen.

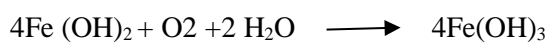
Eg:- Rusting of iron in presence of NaCl solution.



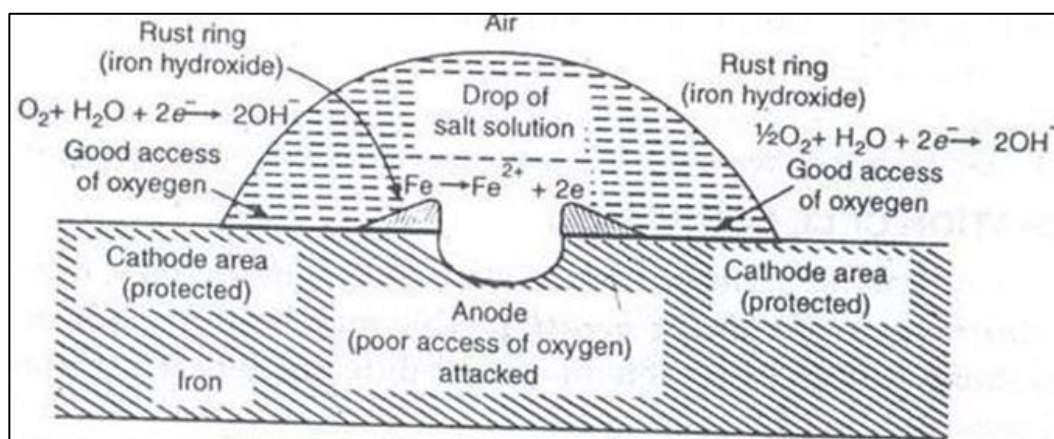
The Fe^{2+} combines with OH^- to form $\text{Fe}(\text{OH})_2$ precipitate.



In presence of sufficient amount of Oxygen,



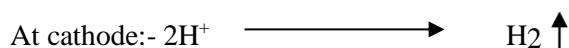
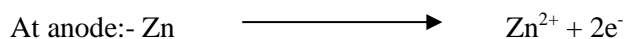
In presence of limited amount of oxygen, black anhydrous magnetite is formed.



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.



Eg:- Corrosion of

- a. Steel screws in a brass marine hardware.
- b. Lead- Antimony solder around copper.

8.2 Factors Affecting the Corrosion:

The rate of corrosion mainly depends on two factors.

1. Nature of the metal
2. Nature of Corroding Environment:

8.2.1 Nature of Metal:

- a. Position in electrochemical series:* When two different metals are in contact in presence of electrolyte, the more active metal undergoes Corrosion. The rate of corrosion depends on difference in their positions
- b. Over voltage:* When Zn is placed in 1N-H₂SO₄, 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.
- c. Relative areas of anodic and cathodic parts:* Smaller the anodic area and larger the cathodic area severe will be the corrosion.
- d. Purity of the metal:* Impurities in a metal cause heterogeneity and forms minute electrochemical cells and anodic area gets corroded.
- e. 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.
- f. 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 in W.

8.2.2 Nature of the Corroding Environment:

- a. Temperature-* The rate of corrosion increases with increase in temperature.
- b. 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.
- c. Presence of impurities in atmosphere-* Presences of gases like CO₂, H₂S and fumes of HCl increases acidity of liquid surrounding metals and increases corrosion.
- d. Presence of suspended particles-* Chemically active particles NaCl absorbs moisture and forms strong electrolyte enhances corrosion.
- e. Influence of pH :-* Corrosion is more in acidic medium than neutral or alkaline medium.
- f.* Eg :- Zn corroded rapidly in weakly acidic solution and suffers minimum corrosion at pH = 11.
- g. Conductance of the medium:* Dry sandy soils are less corrosive than clay.
- h. 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".

Differential aeration corrosion: The most common type of concentration cell corrosion occurs when different parts of the metal are exposed to different O₂ 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.: 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.

8.3 Corrosion Control by Cathodic Protection Method:

8.3.1 Cathodic protection:

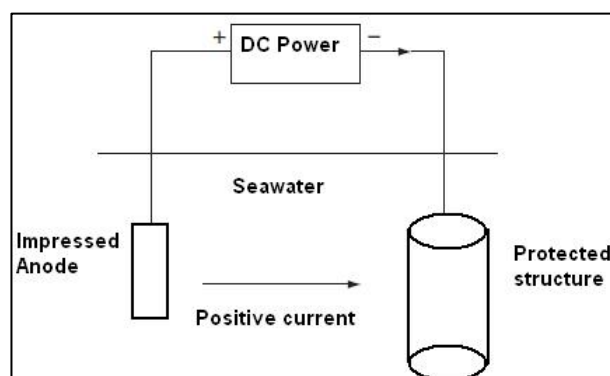
Principle- The metal to be protected is forced to behave like cathode, there by corrosion doesnot occur.

There are two types of cathodic protection

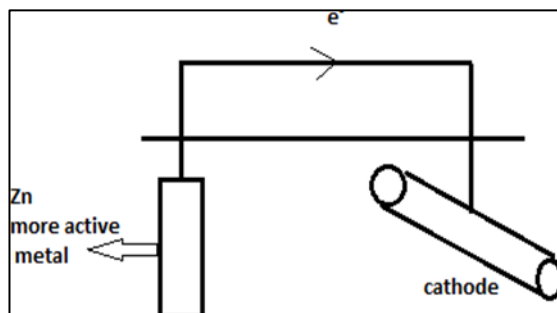
Sacrificial anodic protection- In this method, the metallic structure (to be protected) is connected to more anodic material. So, that the corrosion is concentrated at more active metal. The more active metal sacrifices itself by corrosion and protects the structure (cathode). The sacrificial anode are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

8.3.2 Impressed Current Cathodic Protection:

In this method, an impressed current from external source is applied in opposite direction to neutralize the corrosion current, and convert the corroding metal from anode to cathode. Thus the anodic corroding metal becomes cathodic and protected from corrosion. The impressed current is deriving from the external DC source. The negative terminal of DC source is connected with metal to be protected whereas the positive terminal of DC is connected to the anode. Here anode may be graphite, stainless steel scrap iron etc. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.

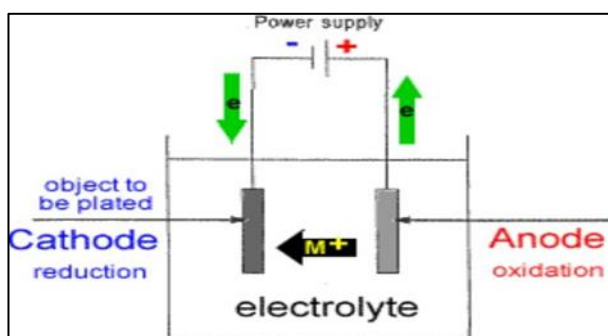


This method is mainly used for protection of underground pipeline, cables, and marine structures.



8.3.3 Electroplating:

In electroplating, electro-deposition of metal (anode) by means electrolysis over surface of metals and alloys (cathode or base metal). The two electrodes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal. When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer. In electroplating metal like Au, Ag, Zn, Sn, Cr, Ni etc. can be placed on the surface of base metal (Cathode).



8.4 Corrosion Control by using 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:

- A. 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.
- B. 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.