

CORROSION ENGINEERING

(As per revised VTU syllabus: 2015-16)

Corrosion: It is defined as destruction of metals or alloys by the surrounding environment through chemical or electrochemical changes.

Example: Rusting of iron [Formation of oxide (ferric oxide) layer on the surface of iron on exposure to air].

Electrochemical theory of corrosion (Taking iron as an example):

When a metal such as iron, is exposed to the environment, according to electrochemical theory the following changes occur.

- [a] Formation of large number of small galvanic cells (anodic and cathodic areas).
- [b] Corrosion (oxidation) takes place at anodic area.
- [c] The electrons released at anodic area are taken up the cathodic area.



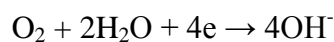
Anodic reaction: At anode, oxidation of iron takes place.



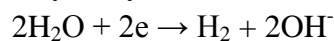
Cathodic reaction:

Electrons flow from anodic to cathodic area and cause reduction depending on the nature of corrosion medium.

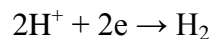
[i] If the corrosion medium is aerated and almost neutral, oxygen is reduced in presence of water to hydroxyl ions.



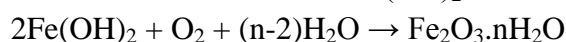
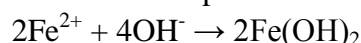
[ii] If the corrosion medium is deaerated and almost neutral, the reaction at cathode involves liberation of hydrogen and hydroxyl ions.



[iii] If the corrosion medium is deaerated and acidic, the H^+ ions are reduced to hydrogen.



The metal ions formed at anode combines with OH^- ions formed at cathode to form corresponding metal hydroxide as the corrosion product.



Galvanic series: It is a series in which metals are arranged in decreasing order of their corrosion capacity. i.e, base metals which corrode faster are placed in the beginning of the series and the metals (mostly noble metals) which do not corrode easily are placed at the end of the series. A typical galvanic series is as given below:

Mg, Zn, Al, Cd, cast Iron, Pd, Sn, Cu, Ni, Ag, Ti, Au, Pt.

According to this series, Mg, Zn corrodes faster than Au or Pt. Thus, galvanic series is more useful in studying corrosion of metals.

Factors affecting the rate of corrosion:

- | | |
|---------------------------------|----------------------------|
| (a) Anodic and cathodic areas | (d) pH |
| (b) Nature of metal | (e) Conductivity of medium |
| (c) Nature of corrosion product | (f) Temperature |

(a) Anodic and Cathodic areas: Smaller the anodic area and larger the cathodic area exposed to corrosion environment, more intense and faster is the rate of corrosion at anodic area.

Examples:

Tin coating on iron: Tin is cathodic to iron. During plating of tin on iron, if some areas are left uncoated, there results a small anode and large cathode. In such a case intense corrosion takes place at small anodic area.

Zinc coating on iron: Iron is cathodic to zinc. Even if zinc peels-off at some points on iron, intense corrosion may not occur. This is because of large anodic and small cathodic areas.



(b) Nature of metal: Metals with low reduction potential (Na, Mg, Zn) exhibit high reactivity and hence under corrosion at a faster rate. On the other hand the metals such as the noble metals (Au, Pt) which have high reduction potentials under corrosion at a very lesser rate.

(c) Nature of corrosion product: The corrosion product is usually a metal oxide, which forms a layer on the surface of metal. If the corrosion product is highly insoluble and nonporous with low conductivity, then the layer formed effectively prevents further corrosion.

Example: Aluminum, titanium etc., develop such a layer on their surface and become passive to the corrosion.

On the other hand some metals form a thick porous oxide layer. These oxide layers cannot prevent corrosion on the metal surface, as the access to corrosion environment cannot be completely prevented by the porous layer.

Example: Iron, Zinc etc., form such a porous layer.

(d) pH: Higher the acidity (low pH) higher is the rate of corrosion. At pH greater than 10 (highly basic), corrosion of iron ceases due to the formation of a protective coating of hydroxides of iron.

(e) Conductivity of corrosion medium: Presence of conducting species in the environment increases the rate of corrosion. This is because, corrosion is an electrochemical phenomenon which involves transfer of electrons.

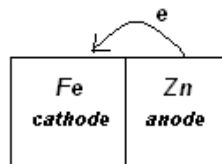
(f) Temperature: As the temperature increases the rate of corrosion also increases. Increase in the temperature increases conductivity of the aqueous corrosion medium and hence an increase in the diffusion rate.

Types of corrosion:

- [1] Differential metal corrosion
- [2] Differential aeration corrosion (Pitting and Water line corrosion)
- [3] Stress corrosion (Caustic embrittlement in boilers)

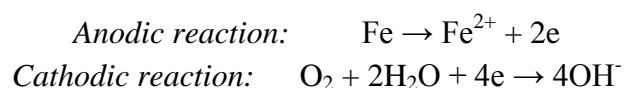
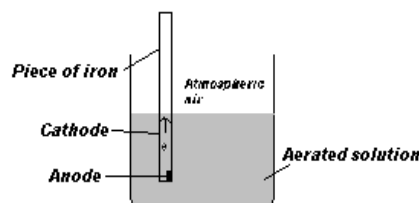
[1] Differential metal corrosion: When two dissimilar metals are in contact with each other a potential difference is set up resulting in a galvanic current. The metal placed higher in the electrochemical series acts as anode and the other metal placed lower in the electrochemical series acts as cathode. The anodic metal undergoes corrosion and cathodic metal remains unaffected.

Example: When iron and zinc are in contact with each other, zinc which is placed higher in electrochemical series acts as anode and corrodes. Iron remains unaffected.

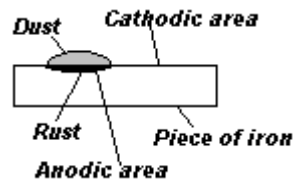


[2] Differential aeration corrosion: The difference in concentration of air over the surface of a metal develops galvanic cells, which initiate corrosion.

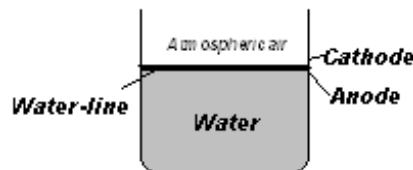
Example: Consider a piece of iron partially dipped in aerated solution. The concentration of oxygen is high at the surface than inside the solution. The area of iron which is less aerated acts as anode and undergoes corrosion. The area of iron which is more aerated acts as cathode and remains unaffected. Since the cathodic reaction involves the consumption of oxygen, the cathodic area tends to concentrate near the water-line as shown in the Figure.



(a) Pitting corrosion: Pitting corrosion results when small dust particles get deposited on a iron/steel surface. Portion of the iron surface covered by dust will be less aerated compared to the exposed surface. The covered portion acts as anode and undergoes corrosion. The exposed surface (free from dust) acts as cathode and remains unaffected. Pitting corrosion is observed on machinery parts, bottom of oil tanks, etc.,.



(b) Water-line corrosion: Water-line corrosion is observed in iron/steel water tanks, ships floating in sea water etc.,. The metal just below the water line is more anodic (less aerated) undergoes corrosion. The meniscus which is just above the water-line is more oxygenated, acts as cathode and remains unaffected.



[3] Stress corrosion: Stress corrosion on the metal occurs due to the combined effect of tensile stress and a specific corrosive environment on the metal. During stress corrosion, the metal or alloy is virtually unaffected over most of its surface, while fine cracks are formed through it normal to the direction of tensile stress.

The stress on the metal may be internal or external and this stress is due to some mechanical or service conditions. The metal atoms under stress are always at higher energy level, such areas act as anode and stress free parts of the metal act as cathode under specific corrosive environmental conditions. This leads to corrosion process.

Example:

- Brass undergoes corrosion in presence of ammonia.
- Stainless steel undergoes corrosion in presence of Cl⁻ and caustics.
- Best example for stress corrosion is *caustic embrittlement*.

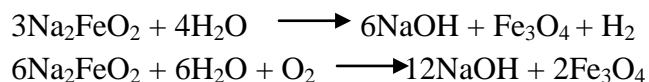
Caustic embrittlement: It is a form of stress corrosion which takes place in boilers operating at high temperature and pressure. Caustic embrittlement occurs at stressed parts of boilers such as cracks, rivets, bents, joints, etc.

The boiler fed water usually contains some residual sodium carbonate (used for softening process). At high temperature and pressure it undergoes hydrolysis to form sodium hydroxide.

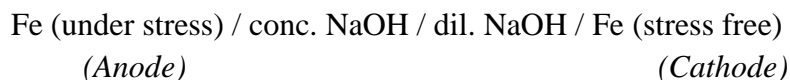


The alkali water enters into minute cracks, crevices between the rivets and joints by capillary action. Inside the cracks water gets evaporated leaving behind NaOH. The concentration of NaOH gradually increases in these sites due to poor circulation of water. When concentration of NaOH reaches a value of 10%, it attacks the metal at stressed region

dissolving it in the form of sodium ferroate (Na_2FeO_2). Sodium ferroate undergoes hydrolysis -depositing magnetite as follows:



The corrosion cell can be represented as:



Caustic embrittlement can be prevented by the addition of compounds like sodium sulphite, tannin, lignin, phosphates, etc. which block the cracks, thereby preventing the infiltration of alkali.

Corrosion Control: The methods commonly used to control corrosion of metals are:

- [1] Inorganic coatings (Surface conversion coatings) – Anodizing and Phosphating
- [2] Metal coatings – Galvanizing and Tinning
- [3] Cathodic protection (Sacrificial anodic and Impressed current methods)

[1] **Inorganic coatings (Surface conversion coatings):** In this method, corrosion of a metal is prevented by converting the surface layer of the base metal (specimen) into a compound.

-	Anodizing of Aluminum	Phosphating
Anode	Base metal (Al)	Base metal (Al, Zn, Steel)
Cathode	Cu	Cu
Electrolytic bath	5-10% HCrO_4	H_3PO_4 + metal phosphate + accelerator (nitrates)
Temperature of the bath	35 °C	35 °C
pH of the bath	-	7.8 – 3.2
Voltage	40 V	-
Current density	10 – 20 mA/cm^2	-
Mechanism	(i) Dissolution of specimen metal as metal ions. (ii) Conversion of metal ions into oxide. (iii) Deposition of metal oxide on the surface of the metal.	(i) Dissolution of specimen metal as metal ions. (ii) Conversion of metal ions into phosphate. (iii) Deposition of metal phosphate on the surface of the metal.

Applications:

- Anodized articles are used as soap boxes, tiffin carriers, etc.
- Phosphating provides corrosion resistance and also imparts a good paint adhesion. Phosphating on steel fabrications such as refrigerators, washing machines and car bodies provide better paint adhesion.

[2] **Metal Coatings:** In this method corrosion of a metal can be prevented by covering the metal with another metal.

(i) *Anodic metal coatings:* This involves coating of a metal with a anodic metal.

Example: Coating of aluminum, magnesium, zinc etc., on iron.

Galvanizing: It is a process of coating zinc on iron by hot dipping. The galvanization process involves the following steps.

- The iron sheet is degreased with organic solvents.
- The sheet is treated with dilute sulfuric acid and washed with water.
- The sheet is then treated with a mixture of solutions of zinc chloride & ammonium chloride.
- The treated sheet is dried and then dipped in molten zinc at 450 °C.
- Excess zinc on the sheet is removed by passing through rollers or by wiping.

Applications: Galvanized iron is used in making pipes, buckets, bolts & nuts, etc.,

(ii) *Cathodic metal coatings:* This involves coating of a metal with a cathodic metal.

Example: Coating of tin on iron.

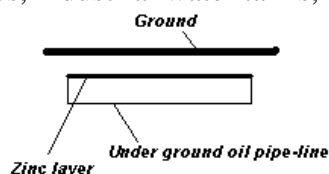
Tinning: It is a process of coating tin on iron by hot dipping. The tinning process involves the following steps.

- The sheet is treated with dilute sulfuric acid at 80 °C and washed with water.
- The sheet is then treated with a mixture of solutions of zinc chloride & ammonium chloride.
- The treated sheet is dried and then dipped in molten tin.
- Finally it is dipped in palm oil to prevent oxidation of tin.
- Excess tin on the sheet is removed by passing through rollers or by wiping.

Applications: Tinned iron is used in making tin cases to store food products.

[3] **Cathodic protection:** In this technique, corrosion of a metal is prevented by supplying electrons from an external source. Electrons for cathodic protection can be supplied by two methods.

(a) *Sacrificial anode method:* Metals like iron, copper etc., are connected to sacrificial anodic metals such as magnesium, aluminum, zinc, etc. Sacrificial anodic metals provide electrons to the specimen metal, thereby converting anodic sites to cathodic sites. However, the sacrificial anode gets corroded and in course of time it has to be replaced. This method is used to protect buried oil pipe lines, industrial water tanks, etc.



(b) *Impressed current method:* In this method, electrons are supplied to the specimen metal from a source of direct current (d.c). This method is used to protect buried oil pipe lines, industrial water tanks, etc.

