

Corrosion

Any process of deterioration (or destruction) and consequent loss of a solid metallic material, through an unwanted (or unintentional) chemical or electrochemical attack by its environment, starting at its surface is called “corrosion”.

Cause of Corrosion:

Most metals exist in nature in their combined form. They are reduced to metallic states from their ores, during their extraction processes. Since considerable amount of energy is required during extraction, the isolated pure metals can be regarded in excited state (a higher energy state) than their corresponding ores, and they have a natural tendency to revert back to combined state (or low energy state). Hence, when metals are exposed to environment, they begin to decay more or less rapidly.

Examples: a. rusting of iron

b. formation of green film of basic carbonate $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$ on the surface of copper

Electrochemical Mechanism of Corrosion (Rusting of Iron)

Electrochemical Corrosion involves:

- The formation of anodic or cathodic areas in contact with each other
- Presence of a conducting medium
- Corrosion of anodic areas only
- Formation of corrosion product somewhere between anodic and cathodic areas

For rusting of iron, we have to consider the following three electrodes:

- $\text{Fe}^{++} + 2\text{e}^- \rightarrow \text{Fe}$ $E^0 = -0.44 \text{ V}$
- $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ $E^0 = -0.42 \text{ at pH}=7$
- $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ $E^0 = +0.40\text{V}$

Combination of electrodes a and b:

a=anode, b=cathode

Rate of reaction is less since reduction reaction potentials are nearly equal.

Combination of electrodes a and c:

The rate of redox reaction is very fast.

Hence, oxygen in the presence of water can easily oxidize iron.

At anode: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^-] \times 2. \quad E^\circ = 0.44 \text{ V}$
 At cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4\text{OH}^- \quad E^\circ = 0.40 \text{ V}$
 Net cell rxn: $2\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Fe}^{2+} + 4\text{OH}^- \quad E^\circ_{\text{cell}} = +0.84 \text{ V}$

$2\text{Fe}^{2+} + 4\text{OH}^- \longrightarrow 2\text{Fe(OH)}_2 \xrightarrow{\text{More O}_2} \text{Fe(OH)}_3 \xrightarrow{\text{More O}_2} \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
 unstable unstable rust

Anode: $\text{Fe(s)} \longrightarrow \text{Fe}^{2+}(\text{aq}) + 2e^-$
 $\text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + e^-$

Cathode: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \longrightarrow 2\text{H}_2\text{O(l)}$

Dry or Chemical Corrosion

It occurs due to direct chemical action of environment/atmospheric gases such as oxygen, halogen, H_2S , SO_2 , nitrogen, etc. with metal surfaces in immediate proximity.

	Electrochemical Corrosion		Chemical Corrosion
i.	It takes place under wet conditions – presence of aqueous solution, or electrolyte.	i.	It takes place in dry conditions.
ii.	It takes place through the formation of a series of galvanic cells.	ii.	It takes place by direct chemical attack of environment on metals.
iii.	Corrosion products accumulate at cathode whereas corrosion occurs at anode.	iii.	Corrosion products accumulate at the same spot where corrosion has occurred.

Other types of Corrosion

1. Galvanic (or Bimetallic Corrosion)

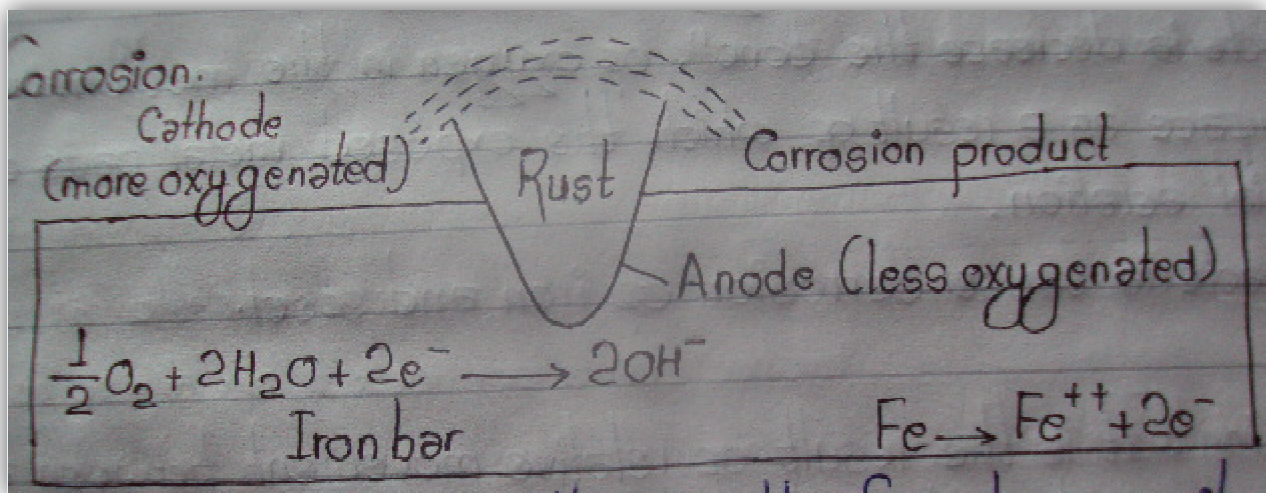
When two dissimilar metals (e.g. zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion. Here, zinc forms the anode and is attacked and gets dissolved whereas copper acts as cathode.

The use of pipelines in conjunction with iron pipes in water distribution systems has been the cause of galvanic corrosion.

2. Crevice/Contact Corrosion

Contact corrosion is produced at the region of contact of metals with metals or non-metals e.g. crevices of different metallic objects such as bolts, rivets, nuts, etc. When these crevices come in contact with the liquids, they become anodic region where corrosion occurs due to restricted supply of oxygen. The exposed surface acts as cathode.

3. Pitting Corrosion

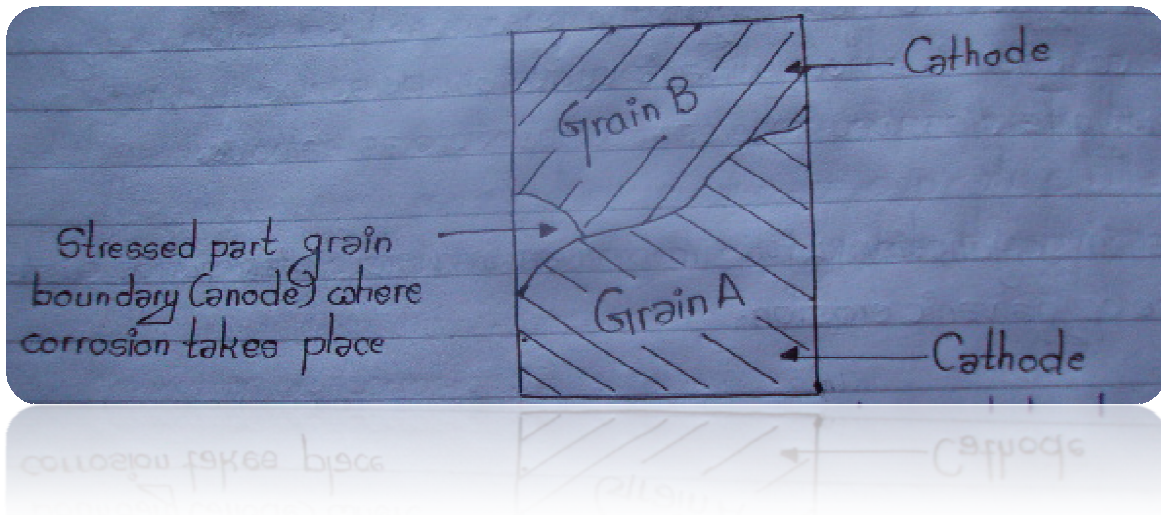


It is a localized corrosion, resulting in the formation of pits. Pitting usually takes place due to the cracking of the protective film on metal surface. An anode is formed where the film has broken. The formation of small anodic region and large cathodic region results in severe anodic corrosion.

4. Intergranular Corrosion

This type of corrosion is due to the fact that grain boundaries contain material, which shows electrode potential more anodic than that of the grain centre. Alloys are generally more susceptible to Intergranular corrosion. E.g. during welding of stainless steel (Fe, C, Cr), chromium carbide is precipitated at grain boundaries, thereby, making the regions adjacent to grain boundaries more anodic.

5. Stress Corrosion



It takes place due to the combined effect of static tensile stresses and corrosive environment on a metal. This type of corrosion is common in fabricated articles of some alloys such as zinc and nickel brasses caused by heavy working like rolling, drawing or insufficient annealing.

6. Microbiological Corrosion

It is the deterioration of materials caused directly or indirectly like microbes.

- Aerobic bacteria decrease the concentration of oxygen in the medium in contact with a metal surface as a result of which the exposed metal parts corrode due to differential aeration.
- Anaerobic bacteria cause corrosion of iron and steel.

7. Erosion Corrosion

It is the result of relative movement between a corrosive fluid and metal surface. All types of equipments exposed to moving fluids are subjected to erosion corrosion. E.g. ship propellers, hydraulic turbine

8. Soil Corrosion

Moisture and dissolved electrolytes present in soil promotes soil erosion. Caused due to:

- Acidity in the soil
- Moisture content of the soil

9. Concentrated Cell Corrosion

This type of corrosion is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration.

Factors Influencing Corrosion

Nature of Metal

- a. **PHYSICAL STATE OF METAL**: The smaller the grain-size of the metal or alloy, the greater will be its solubility and hence, greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.
- b. **PURITY OF METAL**: Impurities in a metal, generally, cause “heterogeneity”, and form minute electrochemical cells (at the exposed parts), and the anodic parts get corroded.
- c. **NATURE OF THE SURFACE FILM**: In aerated atmosphere, practically all metals get covered with a thin surface film of metal oxide. The ratio of the volumes of the metal oxide to the metal is known as a “*specific volume ratio*”. Greater the specific volume ratio, lesser is the oxidation corrosion rate.
- d. **RELATIVE AREAS OF THE ANODIC AND CATHODIC PARTS**: Corrosion is more rapid and severe, and highly localized, if the anodic area is small, because the current density at a smaller anodic area is much greater.

Nature of the Corroding Environment

- a. **TEMPERATURE**: With increase in temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.
- b. **HUMIDITY**: Corrosion of a metal becomes faster in humid atmosphere since the gases (CO₂, O₂, etc.) and vapours, present in atmosphere furnish water to the electrolyte, essential for setting up an electrochemical cell.
 - Critical humidity is defined as the relative humidity above which the atmospheric corrosion rate of metal increases sharply.
- c. **PRESENCE OF IMPURITIES IN ATMOSPHERE**: In presence of gases like CO₂, H₂S, SO₂ and fumes of HCl, H₂SO₄, etc. the acidity of the liquid, adjacent to the metal surfaces, increases and its electrical conductivity also increases. This consequently, results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surfaces.
- d. **PRESENCE OF SUSPENDED PARTICLES IN ATMOSPHERE**: If the suspended particles are chemically active in nature [like NaCl, (NH₄)₂SO₄], they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion.

Prevention of Corrosion

- a. The design of the materials should be such that corrosion, even if it occurs, is uniform and does not result in intense and localized corrosion.
- b. Pure metals having high corrosion-resistance should be used. Purification of metals like Al, Mg, etc. provides a coherent and impervious protective oxide film on their metal surfaces.

- c. Corrosion-resistance of most metals can be increased by alloying them with suitable elements.
- d. **SACRIFICIAL ANODIC PROTECTION METHOD**: In this method, the metallic structure to be protected is connected by a wire to more anodic metal, so that all the corrosion is concentrated at this more active metal. **Application**: protection of buried pipelines, underground cables, water tanks, etc.
- e. **APPLICATION OF PROTECTIVE COATINGS**: A coating surface isolates the underlying metal from corroding environment. The coating applied must be chemically inert under particular conditions of temperature and pressure.