

Corrosion

INTRODUCTION: Corrosion is an undesirable process. Due to corrosion there is limitation of progress in many areas. The cost of replacement of materials and equipment's lost through corrosion is unlimited. Metals and alloys are used as fabrication or construction materials in engineering. If the metals or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. **This phenomenon of destruction of metals and alloys is known as corrosion.** Corrosion of metals is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical or biochemical interactions with the environment.

Example: Rusting of iron, tarnishing of silver, Green coating on brass.

Cause of Corrosion

In nature, most metals are found in a chemically combined state known as an ore. All the metals except gold, platinum and silver exist in nature in the form of their oxides, carbonates, sulphides, sulphates, etc. These combined forms of the metals represent their thermodynamically stable state (low energy state). The metals are extracted from these ores after supplying a large amount of energy. Metals in the uncombined condition have a higher energy and are in an unstable state. It is their natural tendency to go back to the low energy state, i.e., combined state by recombining with the elements present in the environment. This is the main reason for corrosion.

CONSEQUENCES (EFFECTS) OF CORROSION:

The economic and social consequences of corrosion include i) Due to formation of corrosion product over the machinery, the efficiency of the machine gets failure leads to plant shut down. ii) The products contamination or loss of products due to corrosion. iii) The corroded equipment must be replaced iv) Preventive maintenance like metallic coating or organic coating is required. v) Corrosion releases the toxic products. vi) Health (eg., from pollution due to a corrosion product or due to the escaping chemical from a corroded equipment).

THEORIES OF CORROSION

- [1] Direct chemical attack or Dry corrosion
- [2] Electrochemical theory or Wet corrosion
- [3] Differential aeration or, Concentration cell corrosion

[1] Direct chemical attack or Dry corrosion:

This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen, etc. During this solid film of the corrosion product is formed on the surface of the metal which protects the metal from further

corrosion. If a soluble or volatile corrosion product is formed, then the metal is exposed to further attack. For example, chlorine and iodine attack silver generating a protective film of silver halide on the surface. On the other hand, stannic chloride formed on tin is volatile and so corrosion is not prevented.

Oxidation corrosion is brought about by direct action of oxygen at low or high temperatures on metals in the absence of moisture. Alkali metals (Li, Na, K, etc.) and alkaline earth metals (Mg, Ca, Sn, etc.) are readily oxidized at low temperatures. At high temperatures, almost all metals except Ag, Au and Pt are oxidized. Alkali and alkaline earth metals on oxidation produce oxide deposits of smaller volume. This results in the formation of a porous layer through which oxygen can diffuse to bring about further attack of the metal. On the other hand, aluminium, tungsten and molybdenum form oxide layers of greater volume than the metal from which they were produced. These non-porous, oxide films prevent the further attack. The protective or non-protective nature of the oxide film is determined by a rule known as the **Pilling-Bedworth rule**. According to it, if the volume of the oxide layer is greater than the volume of the metal, the oxide layer is protective and non-porous. On the other hand, if the volume of the oxide layer formed is less than the volume of the metal, the oxide layer is nonprotective and porous.

[2] Electrochemical Theory or Wet Corrosion;

According to the electrochemical theory, the corrosion of a metal in aqueous solution may be a two-step process, one involving oxidation and another reduction. It is known that two metals having different electrode potentials form a galvanic cell when they are immersed in a conducting solution. When the electrodes are joined by a wire, electrons flow from the anode to the cathode. The oxidation reaction occurs at the anode, i.e. at the anode the metal atoms lose their electrons to the environment and pass into the solution in the form of positive ions.

$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ Thus, there is a tendency at the anode to destroy the metal by dissolving it as ions. Hence corrosion always occurs at anodic areas. The electrons released at the anode are conducted to the cathode and are responsible for various cathodic reactions such as electroplating (deposition of metals), hydrogen evolution and oxygen absorption:

- (i) Electroplating: The metal ions at the cathode collect the electrons and deposit on the cathode surface. $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
- (ii) Liberation of hydrogen: In an acid solution, (in the absence of oxygen) hydrogen ions accept electrons and hydrogen gas is formed. $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$.
- (iii) Oxygen absorption: In the presence of dissolved oxygen and in an acid medium, oxygen absorption reaction takes place. $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$.

Thus it is clear that the essential requirements of electrochemical corrosion are as follows: (a) Formation of anodic and cathodic areas. (b) Electrical contact between the cathodic and anodic parts to enable the conduction of electrons. (c) An electrolyte through which the ions can diffuse or migrate.

Difference between (dry) chemical and (wet) electrochemical corrosion:

Chemical Corrosion	Electrochemical Corrosion
It occurs in dry condition	It occurs in the presence of moisture or electrolyte
It is due to the direct chemical attack	It is due to the formation of a large number

of the metal by the environment.	of anodic and cathodic areas
Even a homogeneous metal surface gets corroded.	Heterogeneous (bimetallic) surface alone gets corroded.
Corrosion products accumulate at the place of corrosion.	Corrosion occurs at the anode while the products are formed elsewhere
It is a self-controlled process	. It is a continuous process.
Formation of mild scale on iron surface is an example.	Rusting of iron in moist atmosphere is an example.

[3] Differential Aeration or Concentration Cell Corrosion;

Anodic and cathodic areas may be generated even in a perfectly homogeneous and pure metal due to different amounts of oxygen reaching different parts of the metal which form oxygen concentration cells. In such circumstances, those areas which are exposed to greater amount of air become cathodic while the areas which are little exposed to air become anodic and suffer corrosion.

Explanation: If a metal is partially immersed in a conducting solution the metal part above the solution is more aerated and becomes cathodic. The metal part inside the solution is less aerated and thus becomes anodic and suffers corrosion.

At anode: Corrosion occurs (less aerated) $M \rightarrow M^{2+} + 2e^{-}$

At cathode: OH⁻ ions are produced (more aerated) $\frac{1}{2} O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-}$

Which is further oxidized to Fe(OH)₃. Since the anodic area is small and the cathodic area is large, corrosion is more concentrated at the anode. Thus, a small hole is formed on the surface of the metal. This type of intense local corrosion is called **pitting**.

Factors influencing corrosion:

There are two factors that influence the rate of corrosion. Hence knowledge of these factors and the mechanism with which they affect the corrosion rate is essential because the rate of corrosion is different in different atmosphere.

1. Nature of the metal
2. Nature of the corroding environment.

Nature of the metal:

a) Physical state: The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc.). The smaller the grain size of the metal or alloy, the greater will be its solubility and hence greater will be its corrosion.

b) Purity of metal: Impurities in a metal cause heterogeneity and form minute/tiny electrochemical cells (at the exposed parts), and the anodic parts get corroded. The higher the percentage of impurity present in a metal, the faster is the rate of corrosion of the anodic metal.

c) Over voltage: The over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate.

d) Nature of oxide film: In aerated atmosphere, practically all metals get covered with a thin surface film of metal oxide, lesser is the oxidation corrosion rate.

e) Position in the galvanic series: The extent of corrosion depends upon the position of the metal in the galvanic series. Greater the oxidation potential, the greater is the rate of corrosion. When two metals are in electrical contact, the metal higher up in the galvanic series becomes anodic and suffers corrosion.

f) Relative areas of the anode and cathode: The rate of corrosion is more when the area of the cathode is larger.

g) Passive character of metal:

h) Solubility of corrosion products: If the corrosion product is soluble in the corroding medium, the corrosion of the metal will proceed faster

Nature of the Environment:

a) Temperature: The rate of chemical reactions and the rate of diffusion of ions increase with temperature. Hence, corrosion increases with temperature.

b) Humidity of air: The rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as a solvent for oxygen, carbon dioxide, sulphur dioxide etc. in the air to produce the electrolyte which is required for setting up a corrosion cell.

c) Presence of impurities in atmosphere: Atmosphere in industrial areas contains corrosive gases like CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 etc. In presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby the rate of corrosion increases.

d) Presence of suspended particles in atmosphere: In case of atmospheric corrosion: (i) if the suspended particles are chemically active in nature (like NaCl , Ammonium sulphate), they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion; (ii) if the suspended particles are chemically inactive in nature (eg., charcoal), they absorb both sulphur gases and moisture and slowly enhance corrosion rate.

e) Influence of pH: Generally acidic media (ie., $\text{pH} < 7$) are more corrosive than alkaline and neutral media.

f) Nature of ions present: g) Conductance of the corroding medium:

h) Formation of oxygen concentration cell: i) Flow velocity of process stream:

j) Polarization of electrodes:

CORROSION CONTROL:

Corrosion can be controlled by the following ways:

[1] **By selection of the material:** Selection of the right type of the material is the main factor for corrosion control. Thus, noble metals are used for surgical instruments and ornaments as they are most immune to corrosion.

[2] **By using pure metals:** Pure metals have higher corrosion resistance. Even minute amount of impurities may lead to severe corrosion,

[3] **By alloying:** Both corrosion resistance and strength of many metals can be improved by alloying, e.g. stainless steels containing chromium produce a coherent oxide film which protects the steel from further attack.

[4] **By annealing:** Heat treatment like annealing helps to reduce internal stresses and reduces corrosion.

[5] **By eliminating galvanic action:** If two metals have to be in contact, they should be so selected that their oxidation potentials are as near as possible. Further, the area of the cathode metal should be smaller than that of the anode, e.g. copper nuts and bolts on large steel plate. The corrosion can also be reduced by inserting an insulating material between the two metals.

[6] **By cathodic protection:** The principle involved in cathodic protection is to force the metal behave like a cathode. Since there will not be any anodic area on the metal, corrosion does not occur.

There are two types of cathodic protection. (a) Sacrificial anodic protection

(b) Galvanization.

(a) **Sacrificial anodic protection:** In this technique, a more active metal is connected to the metal structure to be protected so that all the corrosion is concentrated at the more active metal and thus saving the metal structure from corrosion. This method is used for the protection of sea going vessels such as ships and boats. Sheets of zinc or magnesium are hung around the hull of the ship. Zinc and magnesium being anodic to iron get corroded. Since they are sacrificed in the process of saving iron (anode) they are called sacrificial anodes. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.

(b) **Galvanizing:** The process of coating a layer of zinc on steel is called galvanizing. It is used to protect roofing sheets, wires, pipes, tanks, nails, screws, etc.

[7]. **Proper Designing:** Proper geometrical design plays a vital role in the control of corrosion of equipments and structures. The general guidelines of the design of materials and components to control corrosion are the following: a. Use always simple design and structure b. The design must avoid more complicated shapes having more angles, edges, corners etc. c. Avoid the contact of dissimilar metals as they may lead to galvanic type corrosion.

[8]. **Protective Protective Coatings** : Protective coatings are used to protect the metals from corrosion. The main types of protective coatings are classified as follows.

i) Metallic coating-Electroplating, Galvanisation, Metal spraying etc.

ii) Nonmetallic coating: Oxide coating, Phosphate coating etc.

iii) Organic coating: Paints, Varnish etc.