

# CORROSION

## □ INTRODUCTION TO CORROSION

Corrosion is exactly the reverse of extraction of metals and also known as *weeping of metals*. When metals are exposed to the environment, the metal surfaces start decaying by converting into more stable metal compounds more or less rapidly. Corrosion may be defined as, "*the gradual eating away, disintegration, decaying or deterioration of a metal by chemical or electro-chemical reaction with its environment*". The environment could be of any type such as atmosphere, water, seawater, acids, alkalies, steam, gases, soils and liquid metals etc, and the interaction of metal with the environment could take place at any temperature. Thus, according to modern definition, "*corrosion is the deterioration of a substance due to its reaction with its environment*". Corrosion is either chemical or electrochemical in nature.

### [I] Some Examples of Corrosion

- (i) Rusting of iron.
- (ii) Reaction of chlorine gas with magnesium or tin.
- (iii) Formation of green layer of basic carbonate.

**Note :** The undesirable destruction or alteration in non-metallic materials by weathering or other agents is not generally classified as corrosion.

### [II] Causes of Corrosion

In nature, most metals (except noble metals) exist in combined states as their compounds, called ores and minerals *i.e.*, oxides, hydroxy carbonates, carbonates, chlorides, sulphides, silicates etc. These compounds represent their thermodynamically stable state. The metals are extracted from these ores after expending lot of energy. Hence, unless the nature of the metal is substantially changed (*e.g.*, by alloying), the metal will have a natural tendency to convert back to its natural thermodynamically stable state, *i.e.*, combined state. This is the basic reason for metallic corrosion.

**Note :** Metals that exist in elemental state in nature as gold, naturally, have excellent corrosion resistance in natural environment.

## FACTORS INFLUENCING CORROSION

Usually corrosion depends on the nature of metal and the nature of the environment.

### (i) Nature of the Metal

**(i) Oxidation potential :** The extent of corrosion depends upon the position of the metal in the electrochemical series and galvanic series. When two metals are in electrical contact in presence of an electrolyte, the metal higher up in the galvanic series becomes anodic and suffers corrosion. Further, the more the two metals are apart in the galvanic series, the greater will be the corrosion of the anodic metal.

**(ii) Overvoltage :** When a metal which occupies a high position in galvanic series (say zinc) is placed in 1N-H<sub>2</sub>SO<sub>4</sub>, it undergoes corrosion forming a film and evolving hydrogen gas. The initial rate of reaction is quite slow, because of high overvoltage (= 70V) of zinc metal, which reduces the effective electrode potential to a small value. However, if a few drops of copper sulphate are added, the corrosion rate of zinc is accelerated, because some copper gets deposited on the zinc metal, forming minute cathodes, where the hydrogen overvoltage is only 0.33V. Thus, reduction in overvoltage of the corroding metal alloy accelerates the corrosion rate.

**(iii) Relative areas of anode and cathode :** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part. It may be broadly concluded that when anodic polarization is negligible and conductance remaining more or less constant, corrosion of the anode is directly proportional to the area of the cathode.

Although the corrosion current is same at both cathode and anode, the current density at the smaller anode will be much greater and the demand for electrons (by the large cathodic areas) can be met by smaller anodic areas only by undergoing corrosion more briskly.

**(iv) Purity of metal :** Impurities in a metal, generally, cause heterogeneity and form minute/tiny electrochemical cells (at the exposed parts) and the anodic parts get corroded. For



example, the impurities such as Pb, Fe or C in zinc lead to the formation of tiny electrochemical cells at the exposed part of the impurity and the corrosion of zinc around the impurity takes place due to local action. The rate of corrosion increases with the increasing exposure of the impurities.

(v) **Physical state of the metal** : The rate of corrosion is influenced by the 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.

(vi) **Nature of surface film** : In aereated atmosphere, practically all metals get covered with a thin surface film of metal oxide having a thickness of a few angstroms. The film may contain one or more forms of the metal oxide and its thickness depends upon the nature of the metal and temperature. 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. For example, the specific volume ratios for W, Cr and Ni are 3-6, 2-0 and 1-6, respectively, which indicates that the rate of oxidation at elevated temperatures is least for W.

(vii) **Passive character for metal** : Metals like Ti, Al, Cr, Mg, Ni and Co are passive and they show much higher corrosion resistance than expected from their positions in galvanic series, due to the formation of highly protective, but very thin film (of oxide) on the metal or alloy surface. Moreover, the film is of such a self-healing nature, that if broken, it repairs itself, on re-exposure to oxidising conditions. Thus, corrosion resistance of stainless steel is due to the passivating character of chromium present in it.

(viii) **Solubility of corrosion products** : If the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate. On the contrary, if the corrosion product is insoluble in the medium or it interacts with the medium to form another insoluble product (e.g.,  $\text{PbSO}_4$  formation in case of Pb in  $\text{H}_2\text{SO}_4$  medium), then the corrosion product acts as a physical barrier, thereby suppressing further corrosion.

(ix) **Volatility of corrosion products** : If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion, leading to excessive corrosion. For example, molybdenum oxide ( $\text{MoO}_3$ ), which is the oxidation corrosion product of Mo is volatile.

### [III] Nature of Environment

(i) **Temperature** : The rate of chemical reactions and the rate of diffusion increase with temperature and polarization decreases, hence, corrosion increases with temperature.

(ii) **Presence of moisture** : Humidity of air is the deciding factor in atmospheric corrosion. Critical humidity is defined as the **relative humidity above which the atmospheric corrosion rate of metal increases sharply**. The value of critical humidity depends on the physical characteristics of the metal as well as nature of the corrosion products. The reason why corrosion of a metal becomes faster in humid atmosphere is that gases like  $\text{CO}_2$ ,  $\text{O}_2$  etc. and vapours, present in atmosphere furnish water to the electrolyte, which are essential for setting up an electrochemical corrosion cell.

(iii) **Presence of impurities in atmosphere** : Atmosphere, in the vicinity of industrial areas, contains corrosive gases like  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and fumes of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , etc. In presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby corrosion is increased.

(iv) **Presence of suspended particles in atmosphere** : (a) If the suspended particles are chemically active in nature like  $\text{NaCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ , they absorb moisture and act as strong electrolytes, thereby causing increased corrosion.



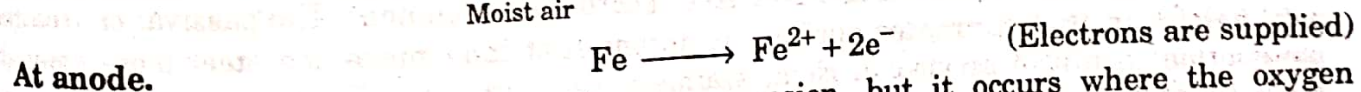
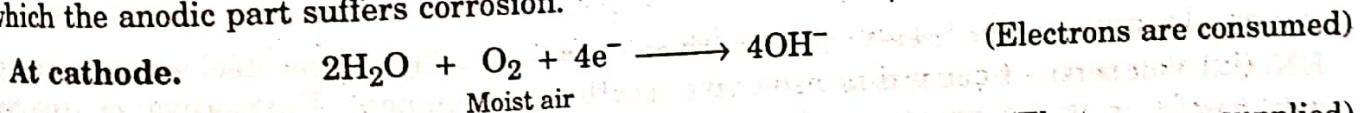
(b) If the suspended particles are chemically inactive in nature *i.e.*, charcoal, they absorb both gaseous and moisture and slowly increase the corrosion rate.

(v) **Effect of pH** : The hydrogen ion concentration of the medium is another important factor in corrosion reactions as well as corrosion control. Acidic media are generally more corrosive than alkaline and neutral media. However, amphoteric metals (like Al, Zn, Pb etc.) dissolve in alkaline media as complex ions. The corrosion rate of iron in oxygen-free water is slow, until the pH is below 5.0. The corresponding corrosion rate in presence of oxygen is much higher. Consequently, corrosion of metals, readily attacked by acid, can be reduced by increasing the pH of the attacking environment, *e.g.*, Zn (which is rapidly corroded, even in weakly acidic solutions such as carbonic acid) suffers minimum corrosion at pH = 11.

(vi) **Nature of ions present** : Chloride ions present in the medium destroy the passive film and corrode many metals and alloys. On the other hand, the presence of anions like silicates in the medium leads to the formation of insoluble reaction products, *e.g.*, silica gel, which inhibits further corrosion.

(vii) **Conductance of the medium** : In corrosion of underground or submerged structures, the conductance of the medium is of prime importance. Conductance of dry sandy soils is lower than those of clayey and mineralized soils. Consequently, stray currents (from power leakages) will cause more severe damage to the metallic structures, buried under clayey and mineralized soils than those under dry sandy-soils.

(viii) **Concentration of oxygen and formation of oxygen concentration cell** : The rate of corrosion increases with increasing supply of oxygen. Less oxygen concentration, *e.g.*, oxide-coated part or less-exposed parts becomes anodic, while the more oxygenated regions or parts more exposed to oxygen become cathodic. This leads to the formation of oxygen-concentration cell in which the anodic part suffers corrosion.



Thus, oxidation concentration cell promotes corrosion, but it occurs where the oxygen concentration is lower.

(ix) **Flow velocity of process stream** : In order to understand the effects of velocity, we must remember that corrosion is controlled by polarization (*i.e.*, slowing down of the reactions) at the anodes and the cathodes. When a metal that does not passivate, is under diffusion control, an increase in flow velocity of the medium enhances diffusion rate, thereby increasing the corrosion rate. Thus, in non-passivating type of corroding metals, minimization of flow velocity may decrease the corrosion rates. However, no generalization can be made in case of passive metals without proper data.