

## Lecture 1

### Corrosion: Introduction – Definitions and Types

*Keywords: Definition of Corrosion, Corrosion Types, Environment.*

Corrosion can be viewed as a universal phenomenon, omnipresent and omnipotent. It is there everywhere, air, water, soil and in every environment, we encounter.

There is no single figure for loss to the nation due to corrosion. It can be a minimum of 3.5% of the nation's GDP. Losses due to corrosion could be around Rs. 2.0 lakh crores per annum in India. Corrosion costs manifest in the form of premature deterioration or failure necessitating maintenance, repairs and replacement of damaged parts.

In the US, total direct cost of corrosion is estimated at about 300 billion dollars per year; which is about 3.2% of domestic product. Corrosion has a huge economic and environmental impact on all facets of national infrastructure; from highways, bridges, buildings, oil and gas, chemical processing, water and waste water treatment and virtually on all metallic objects in use. Other than material loss, corrosion interferes with human safety, disrupts industrial operations and poses danger to environment. Awareness to corrosion and adaptation of timely and appropriate control measures hold the key in the abatement of corrosion failures.

#### **Definitions:**

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means.

In simple terminology, corrosion processes involve reaction of metals with environmental species.

As per IUPAC,

“Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in its consumption or dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as melting and evaporation, abrasion or mechanical fracture are not included in the term corrosion”

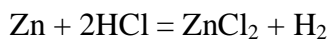
With the knowledge of the role of various microorganisms present in soil and water bodies, the definition for corrosion need be further widened to include microbially-influenced factors.

Corrosion can be classified in different ways, such as

- Chemical and electrochemical
- High temperature and low temperature
- Wet corrosion and dry corrosion.

Dry corrosion occurs in the absence of aqueous environment, usually in the presence of gases and vapours, mainly at high temperatures.

Electrochemical nature of corrosion can be understood by examining zinc dissolution in dilute hydrochloric acid.



Anodic reaction is  $\text{Zn} = \text{Zn}^{++} + 2\text{e}$  with the reduction of  $2\text{H}^+ + 2\text{e} = \text{H}_2$  at cathodic areas on the surface of zinc metal. There are two half reactions constituting the net cell reaction.

Environmental effects such as those of presence of oxygen and other oxidizers, changes in flow rates (velocity), temperature, reactant concentrations and pH would influence rates of anodic and cathodic reactions.

Even though the fundamental mechanism of corrosion involves creation or existence of corrosion cells, there are several types or forms of corrosion that can occur. It should however be borne in mind that for corrosion to occur, there is no need for discrete (physically independent) anodes and cathodes. Innumerable micro level anodic and cathodic areas can be generated at the same (single) surface on which anodic (corrosion) and cathodic (reduction) reactions occur.

Each form of corrosion has a specific arrangement of anodes and cathodes and specific patterns and locations depending on the type can exist.

The most important types are

- Uniform corrosion.
- Galvanic corrosion, concentration cells, water line attack
- Pitting.
- Dezincification, Dealloying (selective leaching)
- Atmospheric corrosion.
- Erosion corrosion
- Fretting
- Crevice corrosion; cavitation
- Stress corrosion, intergranular and transgranular corrosion, hydrogen cracking and embrittlement
- Corrosion fatigue.

**Table 1.1 ASM classifications of corrosion types**

<b>General Corrosion:</b>	<b>Localized Corrosion:</b>	<b>Metallurgically Influenced Corrosion:</b>	<b>Mechanically Assisted Degradation:</b>	<b>Environmentally Induced Cracking:</b>
Corrosive attack dominated by uniform thinning <ul style="list-style-type: none"> <li>• Atmospheric corrosion</li> <li>• Galvanic corrosion</li> <li>• Stray-current corrosion</li> <li>• General biological corrosion</li> <li>• Molten salt corrosion</li> <li>• Corrosion in liquid metals</li> <li>• High – temperature corrosion</li> </ul>	High rates of metal penetration at specific sites <ul style="list-style-type: none"> <li>• Crevice corrosion</li> <li>• Filiform corrosion</li> <li>• Pitting corrosion</li> <li>• Localized biological corrosion</li> </ul>	Affected by alloy chemistry & heat treatment <ul style="list-style-type: none"> <li>• Intergranular corrosion</li> <li>• Dealloying corrosion</li> </ul>	Corrosion with a mechanical component <ul style="list-style-type: none"> <li>• Erosion corrosion</li> <li>• Fretting corrosion</li> <li>• Cavitation and water drop impingement</li> <li>• Corrosion fatigue</li> </ul>	Cracking produced by corrosion, in the presence of stress. <ul style="list-style-type: none"> <li>• Stress – Corrosion Cracking (SCC)</li> <li>• Hydrogen Damage</li> <li>• Liquid metal embrittlement</li> <li>• Solid metal induced embrittlement</li> </ul>

(Ref: Sully J R, Taylor D. W, Electrochemical Methods of Corrosion Testing, Metals Hand Book. Vol 13, 1987.)

Crevice corrosion is a localized attack on a metal adjacent to the crevice between two joining surfaces (two metals or metal-nonmetal crevices). The corrosion is generally confined to one localized area to one metal. This type of corrosion can be initiated by concentration gradients (due to ions or oxygen). Accumulation of chlorides inside crevice will aggravate damage. Various factors influence crevice corrosion, such as.

- Materials: alloy composition, metallographic structure.
- Environmental conditions such as pH, oxygen concentration, halide concentrations, temperature.
- Geometrical features of crevices, surface roughness.
- Metal to metal or metal to nonmetal type.

Filiform corrosion is a special type of crevice corrosion.

Pitting corrosion is a localized phenomenon confined to smaller areas. Formation of micro-pits can be very damaging. Pitting factor (ratio of deepest pit to average penetration) can be used to evaluate severity of pitting corrosion which is usually observed in passive metals and alloys. Concentration cells involving oxygen gradients or ion gradients can initiate pitting through generation of anodic and cathodic areas. Chloride ions are damaging to the passive films and can make pit formation auto-catalytic. Pitting tendency can be predicted through measurement of pitting potentials. Similarly critical pitting temperature is also a useful parameter.

Uniform corrosion is a very common form found in ferrous metals and alloys that are not protected by surface coating or inhibitors. A uniform layer of 'rust' on the surface is formed when exposed to corrosive environments Atmospheric corrosion is a typical example of this type.

Galvanic corrosion often referred to as dissimilar metal corrosion occurs in galvanic couples where the active one corrodes. EMF series (thermodynamic) and galvanic series (kinetic) could be used for prediction of this type of corrosion. Galvanic corrosion can occur in multiphase alloys.

Eg: - Copper containing precipitates in aluminium alloys.

Impurities such as iron and copper in metallic zinc.

Differential aeration (oxygen concentration cell) and ion concentration (salt concentration) cells create dissimilar polarities (anodic and cathodic areas)

Eg:-Pitting of metals. Rusting of iron (Fig. 1.1).

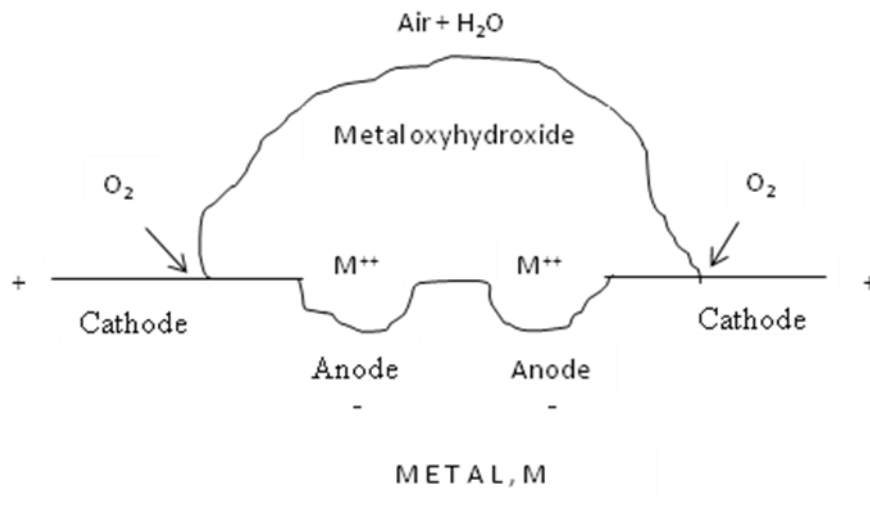


Fig. 1.1 Differential oxygen cells in rusting of iron

Selective leaching (Dealloying) refers to selective dissolution of active metal phase from an alloy in a corrosive environment.

Examples:

- a) Brass containing copper and zinc. Since zinc is anodic to copper, selective dezincification occurs in a corrosive medium, enriching the cathodic copper in the matrix (colour of brass turns red from yellow).
- b) Graphitization of grey cast iron-graphite being cathodic enhances dissolution of iron in the matrix, leaving behind a graphite network.

There are several other examples of dealloying besides the above.

- Tin Bronzes in hot brine or steam-Destannification.
- Precious metal alloys such as gold containing copper or silver – strong acids, sulfide environment - preferential dissolution of copper or silver.
- Cupro-nickel alloys in condenser tubes-denickelisation.

Localised attack at or nearer to grain boundaries in a metal or alloy can be termed as intergranular corrosion. Generally the following factors contribute to intergranular corrosion.

- Impurities and precipitation at grain boundaries.
- Depletion of an alloying element (added to resist corrosion) in the grain-boundary area.

A typical example is sensitized 18-8 stainless steels when chromium carbide is precipitated along grain boundaries. Lowered chromium content in the area adjacent to grain boundaries, leads to formation of anodic and cathodic areas.

Such intergranular corrosion is common in stainless steel welded structures and is referred to as weld decay. Intergranular attack can occur in other alloys as well.

For example, Duralumin-type alloys (Al – Cu) due to precipitation of  $\text{CuAl}_2$ .

Erosion corrosion is the deterioration of metals and alloys due to relative movement between surfaces and corrosive fluids. Depending on the rate of this movement, abrasion takes place. This type of corrosion is characterized by grooves and surface patterns having directionality. Typical examples are

- Stainless alloy pump impeller,
- Condenser tube walls.

All equipment types exposed to moving fluids are prone to erosion corrosion.

Many failures can be attributed to impingement (impingement attack). Erosion corrosion due to high velocity impingement occurs in steam condenser tubes, slide valves in petroleum refinery at high temperature, inlet pipes, cyclones and steam turbine blades.

Cavitation damage can be classified as a special form of erosion corrosion. This is usually caused by formation and collapse of vapour bubbles in liquids closer to a metal surface. Typical examples include ship's propellers, pump impellers and hydraulic turbines. Surface damage similar to that of pitting can occur and both corrosion and mechanical factors are involved.

Corrosion occurring at contact regions between materials under load subjected to slip and vibration can be termed Fretting. Such friction oxidation can occur in engine and automotive parts. Fretting is known to occur at bolted tie plates on rails.

Parameters promoting fretting include:

- Relative motion between two surfaces.
- Interface under load.

Both the above produce slip and deformation of surfaces. Wear-oxidation and oxidation-wear theories are proposed to explain fretting corrosion.



Stress corrosion cracking (SCC) refers to failure under simultaneous presence of a corrosive medium and tensile stress. Two classic examples of SCC are caustic embrittlement of steels occurring in riveted boilers of steam-driven locomotives and season cracking of brasses observed in brass cartridge cases due to ammonia in environment. Stress cracking of different alloys does occur depending on the type of corrosive environment. Stainless steels crack in chloride atmosphere. Major variables influencing SCC include solution composition, metal/alloy composition and structure, stress and temperature. Crack morphology for SCC failures consists of brittle fracture and inter - or trans-granular cracking could be observed. Higher stresses decrease time before crack initiation. Tensile stresses of sufficient threshold levels are involved (applied, residual or thermal stresses).

Hydrogen embrittlement although many a time classified under stress corrosion, need be considered separately since the two types respond very differently to environmental factors.

Fracture of metals and alloys under repeated cyclic stresses is termed fatigue and corrosion under such circumstances is corrosion fatigue (reduction of fatigue resistance).

Electrochemical factors come into play in many of the above corrosion forms. Both thermodynamic and kinetic aspects of electrochemistry of corrosion are discussed in the following lectures with respect to both corrosion mechanisms and corrosion protection.