

Summary | Degradation

Introduction

Corrosion

Deterioration of metals due to the reaction with the environment.

All corrosion reactions are electrochemical in nature.

Electrochemical reactions

Pair of reactions in which electron transfer occurs from one reaction to another.

Oxidation

The reaction where an electron is released. Aka. anodic reaction.

Reduction

The reaction where an electron is consumed. Aka. cathodic reaction.

Anode

The site at which oxidation takes place.

Cathode

The site at which reduction takes place.

Common reactions

Hydrogen evolution reaction (HER)



Oxygen reduction reaction (ORR)



Standard Electrode Potential

Whether a metal becomes anode/oxidizes or cathode/reduces depends on its E^0 value. Measured in reference to hydrogen.

The metal with the least E^0 becomes the anode.

Cell

When 2 electrodes are electrically connected.

Cell potential

Absolute difference between the 2 electrode's standard electrode potentials. Denoted by ΔE^0 .

For a corrosion reaction to occur spontaneously, $\Delta E^0 > 0$. Cell potential is an indication of the rate of corrosion.

Forms of Corrosion

8 forms:

1. Uniform / General corrosion
2. Galvanic corrosion
3. Crevice corrosion
4. Pitting corrosion
5. Inter-granular corrosion
6. Erosion corrosion
7. Stress corrosion
8. Selective leaching

Uniform corrosion

Occurs uniformly over the entire exposed area of the metal. Rust forms all over the surface. Leads to 30% of corrosion failures.

Galvanic corrosion

When 2 metals are in contact (electrically) and placed in a corrosive environment, only one metal — the element with most negative potential— corrodes. Aka. two metal corrosion.

Galvanic corrosion can happen even inside 1 metal. In such cases, one part of the metal becomes anodic to the rest. For example, consider a piece of iron, immersed in water. Initially iron goes under uniform corrosion. Once the oxygen in the water is depleted, iron just above the water surface starts to react as a cathode. Severe corrosion occurs just below the water level.

Corrosion will be severe at the junction.

Area effect

Smaller the anode, severe will be the corrosion.

Galvanic series

Designed to be an extension of electrochemical series that includes alloys and non-metals. Materials are ordered in ascending order of reactivity. Materials in the lower position becomes the anode. Specific for a particular environment.

Crevice corrosion

If a crevice (a crack forming a narrow opening) is in contact with a liquid, the crevice undergoes corrosion with virtually no attack in the other region.

Crevice becomes anodic because of low oxygen supply. Exposed area has high oxygen supply and works as a cathode.

Mechanism of CC

Consider a riveted metal-plate section in contact with domestic water.

Initially it will corrode uniformly. After some time, crevice becomes depleted with oxygen due to restricted convection. Now the crevice becomes the anode. As the anode area is much smaller compared to cathode, corrosion will be severe.

If the water contained salt(s), metal chloride(s) will be formed. All metal chlorides other than NaCl, KCl hydrolyze in water. And produces acid. Acids increase the rate of corrosion.

Prevention of Corrosion

Corrosion results in loss of materials and money. It must be minimized or controlled.

To avoid corrosion

- Use noble metals (Au, Pt)
- Use purest possible metal - not possible in real life
- Use corrosion resistant alloys
- Use non-metals (like polymers or ceramics)

Cathodic protection

Corrosion can be prevented by making the metallic structure as cathode.

2 types of cathodic protection is available.

Galvanic protection

Metal to be protected is made cathode by connecting it to an anodic metal (which is called the sacrificial anode). Zn and Mg are commonly used as anodic metals. Aka. sacrificial anodic protection.

Uses

- Protection from soil corrosion of buried pipelines, underground cables
- Protection from marine corrosion of cables, ship hulls, piers
- Prevention of rust in water boilers by inserting magnesium
- Minimizing engine corrosion using calcium

Impressed current cathodic protection

Suppressing corrosion by supplying external current (opposite to corrosion). The applied current converts corroding metal from anode to cathode.

Usually current is derived from DC sources with an inert anode.

Modifying the environment

Corrosion can be prevented by adding inhibitors to the environment.

Examples:

- Hydrogen evolution reactions - used when cathodic reactions are HER.
- Oxygen scavengers - eliminates oxygen from the corroding medium. used when cathodic reactions are ORR.

Protective coatings

Preventing corrosion by covering the surface by means of protective coatings.

The coating acts as a physical barrier between the coated metal surface and the environment.

2 types:

- Inorganic
 - Metallic
 - Non-metallic
- Organic
 - Paints

Galvanizing

The process of coating steel sheets with a thin coat of zinc to prevent them from rusting.

Steel article is:

1. cleaned with diluted sulfuric acid
2. washed with distilled water
3. dried
4. dipped in a bath of molten zinc

Now zinc is coated on the steel article.

Paints

Paint is a viscous, opaque mechanical dispersion mixture of one or more pigments (dye) in a vehicle (drying oil).

Corrosion inhibitors are added to paints.

Degradation of Polymers

Change in the chemical and/or physical structure of the polymer chain.

Degradation is undesirable during use but desirable after use (as in biodegradation).

Types of degradations

Type of degradation	Agent
Thermal degradation	Heat
Chemical degradation	Chemical
Photo-degradation	UV & other radiations
Mechanical degradation	Stress
Biodegradation	Bacteria and other organisms

Note

UV stabilized - the polymer is protected from UV degradation.

Susceptibility to degradation

Depends on its structure and the type of degradation.

- Chains containing aromatic functionality are susceptible to ultraviolet degradation
- Hydrocarbon-based polymers are susceptible to thermal degradation

Bond rupture or scission

Breaking into smaller polymer chains. Molecular weight of the polymer decreases.

Swelling & dissolution

Main form of degradation when a polymer is exposed to liquids.

Swelling

The liquid or solute diffuses into the polymer. Polymer absorbs the liquid or solute. Chain separation increases. Secondary inter-molecular bonding forces decreases.

Dissolution

Extreme state of swelling. Occurs when the polymer is completely soluble.

Corrosion of Ceramics

Resistant to corrosion. Because of this, glass is often used to contain liquids.

Refractory ceramics

Ceramics that can withstand high temperatures. Can provide thermal insulation.