SMM 3622

Materials Technology

4.1 Corrosion

WHAT IS CORROSION?

- Corrosion is defined as the *destruction of a metal by chemical or electrochemical reaction with its surrounding (environment)*
- It is an electrochemical process involving metals: electricity and chemical reactions are involved and metal material is lost.
- Corrosion can occur in a gaseous environment (dry corrosion) or a wet environment (wet corrosion).
- The term corrosion is restricted to attack of metals.
- Rusting, applies to corrosion of iron and steel. Non-ferrous metals corrode but do not rust.

- Aqueous corrosion (with water) (occur at ambient temperature)
- Atmospheric corrosion (with air + water + salt)
- High temperature corrosion
  - *Oxidation* (with oxygen)
  - *Hot corrosion* (with other gases)

Importance of Corrosion study:

- Corrosion is a very serious problem. Three areas in which corrosion study is important:

  1. Economic
  2. Improved safety
  3. Conservation of resources

- In addition to the cost of replacements (direct losses), corrosion costs also include (indirect losses):
  1. lost of production shutdown or failure
  2. Lost of product: oil, gas, water due to corroded pipe system
  3. Loss of efficiency
  4. High maintenance costs
  5. Loss of product quality due to contamination of product from the corrosion of materials.
  6. High cost of fuel and energy as the result of leakage of corroded pipes

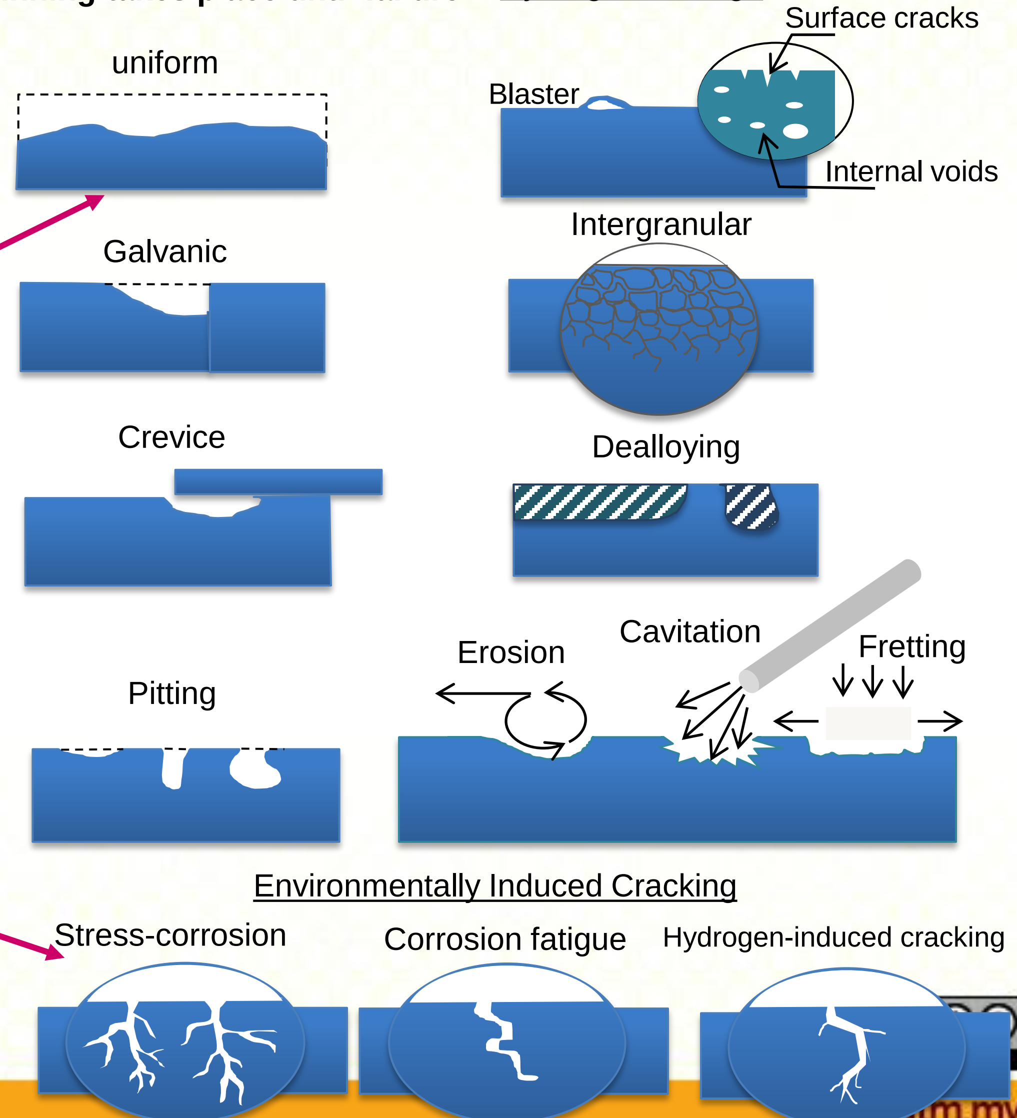
- Corrosion falls into two main categories:

1. General or uniform corrosion

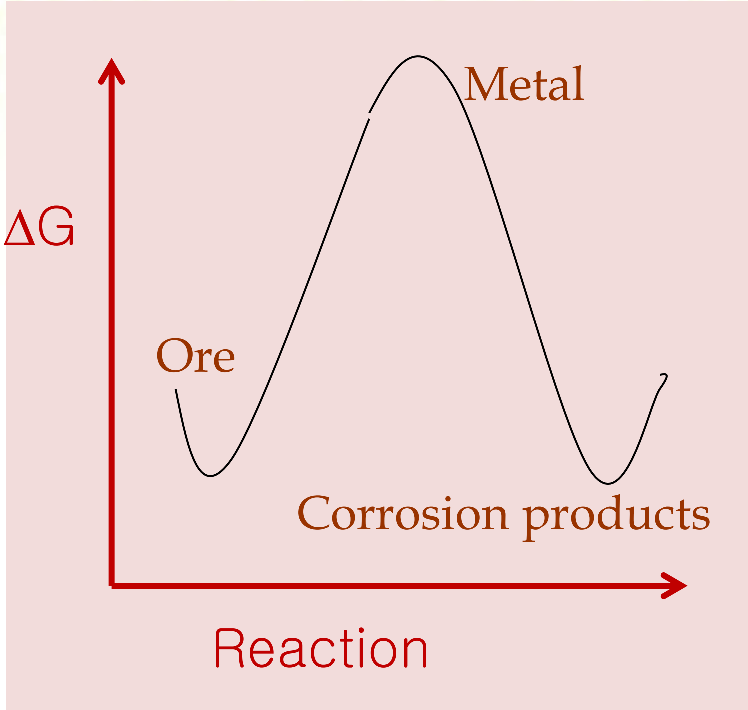
Uniform corrosion is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the total area. General thinning takes place until failure.

2. Localised corrosion

Selective removal of metal by corrosion at small areas or zones on a metal surface in contact with a corrosive environment e.g. liquid.



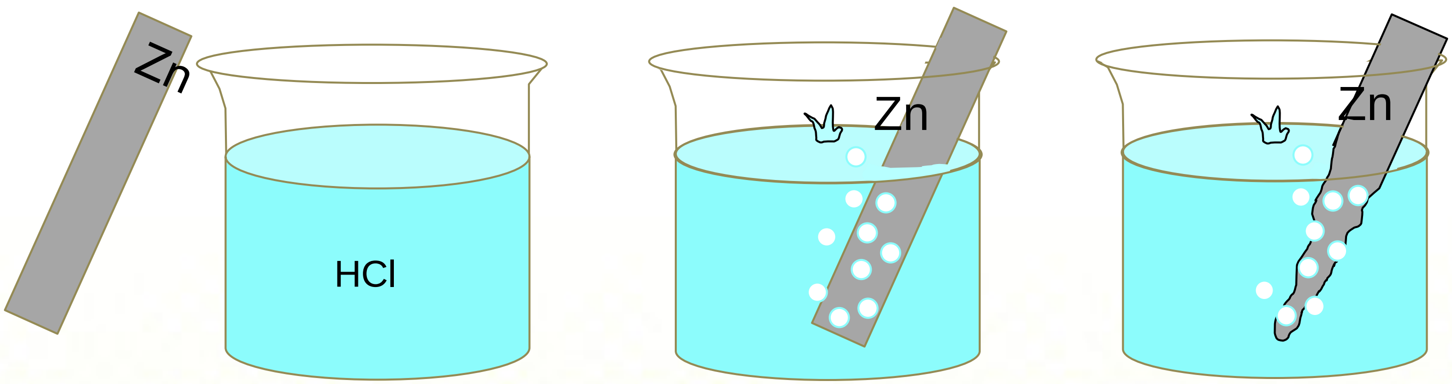
- All metals have a tendency to corrode, with some corroding more easily than others.
- Metals are extracted from ores (oxides, sulfides and others).
- Production of these metals from their ores requires energy (heating and melting).
- Certain environments offer opportunities for these metals to recombine and revert to their lower energy states.
- Thus, corrosion can be described as "extractive metallurgy in reverse"



Aqueous Corrosion:

Electrochemical reactions:

- Aqueous corrosion can be best described by this simple example:
  - If we take a piece of zinc (Zn) and place it in HCl, we will quickly notice a vigorous reaction and formation of bubbles on the surface of the Zn.



- What happens is the following reaction:

$Zn + HCl \rightarrow ZnCl_2 + H_2(g)$ (1)

In ionic form:

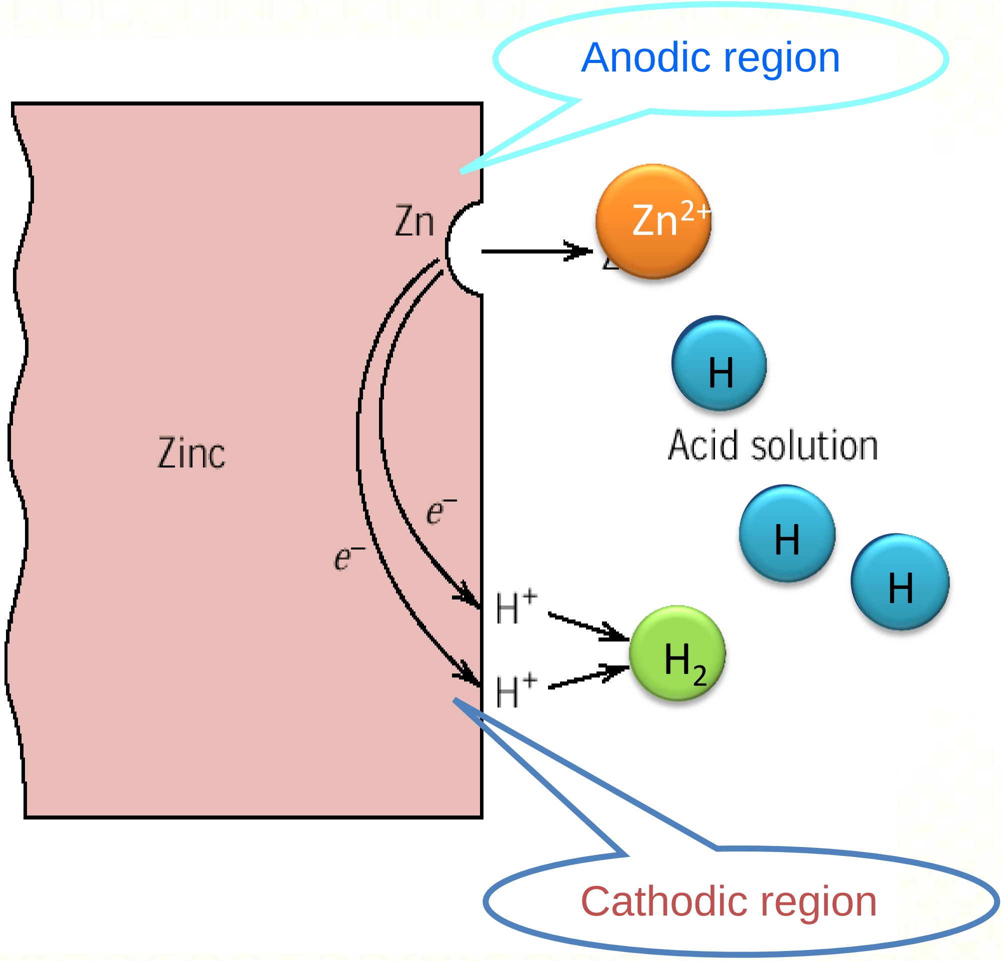
$Zn(s) + 2H^+ + 2Cl^- \rightarrow Zn^{++} + 2Cl^- + H_2(g)$

- The above equation can be represented by two partial reactions:

$Zn \rightarrow Zn^{+2} + 2e^-$ (2) "anodic": Oxidation

$2H^+ + 2e^- \rightarrow H_2$ (3) "cathodic": Reduction

- The complete reaction involving exchange of electrons is shown in Figure below.



- Corrosion involves both an anodic and cathodic reaction
- The anodic reaction involves metal dissolution ("corrosion") (reaction 2)

$M \rightarrow M^{n+} + ne^-$ (Loss of electrons)

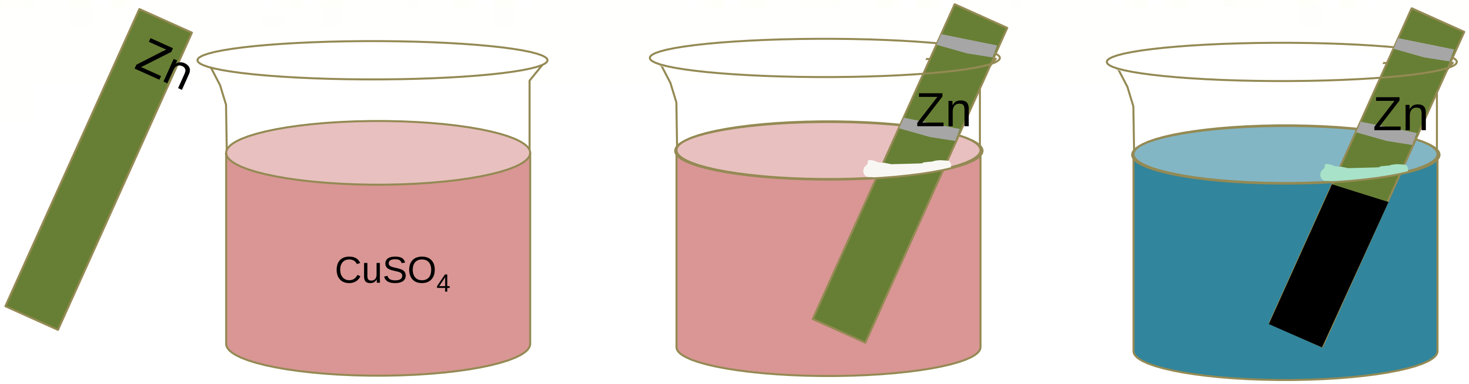
- The cathodic reaction consumes (gain electrons) the electrons (reaction 3)
- The cathodic reaction depends on the type of environment:

1. In acid environments:
   - Hydrogen evolution

     $2H^+ + 2e^- = H_2$
2. Neutral & Alkaline
   - $O_2 + 2H_2O + 4e^- = 4OH^-$ (*if oxygen is present*)

- In the above example, the metal (Zn) dissolves by reaction (2), liberating electrons.
- These electrons react with atomic hydrogen, H^+, in solution to form molecular hydrogen, H_2, by reaction (3).
- *Both reactions (2) & (3) must occur simultaneously and at the same rate.*
- Thus, "the rate of oxidation = rate of reduction"

- If we now place the piece of Zn in a solution containing copper sulfate ($CuSO_4$) (blue solution).



- What is observed is a dark deposit of Cu on Zn, and fading of the blue solution.

- The overall reaction is:

$$Zn + Cu^{+2} \rightarrow Cu + Zn^{+2} \qquad (1)$$

  - The oxidation reaction:

$$Zn \rightarrow Zn^{+2} + 2e^{-} \qquad (2)$$

  - The reduction reaction:

$$Cu^{+2} + 2e^{-} \rightarrow Cu \qquad (3)$$

- Any reaction that can be divided into two (or more) partial reactions of oxidation and reduction is called electrochemical.

- The example presented for the corrosion of Zn in HCl is applicable for the corrosion of any metal.

- In all cases, the metal will enter the solution as ions through anodic reactions:

$$Fe \rightarrow Fe^{+2} + 2e^{-}$$
$$Al \rightarrow Al^{+3} + 3e^{-}$$

- With the liberation of hydrogen gas (H_2) through the cathodic reaction.

- The anodic reaction in every corrosion is the oxidation of a metal to its ions.

- This can be written in the general form:

$M \rightarrow M^{+n} + ne^-$

- The cathodic reaction varies according to the corrosive medium.

1. In acid medium (without O_2):

$2H^+ + 2e^- \rightarrow H_2$

2. In acid medium with O_2: the dominant is:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

3. In neutral and alkalike media:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Corrosion (rusting) of steel:

- Corrosion of steel is an electrochemical reaction followed by a chemical reaction:

Anodic reaction:

$Fe \rightarrow Fe^{+2} + 2e^-$

Cathodic reaction:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Additional cathodic reaction:

$2H^+ + 2e^- \rightarrow H_2$

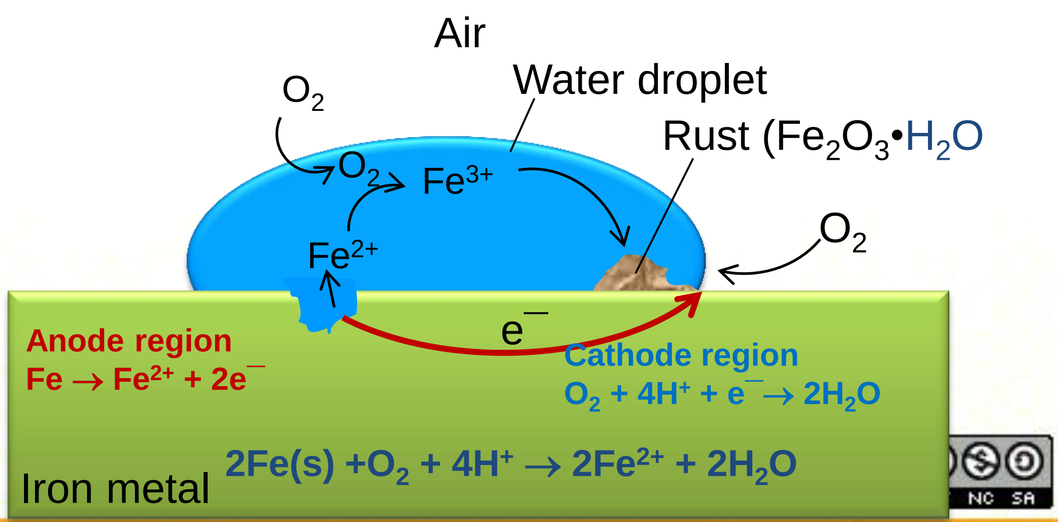
- This is followed by chemical reaction:

$4Fe^{+2} + O_2 + 4H^+ \rightarrow 4Fe^{+3} + 2H_2O$

- And then:

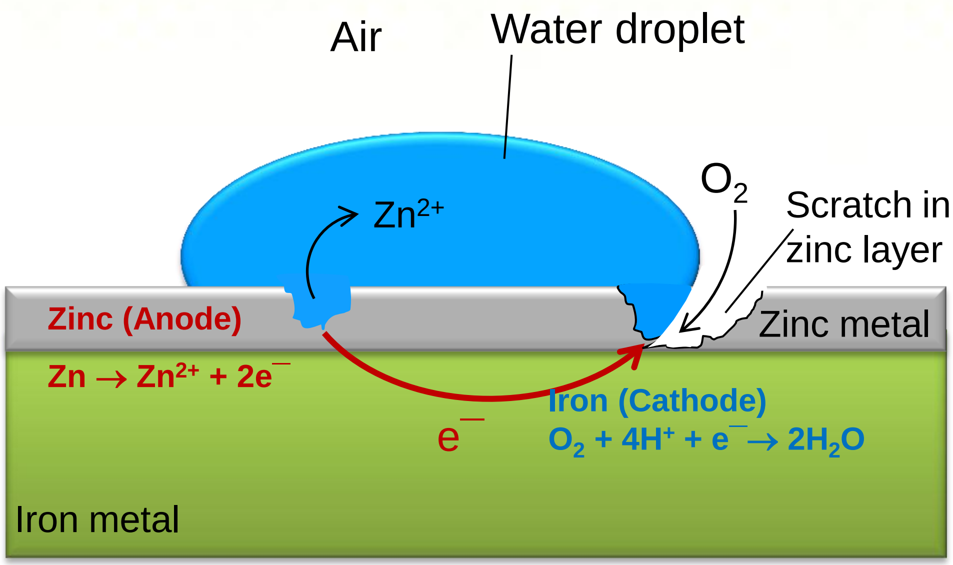
$2Fe^{+3} + 4H_2O \rightarrow Fe_2O_3 + 6H^+$

Rust



Protection of steel from corrosion:

- Steel can be protected by placing it in contact with a more active metal (like Zn which acts as sacrificial anode)



Anodic reaction (sacrificial anode):

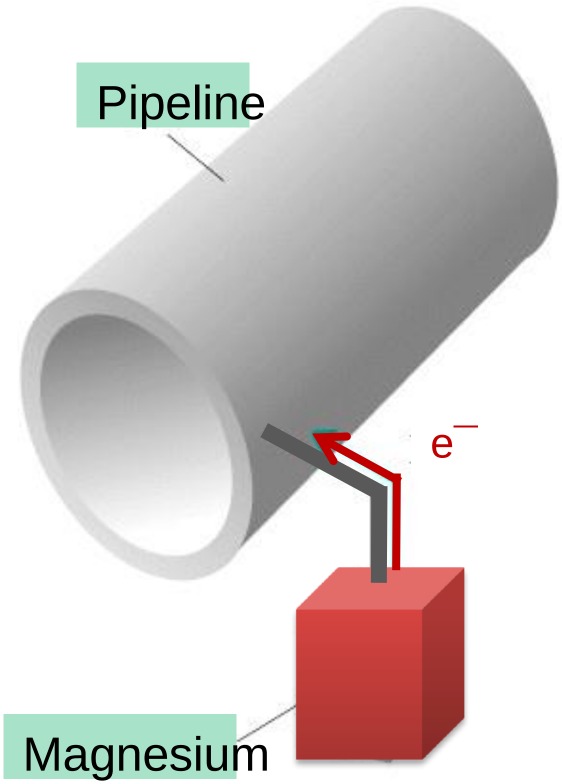
$Zn \rightarrow Zn^{+2} + 2e^-$

Cathodic reaction (acidic conditions):

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Protection of steel from corrosion:

- Steel can be protected by placing it in contact with a more active metal (like Mg)



Anodic reaction:

$Mg \rightarrow Mg^{+2} + 2e^-$

Cathodic reaction (acidic conditions):

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Requirements for Corrosion to occur:

- In order for corrosion to occur, we need the following:

1. **Anode** or anodic sites on the surface of the metal (electrode on which oxidation or corrosion occurs)
2. **Cathode** or cathodic sites on the surface of the metal (electrode on which reduction occurs)
3. **Electrolyte** in contact with both anode and cathode (provides a path for ionic conduction)
4. **Electrical** connection between anode and cathode (provides path for the flow of electrons)