CHAPTER ONE

Introduction
Corrosion is the destructive result of chemical reaction between a metal or metal alloys and its environment.
Metal atoms in nature are present in chemical compounds (i.e. minerals), the same amounts of energy needed to extract metals from their minerals are emitted during the corrosion chemical reaction, corrosion returns metal to its combined state in chemical compounds that are similar or even identical to minerals form which the metal were extracted.
Corrosion is defined in different ways, but the usual interpretation of the term is “an attack on a metallic material by reaction with its environment”. The concept of corrosion can also be used in a broader sense, where this includes attack on nonmetallic materials, but such attacks are outside the scope of this book.
Corrosion of metallic materials can be divided into three main groups
1. Wet corrosion, where the corrosive environment is water with dissolved species.
The liquid is an electrolyte and the process is typically electrochemical.
2. Corrosion in other fluids such as fused salts and molten metals.
3. Dry corrosion, where the corrosive environment is a dry gas. Dry corrosion is also frequently called chemical corrosion and the best-known example is high temperature corrosion.

Corrosion science and corrosion engineering
Corrosion science terms covers theories, laws and explanation of phenomena confirmed by inter subjective observation or experiments, for instance the explanation of different forms of corrosion, rate of corrosion, and mechanism of corrosion provide by corrosion science, corrosion science "knowing why", while corrosion engineering "knowing How "because corrosion engineering apply applications of principles evolved from corrosion science to minimize or prevent corrosion
Corrosion engineering involving designing of corrosion prevention schemes and implementation of specific codes and practices.

Costs of corrosion
1- Economics:
   a. Plant shut down, shut down of nuclear plant, process plant, power plant and refineries may cause severe problems to industry and consumers.
   b. Loss of products, leaking containers, storage tanks, water and oil transportation lines, fuel tanks cause loss of products and may generate severe accidents and hazard i.e. it well known that at least 25% of water is lost by leakage.
   c. Loss of efficiency, insulation of heat exchanger tubes.
   d. Contamination, corrosion products may contaminate chemicals, dyes, etc.
   e. Nuclear hazard i.e. Chernobyl destroy is good example of transport radioactive corrosion products
   f. Over design
Corrosion is a potent force which destroys economy, depletes resources and cause costly and untimely failure of plants, equipments and components.
In absence of adequate corrosion rate information, over design is required to ensure reasonable service life resulting in

2- Human life and safety

Why we study corrosion?
1- To understand how material destroys by corrosion and how they must be protected by applying corrosion protection technology "keep material and precious resources"
2- Engineering knowledge is incomplete without understanding corrosion, aeroplanes, ships automobiles and others cannot be designed without knowledge to corrosion behavior of material used in these structure
3- Corrosion is a treat to the environment i.e. water can become contaminated by corrosion products and unsuitable for consumption.

Electrochemical nature of aqueous corrosion

Nearly all metallic corrosion processes involves transfer of electronic charge in aqueous solutions.

Consider an example of zinc corrosion in hydrochloric acid solution, it take the following over all reaction

\[ \text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2 \]  

(1)

And in ionic form we can write it as below

\[ \text{Zn} + 2\text{H}^+ + 2\text{Cl}^- \rightarrow \text{Zn}^{2+} + 2\text{Cl}^- + \text{H}_2 \]  

(2)

And this reaction is assumed to be separated as two reactions

- Anodic reaction
  \[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]  
  (3)

- Cathodic reaction
  \[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \]  
  (4)

Reaction (3) defined as anodic reaction is an oxidation reaction in which zinc valence increase from 0 to +2 by liberating electrons, while reaction (4) defined as cathodic reaction, is a reaction in which the oxidation state of hydrogen decrease from +1 to 0 i.e. consuming electrons.

Water is required as a carrier for ions such as \( \text{Zn}^{2+} \) and \( \text{H}^+ \) and is called the electrolyte.

What is happen when an excess of electrons are supplied to the metal in above figure (1-1)?

Generally anodic reaction is took a below form

\[ \text{M} \rightarrow \text{M}^{\text{z}^+} + ze^- \]  

(5)

Examples

\[ \text{Fe} \rightarrow \text{Fe}^{\text{z}^+} + 2e^- \]
\[ \text{Ni} \rightarrow \text{Ni}^{\text{z}^+} + 2e^- \]
\[ \text{Al} \rightarrow \text{Al}^{\text{z}^+} + 2e^- \]
Figure (1-1) schematic diagram of metal M dissolution, liberating solution a metal ion M$^{+2}$ and into the metal electrons e$, which are consumed by reduction of H$^+$ to H$_2$.

**Anodic and cathodic reactions**

Anodic (oxidation) reaction is the corrosion reaction and it take place at anodic area and characterized by

1- Oxidation of metal to an ion with positive charge
2- Released electrons
3- Shift to a higher valance state

The process of oxidation in most metals and alloys represents corrosion reaction, hence if oxidation is stopped corrosion is stopped.

On other hand cathodic reaction is the reaction that must be found to corrosion process continue and it is called reduction reaction which occur at cathodic area where electrons are consumed, unlike anodic reaction there is a decrease in valance state

The most common cathodic reaction are

1- \( Cu^{+2} + 2e^- \rightarrow Cu \) (metal deposition)
2- \( 2H^+ + 2e^- \rightarrow H_2 \) (in acid solution)
3- \( O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \) (in acid solution contain dissolved oxygen)
4- \( O_2 + H_2O + 4e^- \rightarrow 4OH^- \) (in neutral or base solution contain dissolved oxygen)
5- \( Fe^{+3} + e^- \rightarrow Fe^{+2} \) (metal ion reduction, valance state reduction of a multivalent metal ion to lower)

**Basic wet corrosion cell**

For corrosion to take place, the formation of corrosion cell is essential, corrosion cell components are

1- Anode: represents the negative terminal at the cell, electrons released at anode which is more reactive metal, Electrons are insoluble in aqueous solution and they only move through the metallic bath, i.e. zinc casting acts as the anode in a battery.
2- Cathode: represents the positive terminal at the cell, reduction take place at it and electrons consumed i.e. carbon electrode in dry cell battery.
3- Electrolyte: it is the electrically conductive solution (i.e. salt solution) that must be present for corrosion to occur.
4- Metallic bath: the two electrodes are connected externally by a metallic conduction.

What is happen when one from these above items was lost?

Types of corrosion cells
These are the main types of cells that take part in corrosion reaction:
1- Galvanic cell: dissimilar metals in an electrolyte or the same metal in dissimilar conditions in a common electrolyte lead to cell formation i.e. steel and copper electrodes immersed in an electrolyte, the more active metal acts anode and more noble metal acts the cathode.

2- Concentration cell: these are cell with two identical electrodes but in contact with a solution of a different composition, there are two kinds of concentration cells:
   a. Salt concentration cell i.e. copper electrode is exposed to concentrated copper sulfate solution and another copper electrode exposed to dilute copper sulfate solution copper dissolve from the electrode in contact with dilute solution (act anode) and plate on copper electrode in contact with concentrated solution (act cathode).
   b. Differential aeration cells, they may include two iron electrodes in NaCl solution the electrolyte around one of these two electrodes are being thoroughly aerated (anode) and other deareated (cathode) for example the bubbling nitrogen through the solution. The difference in oxygen concentration produces a potential difference and cause current to flow, this type of cell accounts for the phenomena damage at crevices which is called crevice corrosion.

Consider the corrosion of pipe in the soil, concentration cell may be set up by:
   c. Variation in the amount of oxygen in soil.
   d. Differences in moisture content in soil.
   e. Differences in compositions of soil.

3- Electrolytic cell: this type of cell is formed when an external current is introduced into the system it may consist of all the basic components of galvanic cell and concentration cell plus an external source of electrical energy i.e. cathodic protection.

4- Differential temperature cells: components of these cells are electrodes of same metal, each of them which is at a different temperature immersed in an electrolyte of the same initial composition heaters and similar equipments.
Corrosion rate determination

Methods of exposure for corrosion measurement are fundamental in corrosion engineering. Exposure may be conducted in the laboratory or in service. Laboratory tests are more flexible and less expensive, however it is nearly impossible to simulate plant conditions i.e. time is usually at premium and accelerating factors such as increased temperature.

Objective of corrosion tests
1. Screen available materials (alloys) to determine the best for specific application.
2. Determine probable service life of equipment.
3. Evaluate new commercial alloys or processes.
4. Assist in the evaluation and development of new corrosion resistant alloys.
5. Verify that the product meets quality control specification before either acceptance or release.
6. Evaluate environmental controls and variations i.e. inhibitor.
7. Determine the most economical means for reducing corrosion.
8. Study corrosion mechanisms.

There are three main methods that are used to express the corrosion rate:
1. Thickness reduction of the material per unit time.
2. Weight loss per unit area and unit time.
3. Corrosion current density.

The corrosion rate or the rate of material removal as a consequence of the chemical action is an important corrosion parameter, this may be expressed as the corrosion penetration rate $CPR$, or the thickness loss per unit of time, the formula for this calculation is

$$CPR = \frac{KW}{DAT}$$

(6)

Where $W$ is weight loss after exposure time $T$, while $D$ and $A$ represent the density and exposed specimen area respectively and $K$ is constant, its magnitude
depend on the system of units used. The CPR is conveniently expressed in terms of either mils (1/1000 inch) per year (mpy) or millimeters per year (m/yr). K=534 to give CPR in mpy and W,D,A and T are specified in units milligrams, gram per cubic centimeter, square inches and hours respectively, in second case K=87.6 for CPR in mm/yr and unit for the other parameters are the same for first case except that A is given in square centimeters. For most application a corrosion penetration rate less than 20 mpy (0.5 mm/yr) is acceptable

Example (1-1):
A piece of corroded metal alloy plate was found in a submersed ocean vessel, it was estimated that the original area plate was 800 cm² and that approximately 7.6 Kg had corroded away during the submersion, assuming a corrosion penetration rate of 4 mm/yr for this alloy in seawater, estimate the time of submersion in years, the density of alloy is 4.5 g/cm³.

\[
CPR = \frac{KW}{DAT}
\]

\[
T = \frac{87.6W}{DA(CPR)}
\]

\[
= \frac{87.6 \times 7.6 \times 10^6 \text{mg}}{4.5 \text{g/cm}^3 \times 800 \text{cm}^2 \times 4 \text{mpy}} = 46233.3 \text{hr}
\]

\[
= 5.27 \text{ year}
\]

A thick steel sheet of area 100 in² is exposed to air near the ocean, after one year period it was found to experience a weight loss of 485 g due to corrosion, to what rate of corrosion in mpy and mm/yr does this correspond?