CHAPTER (I)

1. General Introduction:

Corrosion can be defined in many ways. The most preferred one in literature is the loss of useful properties of a material as a result of chemical or electrochemical reaction with its environment. Loss due to purely mechanical force is not called corrosion but is known as wear, fretting, etc. In some cases chemical or electrochemical attack may be accompanied by physical deterioration and is described by terms: corrosion – errosion, corrosive – wear or fretting corrosion.

Electrochemical reactions are the main causes of processes of degradation and deterioration of metallic construction. Electrochemical techniques can be used for studying and predicting corrosion behaviour as well as passivation phenomenon. They permit rapid corrosion rate measurments and can be used for monitoring purposes. They could be used to accurately, measure very low corrosion rates which are both difficult and tedious to perform with conventional weight loss or chemical analysis techniques. Electrochemial measurments focus on measuring Potentials and Currents. Corrosion today can be understood in terms of potential – pH (or Pourbaix) diagrams as well as in terms of Potential – Current (or Evans) diagrams.

1.1. The Electrochemical and corrosion properties of copper.

Copper is a semi noble metal and has a more positive potential than hydrogen but is more negative than oxygen electrode. The normal electrode potential of copper for the reaction $Cu \rightarrow Cu^{+} + e^{-}$ is +0.52 V, and for $Cu \rightarrow Cu^{++} + 2e^{-}$ it is +0.35V. Thus the more thermodynamically favorable reaction under most conditions is the formation of bivalent copper ions. The static potential of copper in 3% NaCl solution, as an example, is about +0.05V and about +0.15V in 1.0M HCl. For this reason, copper under usual conditions can not displace hydrogen from acids, that is, can not corrode by hydrogen depolarization. However, copper can corrode electrochemically by cathodic oxidation depolarization *(Tomashov, 1967).* Usually corroding copper goes into solution with the formation of Cu^{++}. Removal of these ions from the electrical double layer by stirring or by the addition of complexing agents (KCN, NH_3), severely denobles the potential of the copper electrode. Because of this, the stability of copper in solutions containing KCN, NH_4OH, or ammonium salts is lowered considerably. The chemical stability of copper is to a large degree determined by its thermodynamic stability. It has little tendency to passivate. These properties determine the nature of the corrosion resistance of copper and copper alloys. They are quite resistant to low and medium concentrations of non oxidizing acids (HCl, H_2SO_4, acetic and citric). However, the presence of oxidants (for example, HNO_3 or H_2O_2) or even bubbling oxygen or air through such solutions, considerably increases their rate of corrosion. In oxidizing acids such as HNO_3 copper is completely unstable. Beside oxygen, copper easily reacts with sulfur or compounds that readily release sulfur.

Table (1) amplify the effect of oxygen supply on the corrosion rate of copper.

Table (1): Rate of corrosion of copper in non oxidizing acids.

Acid	Concentration %	Rate of corrosion, mg/cm^2/day	
		By passing hydrogen	*By passing oxygen*
Hydrochloric	4	150	8600
Sulfuric	6	22	920
Citric	50	29	170
Acetic	6	8	143

The corrosion of copper is higher in HCl than in H_2SO_4 because of formation of complex ($CuCl^-_2$). Oxidizing acids (HNO_3 and chromic acid), even dilute, act strongly on copper and copper alloys. Copper is quite stable in water and in solutions of neutral salts, but it considerably less so in the presence of air and oxidizers. Copper is stable in alkaline solutions and is highly resistant to solutions of many organic acids in the presence little oxygen.

In atmospheric environments, copper is highly stable, forming protective surface layers of basic copper carbonates [$CuCO_3.Cu(OH)_2$]. In marine atmospheres the corrosion products, also, contain basic copper chlorides. The presence of SO_2 in the air accelerate corrosion of copper. At high rate of flow of the corrosive medium (sea water), corrosion of copper is enhanced considerably.

1.2. Nature of the protective film on copper:

Copper and its alloys are unique in that their superior performance is associated with two factors. The first is that in accordance with the electromotive (or galvanic) series, they display noble potentials. Second, they form cuprous oxide (Cu_2O) as a corrosion product film that is responsible for their protection. This Cu_2O film is adherent and follows parabolic growth kinetic. Cuprous oxide is a p-type semiconductor formed by the following electrochemical processes:

$$4Cu + 2H_2O \longrightarrow 2Cu_2O + 4H^+ + 4e^- \qquad (1)$$

(anodic reaction)

and

$$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH)^- \qquad (2)$$

(cathodic reaction)

with the net reaction:

$$4Cu + O_2 \longrightarrow 2Cu_2O \qquad (3)$$