Chapter I

Introduction

Chapter I

Introduction

1.1-Prelimenary Consideration

Corrosion can be defined in many ways; the most preferred in literature (1) is the loss of useful properties of a material as a result of chemical or electrochemical reaction with environment. Corrosion is a heterogeneous reaction, which is often diffusion controlled. There are three necessary conditions, which must be met simultaneously to proceed the reaction electrochemically. There must be a potential difference, mechanisms for charge transfer between electronic and electrolytic conductors existing, and continuous path, which must be available.

A corrosion cell consists of anode, cathode and electrolyte for electrical connection. The absence of one parameter prevents corrosion to occur. The most common types of corrosion are galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, and stress corrosion cracking. There are numerous methods for measuring the corrosion rates and comparing the efficiency of the inhibition by additives. These include weight loss, hydrogen evolution, thermometric (2), electrode potential measurements (3), construction of electro-capillary curves (4), depression of polarographic maxima (5), determination of electrode reaction parameters (6), linear polarization measurements (7), and improved electrochemical methods including electrode impedance technique and cyclic voltammetry. However, the work in the present thesis is concerned with corrosion inhibitors for carbon steel applying the weight loss and polarization measurements. An inhibitor is a chemical substance which, when added in small concentration to an environment, effectively checks, decreases, or even prevents the reaction of the metal with the environment.

Inhibitors fall into several classes (8), which include passivators, precipitators, vapour phase, cathodic, anodic, nautralizing and adsorbents inhibitors.

1.2- Electrochemical Nature of Steel Corrosion

In iron or steel corrosion, electrochemical reactions may take place as follow at the anodic area :

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (1)$$

This reaction is rapid in most media, as shown by the lack of pronounced polarization when iron is made anode employing an external current. When iron corrodes, the rate is usually controlled by the cathodic reaction, which in general is much slower (cathodic control). In the deaerated solutions, the cathodic reaction is :

$$H^{+} + e^{-} \rightarrow {}^{1}/_{2}\, H_2 \qquad (2)$$

This reaction proceeds rapidly in acids, but slowly in alkaline or neutral aqueous media. The rate of hydrogen evolution at specific pH depends on the presence or absence of low hydrogen over potential and impurities in the metal or pure iron. The metal surface itself is provided with sites of hydrogen evolution, hence high purity iron continues to corrode in acids but at a measurable lower rate than does the commercial iron.

The cathodic reaction can be accelerated by dissolved oxygen in accordance with the following reactions (a process called depolarization) (9) :

$$2H^+ + {}^1\!/_2\, O_2 + 2e^- \rightarrow H_2O \qquad (3)$$

$$H_2O + {}^1\!/_2\, O_2 + 2e^- \rightarrow 2OH^- \qquad (4)$$

Although the overall anodic and cathodic reactions are those given in equations (1- 4), it is usually considered that the equations take place in a series of steps, one of which is the rate –determining step (RDS). The most widely accepted anodic scheme is that proposed by Kelly (10) and is practically applicable in acid solutions.

The two main cathodic reactions involved in the process are the reduction of H^+ to H_2 and the reduction of dissolved O_2 to OH^-.

The following scheme had been postulated:

1.2-(i) Hydrogen Ion Reduction:

$$H^+_{aq} + e^- \rightarrow H_{ads} \qquad (5)$$

$$H_2O + e^- \rightarrow H_{ads} + OH^-_{aq} \qquad (6)$$

$$H_{ads} + H_{ads} \rightarrow H_2 \qquad (7)$$

$$H^+_{aq} + H_{ads} + e^- \rightarrow H_2 \qquad (8)$$

$$H_2O + H_{ads} + e^- \rightarrow H_2 + OH^- \qquad (9)$$

At low pH reactions (5) and (8) will predominant over (7) and (9). The rate-determining step depends in part on the catalytic properties of the surface. This is particularly true for the recombination reactions (7) and (8) or (9). In some cases the recombination reactions is more difficult than dissolution of atomic hydrogen into the metal and the following alternative reaction becomes the predominant one.

$$H_{ads} \rightarrow H_{metal} \qquad (10)$$

If catalytic sites for hydrogen atom recombination exist within the metal, such as inclusions, then H_2 gas is formed in the metal and blistering and rupture can occur.

1.2-(ii) Oxygen Reduction

$$O_2 + e^- \rightarrow O_2^-{}_{ads} \qquad (11)$$

$$O_2^-{}_{ads} + H^+ \rightarrow HO_{2ads} \qquad (12)$$

$$HO_{2ads} + e^- \rightarrow HO_2^- \qquad (13)$$

$$HO_2^- + H^+ \rightarrow H_2O_{2aq} \qquad (14)$$

$$H_2O_{2aq} + e^- \rightarrow OH^- + OH \qquad (15)$$

$$OH + e^- \rightarrow OH^- \qquad (16)$$

$$2OH^- + 2H^+ \rightarrow 2H_2O \qquad (17)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (18)$$

Or

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (19)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad (20)$$

These reactions are all quite rapid in comparison to the hydrogen evolution reaction and hence the oxygen is a better cathodic depolarizer than hydrogen ion.

1.3- Forms of Corrosion

Almost all corrosion problems and failures encountered in service can be associated with one or more of the eight basic forms of corrosion:- general corrosion, galvanic corrosion, concentration cell (crevice) corrosion, pitting corrosion, intergranular corrosion, stress corrosion cracking, dealloying and erosion corrosion.

1.3.1- General Corrosion.

With general corrosion (sometimes called uniform corrosion), anodic dissolution is uniformly distributed over the entire metallic surface. The corrosion rate is nearly constant at all locations. Microscopic anodes and cathodes are continuously changing their electrochemical behavior from anode to cathode cells for a uniform attack. The general corrosion rates for metals in a wide variety of environments are known, and common practice is to select materials with rates that are acceptable for the application.

1.3.2- Galvanic Corrosion.

(i) Galvanic (dissimilar metals) corrosion occurs when two electrochemically dissimilar metals are metallically connected and exposed to environment. The less noble metal (anode) suffers accelerated attack and the more noble metal (cathode) is cathodically protected by the galvanic current. The tendency of a metal to corrode in a galvanic cell is determined by its position in the " galvanic series " of metals and alloys and listed in Table (1.1).