

in many instances to provide for an expected service life. There are three groups or classifications for acceptable corrosion rates depending on the applications as follow ⁽⁵⁾:

- < 0.005 ipy (< 5 mpy) good corrosion resistance.
- 0.005 to 0.05 ipy (5 to 50 mpy) piping, valve bodies, vessels ...etc.
- > 0.05 ipy (> 50 mpy) not considered for use in the application.

1.4.1.2 Localized corrosion.

It is the type of corrosion covers only a fraction of the total surface area such as pitting and crevice corrosion.

(I) Pitting corrosion.

It is one of the most destructive and insidious forms ^(6, 7), as the attack is extremely localized resulting holes in metals and causing the equipment failure. The term pitting factor is used to express the ratio of the depth of the deepest pit to the average penetration calculated from weight loss. Pitting is generally associated with halide ions and hydrochlorides. Stainless steel in aqueous solutions containing chlorides will be subjected to pitting corrosion. A clean, smooth metal surface will be more resistant to this type of attack. Also, the addition of inhibitors to the solution will occasionally reduce or prevent pitting.

(II) Crevice corrosion.

It is the type of localized corrosion in which the faying surface become depleted of oxygen which adjacent areas are cathodic because of ready access of depolarizing species ⁽⁷⁾. The most important examples of this type are fibrous gaskets, alloys which depend on oxide films for corrosion resistance and also stainless steels.

1.4.1.3 Galvanic corrosion.

It is a bimetallic corrosion ⁽⁷⁾. When one metal is electrically coupled to another metal or nonmetal in an electrically conducting environment, the more anodic member of the galvanic couple corrodes more rapidly than the other cathodic member, which is protected cathodically. Insulating dissimilar metals from each other can prevent this type of corrosion.

1.4.1.4 Velocity-related corrosion.

Erosion and cavitation corrosions are the two forms of velocity-related phenomena ⁽⁷⁾. Fretting is also corrosion of this type which is caused between two rubbing metallic surfaces while simultaneously exposed to a corrosive environment.

(I) Erosion corrosion.

This type of corrosion occurs when the protective films are mechanically removed by the action of flowing fluids environment.

(II) Cavitation.

This type occurs when the conditions of the liquid flow can set up low-pressure areas between the metal and environment such as when liquid vaporizes and forms bubbles.

1.4.2 Corrosion recognized with the assistance of certain supplementary means of examination.

1.4.2.1 Intergranular corrosion.

It occurs when localized attack at and adjacent to grain boundaries with relatively little corrosion of the grain takes place by the impurities at the grain boundaries ^(7, 8) (enrichment or depletion). The example of this type is austenitic stainless steel (sensitization) and heat affected zones of its welds (HAZ) where the presence of carbon impurities (0.06 – 0.08%) at the grain boundaries of Cr (10%) leads to the formation of Cr_{23}C_6 .

1.4.2.2 Dealloying.

Dealloying is characterized by preferential dissolution of one component of one alloy, typically leaching of a weak pseudo-morph of the original item. This form of attack is observed most often in gray cast iron (Graphitic corrosion) and in yellow brasses (Dezincification).

(I) Graphitic corrosion.

Graphitic corrosion may occur on the outside of cast iron pipe in corrosive soils ^(7, 8) and may be localized because of the difference in soil chemistry. It tends to be more general in distribution when cast iron pipe is attacked internally by aggressive water.

(II) Dezincification.

It occurs in yellow brasses where the zinc rich phase is dissolved and leaves a weak porous deposit of the copper rich phase which has a distinct reddish color ⁽⁷⁾. It is called "layer type" when it is general in distribution and "plug type" when it is localized.

1.4.3 Corrosion identified through microscopic examinations.**1.4.3.1 Cracking.**

There are two major types of cracking corrosion, which they are corrosion fatigue and environmental cracking.

(I) Corrosion fatigue.

It occurs due to the synergistic effects of repeated stress combined with corrosion ⁽⁷⁾.

(II) Environmental cracking.

It is a spontaneous brittle fracture of a susceptible material under tensile stress in a specific environment over a period of time. The environmental cracking is classified to stress corrosion cracking (SCC) ⁽⁷⁾ hydrogen assisted cracking (HAC) ^(7,9) and liquid metal embrittlement (LME) ⁽⁹⁾.

1.4.3.2 High temperature corrosion.

This type of corrosion may be a surface phenomena or an internal effect within the structure of the metal or alloy ⁽⁹⁾. The surface phenomena include oxidation or sulphidation, with an accumulation of metallic corrosion products and dissolution as by halogen attack or molten salt effect. Internal effects are also encountered due to reaction within the matrix with environmental species, which have diffused into the metal structure.

1.4.3.3 Biological corrosion. ⁽⁵⁾

Corrosion of a metal can be caused by the metabolic activity of microorganisms either directly or indirectly. There are two types of microorganisms associated with this type of corrosion, which are aerobic and anaerobic. Aerobic types grow in an atmosphere contains oxygen, while anaerobic species grow in an environment devoid of atmospheric oxygen. The activity of these organisms may cause corrosion by:

- (a) Producing a corrosive environment.
- (b) Altering the resistance of the surface film.
- (c) Having an effect on the rate of anodic or cathodic reactions.
- (d) Creating electrolytic concentration cells on the metal surface.
- (e) Altering the environmental composition.

As example, sulphate reducing bacteria (anaerobic) easily reduces inorganic sulfates to sulfides such as calcium sulfide or hydrogen sulfide. When these compounds come into contact with iron (such as underground iron pipes), conversion of the iron to iron sulfide occurs. Since these bacteria thrive under such conditions, the reaction will continue until the pipe fails. The damage can be reduced by chlorination or the addition of certain bactericides.

1.5 Corrosion monitoring techniques.

1.5.1 Non-electrochemical techniques.

1.5.1.1 Thermometric method.

A simple, rapid and limited method for comparing the inhibition efficiency of different additional agents⁽¹⁰⁾. It originally developed for aluminum and its alloys. According to this test, a piece of the metal of specified area is dropped into a definite volume of a corrosive solution. The variation of the temperature of the system is followed as a function of time. After an initial period of almost constant temperature, it raises quickly to attain a maximum value, which approaches in some cases the boiling point of the solution. A reaction number, R.N., was defined by Mylius as:

$$R.N. = \frac{T_m - T_i}{t} \quad K/min. \quad (1.9)$$

where: T_m = maximum temperature in K.

T_i = initial temperature in K.

t = time in minutes from the start of the experimental to attain T_m .

The reaction number is proportional to the rate of the corrosion of the metal. The extent of corrosion inhibition by a certain concentration of a particular additive is evaluated from the percentage reduction in the reaction number.

$$\% \text{ Reduction in R.N.} = \frac{(R.N.)_{\text{free}} - (R.N.)_{\text{add}}}{(R.N.)_{\text{free}}} \times 100 \quad (1.10)$$

where, $(R.N.)_{free}$ = R.N. in the corrosive medium.
 $(R.N.)_{add.}$ = R.N. in the presence of additive.

1.5.1.2 Hydrogen evolution method.

Reactions in which gases are given off or taken up can be monitored by studying the change of gas amount over time. This method is also limited. The efficiency of a given inhibitor can be evaluated as the percentage reduction in reaction rate (K), so the percentage inhibition efficiency (%IE) can be calculated as follow:

$$\% IE = \frac{K_{free} - K_{add}}{K_{free}} \times 100 \quad (1.11)$$

where: K_{free} = specific reaction rate in the corrosive medium.

$K_{add.}$ = specific reaction rate in the inhibited solutions.

and specific reaction rate constants (K) are calculated from the relation, $V = K.t$, where, (V) is the volume of hydrogen evaluated in cm^3 and (t) is the time in minutes.

1.5.1.3 Loss in mass method.

Loss in mass measurements are comprehensive testes for laboratory and field ⁽¹¹⁻¹⁴⁾. They are useful for metals or alloys, which are not subjected to special types of attack and form, which the products of corrosion are easily removed.

To determine the inhibition efficiency of certain inhibitor using these measurements, the metal sample should be polished, degreased, weighed and then immersed in the corrosive medium with and without inhibitor for certain time intervals at fixed temperature. The weight losses are determined after removing corrosion products and then thoroughly wash the specimens by distilled water dry and weigh.

The efficiency of inhibition is calculated from the mass loss values using the following equation:

$$\% IE = \frac{M_{free} - M_{add}}{M_{free}} \times 100 \quad (1.12)$$

where, M_{free} = mass loss in the corrosive medium in $mg\ cm^{-2}$.

$M_{add.}$ = mass loss in the inhibited solutions in $mg\ cm^{-2}$.

Also, the corrosion rate is determined by the relationship:

$$\text{C. R. (mmpy)} = \frac{\text{wt. loss (mg)} \times 87.6}{\text{area (cm}^{-2}\text{)} \times \text{time (hrs)} \times d \text{ (gm.cm}^{-3}\text{)}} \times 100 \quad (1.13)$$

1.5.1.4 Electrical resistance method.

This method involves the measurements of the change in the resistance of corroded metal by the equation: ⁽¹¹⁻¹³⁾

$$R_{\text{metal}} = \frac{\rho \times L}{A} \quad (1.14)$$

where, R_{metal} = resistance of metal.

ρ = specific resistance.

A = area of cross section.

On corrosion, the area of specimen (A) is decreased. Hence the resistance (R) is increased. This means that the change in R value is correlated to corrosion rate (Kelvin or Wheatstone bridge).

1.5.2 Electrochemical techniques.

1.5.2.1 Open circuit potential method.

This method is used to measure the steady state potential (E_{ocp}), of the metal or alloy in the absence and in the presence of additives ⁽¹⁵⁾. In this method, the potential of the corroding material is measured against a reference electrode at different time intervals until a steady state is reached. The steady state potential represents an equilibrium state at which (I_{ox}) is equal (i_{red}).

1.5.2.2 Potentiodynamic polarization method.

(I) Tafel plots.

In this method, corrosion current can be determined from polarization curves by intercept method based on anodic and / or cathodic Tafel curves ⁽¹⁶⁾. The corrosion rate of the system involves the measurements of potential of the working electrode for various applied current densities.

The relation between (E) and $\log(i)$ gives polarization diagram (Tafel plot). The intercept of anodic and cathodic Tafel lines provides the corrosion current and Tafel slopes give anodic (b_a) and cathodic (b_c) Tafel constants.