CHAPTER - I

INTRODUCTION
1. GENERAL ASPECTS OF CORROSION AND ITS CONTROL THROUGH THE USE OF INHIBITORS

Corrosion [1] is defined as the destruction or deterioration of materials (metals) under the chemical or electrochemical action of the surrounding environments. It is now generally accepted that corrosion is a complete or a partial reversion from the metastable condition of the metal to stable conditions of the mineral accompanied by the reduction in the free energy of the system.

1.1 HISTORICAL BACKGROUND

Trends in corrosion research changed rapidly over the years. In the fifties, polarization studies and their applications had been the topic of interest [12-13]. In the seventies corrosion research was concentrated on the mechanistic studies on metal dissolution, localized corrosion and high temperature corrosion [14-20]. In recent years corrosion research has been diversified into several newer fields. Optical techniques have revolutionized the field. Surface analytical techniques play a major role since they give more insight into the understanding of the nature and influence of surface oxides on the corrosion of metals and alloys. These techniques are helpful to characterize the thickness, the structure and the composition of films. Computers [21,22] and microprocessors [23] find application in analyzing the corrosion data.

The ultimate objective of all these investigations is to minimize corrosion failures based on the thorough understanding of the process of corrosion.

1.2 CLASSIFICATION OF CORROSION

Metallic corrosion can be broadly classified as (i) dry or chemical corrosion (ii) wet or electrochemical corrosion.

The reaction of metals with ‘dry’ air or oxygen is considered as dry or chemical corrosion. High temperature oxidation of metals and tarnishing of metals like Cu, Ag, etc., fall into this category.

Wet or electrochemical corrosion occurs in the presence of electrolytic solutions. The reaction is considered to take place at the metal-
solution interface due to the heterogeneity in the metal surface that creates local cathodic and anodic sites on the metal surface.

1.3 FACTORS INFLUENCING CORROSION

The important factors that may influence the corrosion process are

(i) Nature of the metal
(ii) Nature of the environment
(iii) Electrode potential
(iv) Temperature
(v) Aeration
(vi) Nature of the corrosion products formed
(vii) Agitation
(viii) Concentration of various ions in solution
(ix) pH of the solution
(x) Hydrogen over potential, and
(xi) Amount of dissolved oxygen

1.4 FORMS OF CORROSION PROCESSES

Corrosion manifests in different forms. It is desirable to know the form of corrosion, as it will help to identify the cause of corrosion and in the selection of most effective method of preventing it. Various forms of corrosion [24-26] are: (i) uniform corrosion. (ii) Pitting or localized corrosion (iii) Galvanic corrosion (iv) Crevice corrosion, (v) Stress corrosion cracking (SCC), (vi) Erosion – corrosion, (vii) Fretting corrosion, (viii) Filiform corrosion and (ix) selective corrosion like dezincification (or dealloying / parting) and graphitization etc.
1.5 THEORIES OF CORROSION

Corrosion theories may be classified into

i. Homogeneous theory

ii. Heterogeneous theory

1.5.1 Homogeneous theory

The instability of metals due to the charge transfer at the metal interface rather than the heterogeneity causes corrosion. Dissolution of the metal and electronation at the metal interface as emphasized by Wagner and Traud [9] is responsible for corrosion based on the above theory.

The potential difference across the interface destabilizes the metal due to charge transfer reactions where metal dissolution potential should be more negative and electronation potential be more positive than their respective equilibrium potentials.

1.5.2 Heterogeneous theory

The theory proposes that the presence of impurity on the surface of anodic and cathodic areas to destabilize the metal. This is due to the fact that the heterogeneities tend to fix the de–electronation and electronation reactions to stable sink and source areas.

1.6 METHODS OF CORROSION CONTROL

Both economic and scientific considerations are involved in combating corrosion. A greater knowledge of the electrochemical aspects of corrosion science has paved the way for the development of newer techniques for combating corrosion.
There are various methods for preventing corrosion. The general classification may be given as

**Corrosion Control Method**

- Modification of the Metal
  - By alloying (or) surface modification
- Modification of the Environment
  - By the use of inhibitors
- Change of the metal environment potential
  - Cathodic and anodic protection

The present work investigates the use of inhibitors for reducing the rate of alkaline corrosion of aluminium, which is monitored by various electrochemical and non-electrochemical techniques.

### 1.7 Expressions for Corrosion Rate

Corrosion rates have been expressed in various ways in the literature. The following are the major systems of corrosion units.

- (i) **ipy** = inches per year
- (ii) **mpy** = mils per year
  
  \[ 1 \text{ mil} = 0.001 \text{ inch} = 25.4 \mu\text{m} = 0.0254 \text{ mm} \]
- (iii) **ipmo** = inches per month
- (iv) **mdd** = milligrams per square decimeter per day
Usually corrosion rates are expressed in any one of the two basic units namely mpy or mdd. The corrosion rates of mpy and mdd scales can be directly calculated from the following expressions.

(i) \( \text{mpy} = \frac{82.75 \times w}{a \times t \times d} \)  
(ii) \( \text{mdd} = \frac{53.5 \times w}{a \times t} \)  

\[ (1.1) \]

Where

\( w \) = is the weight loss in grams  
\( a \) = area of the specimen in square centimeters  
\( t \) = time in hours  
\( d \) = density of the specimen in g cm\(^{-3}\)

All the other expressions can be calculated from these two basic units for corrosion rates, using the conversion table

\( \text{mpy} = 1000 \times \text{ipy} = 12100 \times \text{ipmo} = \frac{1.44}{d} \times \text{mdd} \)  

\[ (1.2) \]

1.8 INHIBITION OF CORROSION OF METALS

The definition of an inhibitor favoured by NACE is “A substance which retards corrosion when added to an environment in small concentrations”. Inhibitors may also be defined on electrochemical basis as “substances that reduce the rates of either partial anodic oxidation / or cathodic reduction reaction or both”.

One of the most extensively studied topics in the field of corrosion is inhibition. Putilova et al. [27] have reviewed the metallic corrosion inhibitors. Reviews on organic inhibitors [28-30] and organic sulphur compounds [31] have been published. Several books have been published on
this subject [32-35]. The University of Ferrara, Italy conducts a symposium on corrosion inhibition once in five years [36]. All the International Seminars on corrosion discuss the developments and applications of corrosion inhibitors [37-39]. Trabanelli and Carassiti [29] and Sanyal [30] have reviewed this phenomenon along with Weber [40]. Various books on corrosion, review the subject in a precise manner [41-43]. These facts clearly show that the information on this subject is extensively available and also stress the importance of the topic.

1.9 CLASSIFICATION OF INHIBITORS

Inhibitors are classified as acid, neutral, alkaline and vapour phase inhibitors depending upon the environment. Depending on the mechanism of inhibition they are also classified as cathodic, anodic and mixed type inhibitors [46].

1.9.1 Anodic Inhibitors

Of the various classes of inhibitors the compounds orthophosphates, silicates etc are most widely used in the context of increasing the anode polarization and moving the corrosion potential in positive direction. These are called anodic inhibitors. The undesirable property of such inhibitors when used in very low concentrations cause pitting and are extremely dangerous for application. When not used in proper dosage level.

1.9.2 Cathodic Inhibitors

They cause selective polarization of the cathodic sites that results in the shift in potential in the negative direction.

Eg – action of As$^{3+}$ and Sb$^{3+}$ on dissolution of iron in acids.
1.9.3 Mixed Inhibitors

Mixed inhibitors retard both the anodic and cathodic processes almost to equal extent and hence very safe to apply. With these inhibitors the corrosion potential may not be shifted significantly in any one direction. In the case of mixture of inhibitors synergistic [44,45] and antagonistic [28] behaviours were reported.

1.10 ANOTHER APPROACH TO THE STUDY OF INHIBITORS

In one of the approaches [47] which is based on the mechanism of inhibitive action, the corrosion inhibitors have been divided into four major categories

(i) Barrier layer formers
(ii) Neutralizers
(iii) Scavengers and
(iv) Miscellaneous

1.10.1 Barrier layer formers

This material form barrier layers on the corroding metal surface and reduces the corrosion rate. This type forms the largest category of corrosion inhibitors. Barrier layer formers have been further classified into oxidizers, adsorbed layer formers and conversion layer formers. In general these inhibitors are effective in reducing both the anodic and cathodic reaction rates except for the oxidizing inhibitors which shift the corrosion potential of the metal to more positive values at which a stable oxide or hydroxide is formed and protects the metal surface.
1.10.2 Neutralizers

These inhibitors remove the hydrogen ion from the corrosive environments thereby reducing the corrosivity of the environment and hence the concentration of the cathodic reactant. These inhibitors are used in the treatment of boiler waters, oil field applications and also in ethylene glycol cooling systems.

1.10.3 Scavengers

These are similar to neutralizers but used to remove corrosive species other than hydrogen ions. Typical example is hydrazine in boiler systems that remove traces of oxygen, which is a cathodic reactant.

1.10.4 Miscellaneous

These inhibitors include materials such as scale inhibitors and biological growth inhibitors, which reduce the corrosion by interfering with other processes.

1.11 THEORIES OF INHIBITION

The inhibitive action has been explained by the theory of adsorption and / or the film formation.

1.11.1 Adsorption theory

Organic inhibitors, which presumably are not capable of oxidizing or precipitating the metal ion, must have the ability to adsorb and impede either the cathodic or anodic or both the reactions. Organic inhibitors inhibit corrosion by adsorption at metal / solution interface. Ross and Jones [48,49] demonstrated that the adsorption of the inhibitors on iron is regular and
uniform within 5-10 minutes using radioactive technique employing thioureas labeled with $S^{35}$. Most of the heterocyclic compounds containing nitrogen are believed to be cathodic inhibitors. But it has been shown by Hoar [50] that in some cases anodic inhibition is also observed.

The mode of adsorption depends on

(i) The nature of metal surface
(ii) The chemical structure of the molecule
(iii) The electrochemical potential at the metal /solution interface

The following are the different types of adsorption associated with organic inhibitors.

(i) Electrostatic adsorption or Electrosorption
(ii) Chemisorption and $\pi$-orbital adsorption
(iii) Physical or Vander Waals types of adsorption

1.11.2 Electrosorption

In electrosorption, the coulombic electrical forces that stretch out from the metal are much longer in range, than the chemical forces which affect the molecules in chemisorption.

1.11.3 $\pi$-orbital adsorption

In this type, the adsorption may result from $\pi$-orbital interaction with the metal. Organic compounds with double and triple bond, and those containing aromatic nucleus interact with metal by their $\pi$-bond orbital.
1.11.4 Vander Waals adsorption

The adsorbed molecules are held by weak Vander Waals forces and physically adsorbed molecules on solids form multi layers. As the forces operating are weak Vander Waals type, the adsorbed molecules may easily be removed or desorbed from the surface.

1.11.5 Film theory

In order to explain the inhibitive action of the inhibitors in neutral and alkaline media, Evans [51] has put forward the film formation theory. Evans attributed the inhibition to the formation of an insoluble film. Hausler [52] and Putilova et al. [28] have reported appreciable protection of metals by inhibitors due to the formation of a layer of insoluble or slightly soluble corrosion products on the metal surface. The formation of insoluble or slightly soluble complex compounds of the metal sulphides with compounds like thio-ethers and thio-alcohols as protective thin film on the metal surface have been quoted as examples in support of the film theory.

1.12 ADSORPTION Isotherm

An adsorption isotherm is the mathematical expression, which relates the bulk concentration of an adsorbing species to its surface concentration at constant temperature. Various adsorption isotherms have been formulated. A list of isotherms and their corresponding equations are given in the table 1.1. A common procedure is to convert an isotherm into a linear form and plot the experimental data accordingly. The data can be fitted to any one of the adsorption isotherms and can be made into suitable plot and the free energy of adsorption of the organic inhibitor can be obtained.
### Table 1.1

<table>
<thead>
<tr>
<th>No</th>
<th>Isotherm</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Langmuir</td>
<td>$\beta c = \theta / (1-\theta)$</td>
</tr>
<tr>
<td>2.</td>
<td>Freundlich</td>
<td>$\beta c = \theta \quad (0 &lt; n &lt; 1)$</td>
</tr>
<tr>
<td>3.</td>
<td>Frumkin</td>
<td>$\beta c = \theta / (1-\theta) \exp (-2a \theta)$</td>
</tr>
<tr>
<td>4.</td>
<td>Temkin</td>
<td>$\beta c = [\exp (a \theta) - 1] / [1 - \exp (-a (1- \theta))]$</td>
</tr>
<tr>
<td>5.</td>
<td>Parsons</td>
<td>$\beta c = \theta / (1-\theta) \exp (2 - \theta) / (1 - \theta)^2 \exp (-2a\theta)$</td>
</tr>
<tr>
<td>6.</td>
<td>Bockris – Devanathan and Muller (BDM)</td>
<td>$\log c \pm \log \theta / (1-\theta) = c + \beta \theta^{3/2}$</td>
</tr>
</tbody>
</table>

Note: $\beta \equiv e^{-\Delta G_{ads}} / RT$, $a = \text{Interaction parameter}$

Most of the organic inhibitors obey Langmuir's or Temkin's adsorption isotherm.

An inhibitor is found to obey Langmuir isotherm if a plot of $\log \theta / (1-\theta)$ vs $\log c$ is linear. Similarly for Temkin's a plot of $\theta$ vs $\log c$, for BDM a plot of $(\log c - \log \theta / (1-\theta)$ vs $\theta^{3/2}$ and for the Frumkin's a plot of $\log \theta / (1-\theta)$ c vs $\theta$ will be linear.
1.13. CORROSION MONITORING TECHNIQUES

Techniques employed in studying metallic corrosion and its inhibition

A brief review of A.C., D.C. and non-electrochemical techniques which can be used for determining corrosion rates, has been published by Lorenz et al. [53 – 56] and Epelboin et al. [57]. The advantages and disadvantages of these techniques have been critically analysed in these reviews.

Michel Duprat [58] and Heitz et al. [59] have compiled the various electrochemical corrosion-testing methods.

1.14 TECHNIQUES FOR STUDYING CORROSION

1.14.1. NON-ELECTROCHEMICAL METHODS

1.14.1.1 Coupon method

The corrosion rate is evaluated by measuring the change in the weight of coupon after exposing the metal specimen of known area to the particular environment for a specific period. This method yields the average rate and is inherently inaccurate for measuring very low corrosion rates. Methods of surface preparation and cleaning of corroded specimens are described by Champion [60].

1.14.1.2 Solution analysis

In this method [61] chemical or physical techniques are used to identify and estimate the concentration of ions of the metal or metals under examination that is dissolved in the test environment.
1.14.1.3 Gasometric method

In this method [62] a definite correlation between the cathodic reaction rate and the anodic dissolution rate can be established provided the gas evolution is quantified by definite stoichiometry.

1.14.2. ELECTROCHEMICAL METHODS

1.14.2.1 Electrical resistance method

An increase in the electrical resistance is a measure of corrosion [63]. A decrease in the cross section due to corrosion increases the electrical resistance. The resistance of the exposed element is measured by Kelvin’s bridge along with another element, which is protected against corrosion. Instruments have been developed to measure these resistance ratios, which are calibrated in mpy. The major advantage of this method is its ability to measure corrosion rates in the liquid and vapour phases and in aqueous and non-aqueous media. This method is used for continuous monitoring in chemical processing industries.

1.14.2.2 Tafel extrapolation method

This method [64] is also described as Tafel Plot method or Evan’s diagram method or logarithmic polarization method. Actually the measurement of corrosion rate of the system involves the measurement of potentials of the electrode for various applied current densities. A plot of $E$ vs log $I$ give a figure known as polarization diagram (fig. 1.1.). The intercept of anodic and cathodic Tafel lines provides the corrosion current and the slopes of the above tangents give $b_a$ and $b_c$. In actual practice, polarization curves are obtained from galvanostatic / potentiostatic or potentiodynamic methods.
1.14.2.3 Polarization resistance method

Stern and Geary [65] have shown that there is a linear relationship between current and potential when $\eta < 20$ mV and on measuring $[d\eta / di]$ $\eta \rightarrow o$ the corrosion current can be obtained from

$$i_{corr} = \frac{b_a \times b_c}{2.3(b_a + b_c) R_p}$$
The above relationship is valid only for activation-controlled reactions. Rajagopalan and Rangarajan [66] have derived the relationship with metals undergoing corrosion under different condition.

The simultaneous determination of Tafel slopes and corrosion current at the corrosion potential have been suggested by many authors. Barnartt [67], Reeve and Bech-Nielsen [68], Oldham and Mansfeld [69], Periasamy and Krishnaswamy [70] have made some improvements in this method. Mansfeld [71,72] has developed a computer programme (CORFIT) for the quantitative determination of \(i_{\text{corr}}\) which requires simultaneous determination of both \(R_p\) and \(B\). Various applications and the developments of this technique have been reviewed by Lorenz and Mansfeld [54].

### 1.14.2.4 Coulostatic method

This method [73,74] is suited especially for the measurement of corrosion rates of metals in high resistive media. The polarization resistance \((R_p)\) is measured from the \(\eta\)-t transient of the electrode on discharging a charged capacitor \((C)\) through the cell. The electrode potential decay is

\[
\eta_t = \eta_0 \exp \left( -t / C_{dl} R_p \right)
\]

where \(\eta_t\) = Overpotential at any time “t”

\(\eta_0\) = Overpotential immediately after charging the double layer of the electrode.

\(C_{dl}\) = Differential capacity of the double layer.

The plot of \(\log \eta_t\) vs \(t\) is a straight line and the slope gives the \(1 / 2.3 C_{dl} R_p\) and the intercept is \(\eta_0\).
1.14.2.5 A.C. Impedance measurements

The electrochemical impedance measurements form an appropriate method for corrosion studies, particularly for corrosion rate determinations [75-79], mechanistic studies [80-82], passivating systems [83-85] and for investigation under inhibited conditions [86-91]. The theoretical analysis of A.C. impedance measurements has been proposed by Warburg [92], to explain the frequency dispersion of the electrode-electrolyte interface and impedance in terms of mass transport (diffusion controlled) process. A review of the application of these techniques in corrosion studies has been published by MacDonald et al. [97]. The use of A.C. impedance technique to various cases has been reviewed by Gabrielli [93].

The schematic representations of the interface impedance are shown in Fig. 1.2.

Solution resistance is represented by $R_s$, charge transfer resistance is given by $R_{ct}$ or $R_t$ and the double layer capacitance is represented by $C_{dl}$.

Thus, the cell impedance "Z" consists of real ($Z'$) and imaginary ($Z''$) parts. A plot of $Z'$ vs $Z''$ for various frequencies is a semicircle. At high frequency, $Z'$ corresponds to $R_s$ and at low frequency $Z'$ corresponds to ($R_s + R_t$) and the difference between the two values gives $R_t$. 

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\[ R_s = \text{Solution resistance} \]
\[ C_{dl} = \text{Electrochemical double layer capacitance} \]
\[ R_t = \text{Charge transfer resistance} \]

**Fig. 1.2 Schematic representation of interface impedance**

The double layer capacitance \( (C_{dl}) \) can be calculated from the frequency \( \omega \) at \( Z'' \) maximum.
The main disadvantage of this method is that only \( R_t \) can be determined directly while the Tafel parameters have to be obtained by other methods.

### 1.14.2.6 Faradaic rectification method [99]

In a corrosion process, the anodic and cathodic reactions are unsymmetric (i.e. \( b_a \neq b_c \)) [94-96]. When a sinusoidal voltage is applied, a flow of direct component of current results. On measuring the rectified current and voltage, \( i_{\text{corr}} \) is obtained from the relationship

\[
i_{\text{corr}} = \frac{0.754 \ i_{\text{dc}} (E_2 - E_{\text{corr}})}{E_p^2 (b_a^{-2} - b_c^{-2}) (E_2 - E_1)}\]

Where

\( i_{\text{dc}} = \) Rectified current

\( E_1 = \) Mean potential of working electrode corresponding to the rectified current \( i_{\text{dc}} \)

\( E_2 = \) Mean potential of the working electrode when \( i_{\text{dc}} = 0 \)

\( E_p = \) Peak value of a.c component of potential

This method has been tested for corrosion reactions in which the corrosion potential is near to the equilibrium potential of metal / metal ion reaction.
1.14.2.7 Faradaic distortion method [98]

On superimposing a sinusoidal alternating voltage, i.e. $E_m \sin \omega t$ to the electrode at the corrosion potential, harmonic current components are produced due to the non-linear relationship between the current and the potential. Measurements of fundamental ($i_1$), second harmonic ($i_2$) and third harmonic ($i_3$) current components are made for getting $i_{\text{corr}}$, $b_a$ and $b_c$ from the following relationships

$$i_{\text{corr}} = \frac{i_1^2}{\sqrt{4s \cdot \left(1 + \frac{i_1}{i_{\text{corr}}} \cdot \frac{i_1^2}{2} \right)}}$$  \hspace{1cm} 1.7

$$\frac{1}{b_a} = \frac{1}{4.6 E_m} \left[ \frac{i_1}{i_{\text{corr}}} + \frac{4i_2}{i_1} \right]$$  \hspace{1cm} 1.8

$$\frac{1}{b_c} = \frac{1}{4.6 E_m} \left[ \frac{i_1}{i_{\text{corr}}} - \frac{4i_2}{i_1} \right]$$  \hspace{1cm} 1.9

The advantage of this method is that the measurement of corrosion current is possible at the corrosion potential without the use of anodic and cathodic Tafel slopes.
1.15 OTHER TECHNIQUES FOR STUDYING INHIBITORS

1.15.1. Hydrogen permeation measurements:
A number of methods are available for the measurement of permeation of hydrogen through steel membrane. They are

1. Electrode potential measurements method [100]
2. Pressure measurements method [101]
3. Methods based on reducing action [102] and by
4. Hydrogen permeation current measurements [103,104]

Among these methods, the last method is very useful and it is a versatile electrochemical method. In this method one side of a thin metal membrane is cathodically polarized and the permeation rate is determined from the ionization current on the reverse side of the membrane. The advantages of this method are given below.

(i) This method is 10-100 times more sensitive than the other methods employed and hydrogen permeation rate of about $10^{12}$ g. atom. cm$^{-2}$ sec$^{-1}$ can be measured.
(ii) This method is very useful for the determination of diffusion coefficient for hydrogen in metals [105].
(iii) It is useful as a basis to standardize the hydrogen embrittlement characteristics of different plating baths [106].
(iv) It is also helpful to assess the extent of hydrogen entry during any pickling operations and gives an idea of the
corrosivity of the specimen in the medium. Further, inhibitors can be screened easily.

(v) A study of hydrogen pick up during cathodic protection can be assessed [107].

1.15.2. Radio-Tracer Technique

A better knowledge of inhibition phenomena can be obtained by Ratio-Tracer technique [108] with labeled inhibitor. It is possible to detect traces of substances adsorbed even under extreme dilution. This method can be used for determining the adsorption of stably chemisorbed substances.

1.15.3. Spectroscopic methods

The results of I.R. and U.V. spectra of the adsorbed products are very useful in the interpretation of inhibition phenomena. Suetaka [109] developed a technique to determine directly the amount of inhibitor adsorbed by reflection spectra recorded on metallic electrodes. Mass spectrometry and Mossbauer spectra [110] are the other techniques employed in the study of corrosion inhibition. X-ray, electron diffraction and ellipsometric techniques [111] have been employed to study the films formed on the metal surface by the inhibitors.
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