# CHAPTER-1

INTRODUCTION

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a material that results from a chemical or electrochemical interaction with its environment [Pfeifer (2009)]. In nature, most of the metals are obtained from their ores by the expenditure of huge amount of energy during melting and refining processes. Metals store this energy, and release them during the corrosion process after reacting with the environment. Corrosion products have weak mechanical strength. The whole process of corrosion is shown below (Figure 1.1):
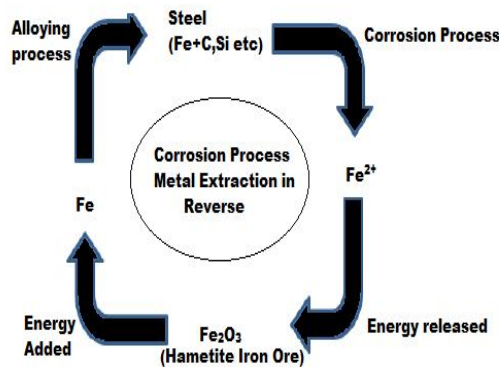
Figure: 1.1: Corrosion cycle

1.1. Economic losses

In 2016, NACE (National Association of Chemical Engineers) estimated that the annual global cost of corrosion is approximately $2.5 trillion. Economic losses can be divided into direct and indirect losses.
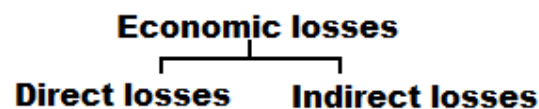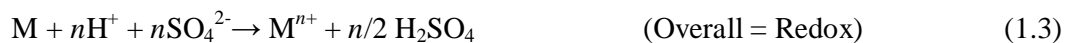
Direct losses:

- Inability to use desirable materials.

- Over-design to allow for corrosion.

- The cost of repair or replacement of the corroded component.

- Cost of anti-corrosive painting or other protection methods**.**

Indirect losses:

- Product contamination.

- Loss of valuable product from a container that is corroded.

- Damage of equipment adjacent to that in which corrosion failure occurs.

- Loss of product.

- Safety, e.g., sudden failure of equipment may cause fire, explosion or release of toxic products.

1.2. General idea of Corrosion

Corrosion is a chemical or electrochemical oxidation process which involves anodic and cathodic reactions. The oxidation of a metal "M" immersed in sulfuric acid (H_2SO_4) solution occurs at anode and reduction occurs at cathode, and these reactions are shown below:

$$M \rightarrow M^{n+} + ne^- \qquad\qquad \text{(Anodic = Oxidation)} \qquad (1.1)$$

$$nH^+ + nSO_4^{2-} + ne^- \rightarrow n/2\ H_2SO_4 \qquad\qquad \text{(Cathodic = Reduction)} \qquad (1.2)$$

$$M + nH^+ + nSO_4^{2-} \rightarrow M^{n+} + n/2\ H_2SO_4 \qquad\qquad \text{(Overall = Redox)} \qquad (1.3)$$

where, M = Metal , H^+ = Hydrogen ion , n = Valence or Oxidation state, M^{n+} = Metal cation, SO_4^{2-} = Sulfate anion

The above equations contain an anodic reaction, which is known as oxidation, where the metal losses electrons and a cathodic reaction, which is equivalent to reduction, where

acceptance or gain of electrons occurs. The combination of anodic and cathodic reactions is known as redox reaction, which is also termed as overall reaction.

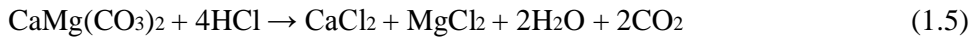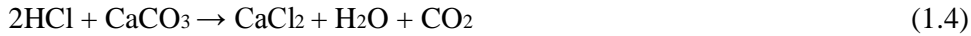## 1.3. Corrosion problems in oil/petroleum industry

In oil/petroleum industry, corrosion of steel and other metal is a common problem such as in gas and oil well equipment, refining operations, pipeline and storage equipment [Houghton and Westmark (1984), Stanford and Campbell (1976), Sharp and Yarborough (1982)]. Damage due to corrosion in petroleum industry occurs mostly due to chemical factors e.g. high mineralization of water, high contents of corrosive gases (CO_2, H_2S, etc.) and the presence of atmospheric oxygen in pipelines; physical factors e.g. flow hydrodynamics, temperature, pressure; and metallurgical factors e. g. characteristics of the metal [Prabha *et al.* (2014)]. In sweet oil wells, pipelines are mostly corroded due to H_2CO_3, which is formed by the reaction between H_2O and CO_2. Sour wells represent a more corrosive environment due to high sulfur content and severely corrode the casing in the upper part of the well. In refineries corrosion of metal occurs due to the presence of carbon dioxide, saltwater, hydrogen sulphide, nitrogen, oxygen, sulphuric acid, ammonia, hydrochloric acid, caustic soda, mercaptan, and naphthenic acid.

1.4. Acidizing treatment in oil wells

Acidizing of oil well is a stimulation technique for increasing oil productivity by enlarging the microscopic flow channels. The acid mixture is helpful in dissolving certain components of the drilling mud which blocks the inflow of oil in the production zone. The treatment fluid typically comprises hydrochloric acid and acidic additives depending upon the underground nature of the oil wells. Acid treatments are commonly designed to include a range of acid types or blends, such as acetic acid, formic acid, hydrochloric acid, hydrofluoric acid and fluroboric acid [Finšgar and Jackson (2014)]. Applications for the various acid types or blends are based on reaction characteristics of the prepared

treatment fluid. Hydrochloric acid is commonly used to remove plugging in the bore well and stimulates production because it is cheap and the ferrous chloride formed on the surface is soluble in water [Jayaperumal *et al.* (2000)].

Generally in the petroleum industry 15% hydrochloric acid is used for the acidizing treatment because it leaves no insoluble reaction products [Rajeev *et al.* (2012)]. In some cases, hydrofluoric acid mixed with other acids is used to dissolve clays and other silicate materials. The acid is pumped inside the well through steel tubing, which enters into the drainage channels tributary and dissolves the exposed limestone surfaces of the rocks. The acid reaction may be represented by the following equations.

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2 \tag{1.4}$$

$$CaMg(CO_3)_2 + 4HCl \rightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2 \tag{1.5}$$

1.5. Types of Corrosion

(a) Chemical Corrosion or Dry Corrosion

(b) Electrochemical Corrosion or Wet Corrosion

(a) Chemical Corrosion or Dry Corrosion

This type of corrosion occurs mainly due the chemical reaction between the atmospheric gasses like O_2, H_2S, SO_2, halogen with the metal. Oxidation corrosion is an example of dry corrosion.

$$2M \rightarrow 2M^{n+} + 2ne^- \qquad \text{(De-electronation)} \tag{1.6}$$

$$nO_2 + 2ne^- \rightarrow 2nO^{2-} \qquad \text{(Electronation)} \tag{1.7}$$

$$2M + nO_2 \rightarrow 2M^{n+} + 2nO^{2-} \qquad \text{(Metal oxide)} \tag{1.8}$$

(b) Electrochemical Corrosion or Wet Corrosion

This type of corrosion arises:

i) When a metal comes in contact with a conducting liquid or

ii) Due to partially dipping of two different metals or alloys in solution

The occurrence of wet corrosion is due to the presence of anodic and cathodic regions between which current flows through the conducting solution. Oxidation reaction occurs in anodic region and reduction occurs in cathodic region. The formed corrosion product is collected somewhere between anode and cathode. In acidic medium following reactions occur:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad\qquad \text{(Oxidation)} \qquad\qquad (1.9)$$

The released electrons flow through the metal from anodic area to cathodic area, whereas H^+ ions of acidic solution are eliminated as hydrogen gas (H_2),

$$2H^+ + 2e^- \rightarrow H_2 \qquad\qquad \text{(Reduction)} \qquad\qquad (1.10)$$

The overall reaction is:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad\qquad\qquad\qquad (1.11)$$

In neutral and alkaline medium following reactions can occur:

At anode: $Fe \rightarrow Fe^{2+} + 2e^-$ \qquad\qquad (Oxidation) \qquad\qquad (1.12)

At cathode: The released electron flow from anode to cathode through iron metal

$$\tfrac{1}{2} O_2 + H_2O + n2e^- \rightarrow 2OH^- \qquad\qquad \text{(Reduction)} \qquad\qquad (1.13)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad\qquad \text{(overall reaction)} \qquad\qquad (1.14)$$

If excess oxygen is present, then ferrous hydroxide is easily oxidized to ferric hydroxide.

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow Fe(OH)_3 \qquad\qquad\qquad (1.15)$$

The product called yellow rust corresponds to $Fe_2O_3 \cdot xH_2O$ (Figure 1.2).
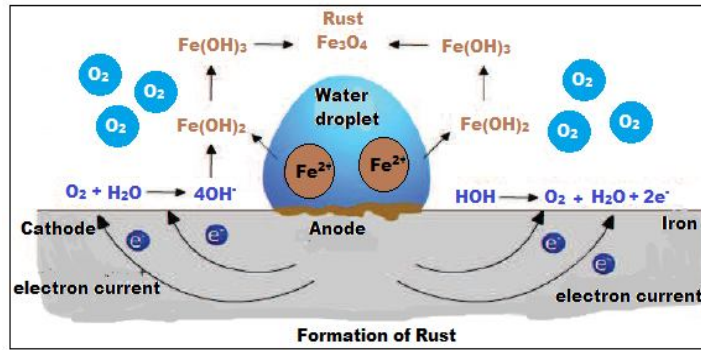
Figure: 1.2: Formation of rust

1.6. Theories of Corrosion

There are three theories of corrosion:

(i) Homogeneous theory

(ii) Heterogeneous theory

(iii) Mixed potential theory

(i) Homogeneous theory: According to this theory corroding metal is treated as a single electrode on which corrosion reactions occur. Due to corrosion charge transfer reaction occurs at the metal solution interface and this makes metal to become unstable. So, it becomes essential to make the potential more negative than the equilibrium potential for cathodic reaction (electronation) or more positive than the equilibrium potential for anodic reaction (metal dissolution).

(ii) Heterogeneous theory: According to this theory, metal corrosion occurs when it comes in contact with moist atmosphere. In this generation of local galvanic cell arises over the corroding metal due to the structural heterogeneity. Though many theories have been put forward, the most acceptable theory is electrochemical or acid theory of corrosion [Walker *et al.* (1907)]. The other old theories such as direct chemical attack theory [Bengoung and Stuart (1922)], Colloidal theory [Friend (1921)] and Biological theory [Reddic and Linderman (1932)] were either proved to form a part of

electrochemical theory or found to be rarely applicable. The factors that are mainly responsible for corrosion are those associated with the metal, environment or both.

(iii) Mixed Potential Theory: According to mixed potential theory, electrochemical reactions are divided into two or more partial oxidation and reduction reactions [Perez (2010)]. During an electrochemical reaction there is no net accumulation of electrical charge, i.e. metal cannot spontaneously accumulate electrical charge when immersed in an electrolyte. For the corrosion of an electrically isolated metal sample, the total rate of oxidation must be equal to total rate of reduction [Husler (1985)]. The polarization curves for corroding metal can be demonstrated by applying the mixed potential theory. More generally polarization of anodic and cathodic reactions occurs to same extent and thus corrosion is said to be under mixed control. The extent of polarization not only depends on the nature of metal and electrolyte, but also depends on the exposed area of the electrode [Putilova *et al.* (1960)].

1.7. Thermodynamic Aspects

Thermodynamics indicate the spontaneous direction of a chemical reaction. It is used to determine whether corrosion is theoretically feasible or not. Different metals have different tendencies to corrode in a given corrosive environment. The corrosion tendency depends upon the energy associated with the chemical reaction taking place during corrosion. By calculating the amount of free energy change associated with a given chemical reaction, it is possible to predict whether natural corrosion can take place in a given set of environmental conditions. Thermodynamic approaches have been also widely used to explain and understand the fundamental of corrosion problems.

Thermodynamic stability of a chemical compound is determined by the sign and the change in free energy (ΔG). If G_1 corresponds to the initial free energy of metals and G_2

to that of the reaction products, then $G_2-G_1=\Delta G$ is the free energy change for the reaction.

In an electrochemical reaction the variation in ΔG can be expressed as follows:

$$\Delta G = -nF\Delta E \tag{1.16}$$

where, ΔE is the potential difference between two half-cells, n is the number of electrons transferred and F is the Faraday constant.

A large negative value of ΔG indicates a pronounced tendency for the reaction to proceed, whereas a positive value indicates no tendency towards reaction. If $\Delta G = 0$, the system is in equilibrium [Davies (1940)].

So, the thermodynamic condition for corrosion reaction includes $\Delta G < 0$ and $\Delta E > 0$

The variation of free energy is expressed by the equation:

$$\Delta G = \Delta G^\circ + RT \ln \frac{\Pi_{prod}}{\Pi_{react}} \tag{1.17}$$

Introducing the potential leads to Nernst's law:

$$E_a = \Delta E_a^\circ + \frac{RT}{zF} \ln \left[M^{z+} \right] \tag{1.18}$$

$$E_c = \Delta E_c^\circ + \frac{RT}{zF} \ln \left[A^{a-} \right] \tag{1.19}$$

This makes it easy to obtain the variation of free energy for the overall reaction as the sum of the variations of the two partial reactions. Using the potentials we obtain:

$\Delta E = E_c - E_a$ or $E_c - E_a > 0$ or $E_c > E_a$

In other words, the corrosion reaction is spontaneous if the potential of the cathodic reaction is nobler than the potential of the anodic reaction. Only in this case is a positive driving force available ($\Delta E > 0$) which makes the reaction possible. Considering the anodic reaction alone, the thermodynamic condition for it to proceed in the anodic direction (corrosion) emerges when its potential "E" is nobler than the equilibrium potential, indicated by E_{eq}, given by:

$$E_{eq} = \Delta E^{\circ} + \frac{RT}{zF} \ln \left[M^{z+} \right] \qquad (1.20)$$

where, E° is the standard potential of the metal and $[M^{z+}]$ the concentration of its ions in the electrolyte in contact with its surface. The thermodynamic condition for the reaction to proceed in the anodic direction (corrosion) is thus, $E > E_{eq}$, corresponding to a negative variation of free energy ($\Delta G < 0$). If, however, $E < E_{eq}$, we have a positive variation of free energy ($\Delta G > 0$), and the reaction proceeds in the cathodic direction (the oxidation of the metal cannot occur, in other words a condition of thermodynamic immunity is created) [McCafferty (2010)].

Other thermodynamic quantities can be derived from electrochemical measurements. For example, the entropy change (ΔS) in a cell reaction is given by the temperature dependence of ΔG:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T} \right)_P \qquad (1.21)$$

Hence,

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P \qquad (1.22)$$

And

$$\Delta H = \Delta G + T \Delta S = nF \left[T \left(\frac{\partial E}{\partial T} \right)_P - E \right] \qquad (1.23)$$

where, ΔH is the enthalpy change and T is the absolute temperature in degrees Kelvin (K). The equilibrium constant (K_{ads}) is correlated with the standard free energy of adsorption (ΔG°_{ads}) and can be given by the following equation:

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5 K_{ads}) \qquad (1.24)$$

where R is the gas constant. The value of 55.5 is the concentration of water in solution in mol L^{-1}.

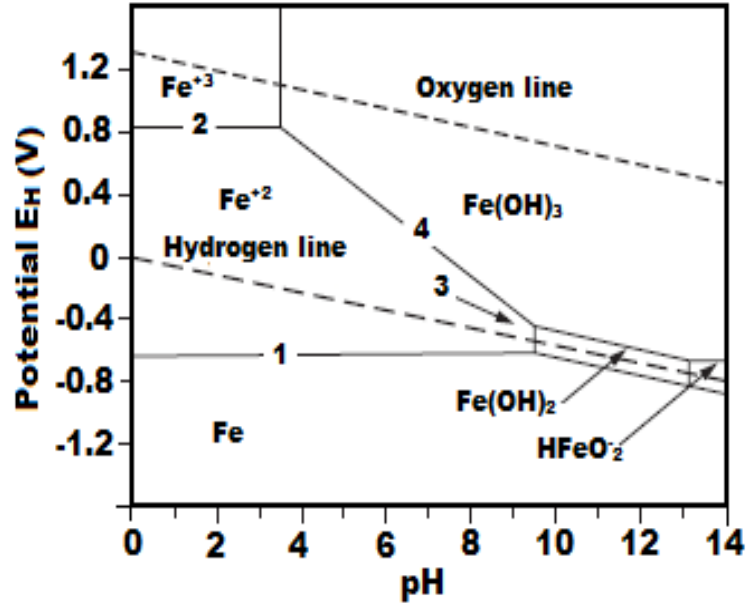## 1.8. Pourbaix diagrams

The stability of a metal when exposed to a given environment depends on a multitude of factors that may vary greatly with the pH (acidity or alkalinity) and oxidizing or reducing power of that environment. One useful concept to represent the effects of aqueous environments on metals became known as potential-pH (E-pH) diagrams, also called predominance or Pourbaix diagrams, which have been adopted universally since their introduction in the late 1940s. The potential is shown on the vertical axis and the pH on the horizontal axis. Such diagrams are constructed from calculations based on the Nernst equation, which is given as follows:

$$E_{eq}^{M^{z+}/M} = \Delta E_{\circ}^{M^{z+}/M} - \frac{0.059}{z} \log a_{M^{z+}} \qquad (1.25)$$

The Pourbaix Diagrams for Fe-H$_2$O system is shown in Figure 1.3. In the diagram, the horizontal lines represent pure electron transfer reactions dependent solely on potential, but independent of pH,

Fe = Fe^{2+} + 2e$^-$

Fe^{2+} = Fe^{3+} + e$^-$
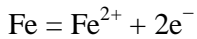
**Figure: 1.3:** Potential-pH (Pourbaix) diagram for Fe-H$_2$O system

These lines extend across the diagram until the pH is sufficiently high to facilitate the formation of hydroxides, represented by vertical lines, thereby reducing the concentration of Fe^{2+} and Fe^{3+} ions.

The vertical lines in Figure 1.3 correspond to the reactions:

$$Fe^{+2} + 2H_2O \rightarrow Fe\,(OH)_2 + 2H^+ \tag{1.26}$$

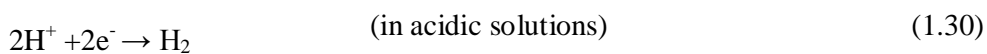$$Fe^{+3} + 3H_2O \rightarrow Fe\,(OH)_3 + 3H^+ \tag{1.27}$$

There is no electron transfer involved and the reactions are solely dependent on pH.

The sloping lines in above figure represent equilibrium involving both electron transfer and pH; for example:

$$Fe^{+2} + 3H_2O \rightarrow Fe\,(OH)_3 + 3H^+ + e^- \tag{1.28}$$

$$Fe + 2H_2O \rightarrow HFeO_2^- + 3H^+ + 2e^- \tag{1.29}$$
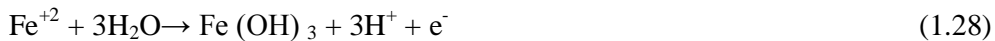
The hydrogen and oxygen are also shown in the diagram by the dotted lines. The hydrogen line represents the equilibrium:

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{(in acidic solutions)} \tag{1.30}$$

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Or

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (in neutral or alkaline solutions)   (1.31)
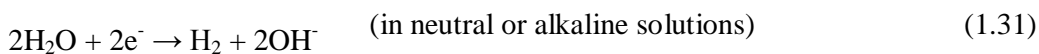
The Pourbaix diagram (potential-pH diagram) has three zones:

➢ **Immunity zone:** Under these conditions of potential and pH, iron remains in metallic form.

➢ **Corrosion zone:** Under these conditions of potential and pH, iron corrodes, forming Fe^{2+} or Fe^{3+} or $HFeO_2^-$.

➢ **Passive zone:** Under these conditions of potential and pH, protective layers of Fe $(OH)_3$ form on iron and further corrosion of iron does not take place.

1.9. Kinetics of Corrosion

When an electrochemical reaction takes place at the metal-solution interface the rate of reaction is proportional to current-potential dependence. Overvoltage (polarization) "η" is the potential change, $E\text{-}E_r$, from the equilibrium half-cell electrode potential E_r, caused by a net surface reaction rate for the half-cell reaction and was introduced by Nernst and Caspari. The dependence of η on the current-density for a hydrogen evolution reaction has been shown to be $\eta = a + b \log i$ by Tafel. Butler gave the kinetic treatment of a reversible electrode in which the concepts of the partial anodic and cathodic currents are related to η through an exponential equation.

1.9.1. Activation controlled corrosion

Activation polarization is generally caused by slow electrode reaction. The reaction at the electrode requires activation energy in order to proceed. The most important example for activation controlled corrosion reaction is that of hydrogen ion reduction at cathode. The relationship between current and potential for a corroding system in which anodic reaction is metal dissolution and cathodic reaction is hydrogen evolution can be derived by the application of electrochemical kinetic theory.

For the metal dissolution reaction,

$$M \rightarrow M^{+2} + 2e^-$$ (1.32)

$$i_c = i_c^o \left\{ \exp\left(\frac{\alpha_c F}{RT}(E - E_c^r) \right) - \exp\left(\frac{-\beta_c F}{RT}(E - E_c^r) \right) \right\}$$ (1.33)

where, E_c^r is the reversible potential of cathodic dissolution reaction, i_c^o is the exchange current density for cathodic reaction and α_c, β_c are transfer coefficients of reduction reaction.

Normally the corrosion potential (E_{corr}) will be far away from the equilibrium potential of the reversible reaction. Hence the contribution from the deposition reaction of metal dissolution and the reduction reaction is negligible. Therefore the net current of the mixed electrode system is given as follows:

$$i = i_a - i_c$$ (1.34)

$$= i_a^o \left\{ \exp\left(\frac{\alpha_a F}{RT}(E - E_a^r) \right) - \exp\left(\frac{-\beta_a F}{RT}(E - E_a^r) \right) \right\}$$ (1.35)

At corrosion potential $E = E_{corr}, i = 0$

i.e. $i_{corr} = i_a^o \left(\exp \frac{\alpha_a F}{RT}(E_{corr} - E_a^r) \right)$ (for anodic reaction) (1.36)

i.e. $i_{corr} = i_c^o \left(\exp \frac{\alpha_c F}{RT}(E_{corr} - E_c^r) \right)$ (for cathodic reaction) (1.37)

Substituting the terms E_a^r and E_c^r in terms of E_{corr}

$$i = i_{corr} \left\{ \exp\left(\frac{\alpha_a F}{RT}(E - E_{corr}) \right) - \exp\left(\frac{-\beta_c F}{RT}(E - E_{corr}) \right) \right\}$$ (1.38)

The above equation can be rewritten in terms of Tafel slopes β_a and β_c as

$$i = i_{corr} \left\{ \exp\left(\frac{2.3(E - E_{corr})}{\beta_a} \right) - \exp\left(\frac{-2.3(E - E_{corr})}{\beta_c} \right) \right\}$$ (1.39)

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Since $E - E_{corr} = \eta$

$$i = i_{corr}\left\{\exp\left(\frac{2.3\eta}{\beta_a}\right) - \exp\left(\frac{-2.3\eta}{\beta_c}\right)\right\} \tag{1.40}$$

The above expression forms the basis of measuring corrosion rate by electrochemical method.

1.9.2. Diffusion controlled corrosion

Concentration polarization or diffusion over potential is the potential difference of a cathode in absence and presence of external current. The corrosion process in neutral media consists of metal dissolution reaction as anodic and oxygen reduction as cathodic reaction. In such cases,

$$i_a = i_{corr}\left(\exp\frac{\alpha_a F}{RT}(E - E_{corr})\right) \tag{1.41}$$

$$i_c = i_d = \frac{\eta F D C_b}{\delta} \tag{1.42}$$

where, D is diffusion coefficient, δ is diffusion layer thickness and C_b is the concentration of reduced species.

$$i = i_a - i_c \tag{1.43}$$

$$i_a = i_{corr}\left(\exp\frac{\alpha_a F}{RT}(E - E_{corr})\right) - i_d \tag{1.44}$$

i_d = limiting diffusion current density

At corrosion potential $E = E_{corr}$, $I = 0$, therefore $i_{corr} = i_d$

It follows that the i_d is the most significant parameter in the corrosion reaction in which the cathodic reaction is diffusion controlled and any factor that increases i_d will increase the corrosion rate.

1.10. Diagrams associated to Kinetic parameters

Polarization diagram of corroding metals is sometimes called Evans diagram or mixed-potential diagrams. This polarization diagram was originally developed by U. R Evans of Cambridge University, England.

1.10.1. Evans Diagram

This is the plot which is drawn between potential versus log current or log current density. To establish a plot of Evans diagram, the usual electrodes that are employed, in addition to the electrode being studied (the "working "electrode), are the reference electrode and the inert counter (or auxiliary) electrode that is usually made of platinum. Alternatively, depending on the type of measurements to be made, a galvanostatic circuit, consisting of a power supply, resistor, ammeter, and potentiometer can be used. The current between working and counter electrodes is controlled, and the potential of the working electrode with respect to the reference electrode is measured [Revie (2008)]. Figure 1.4, shows Evans diagram of metal M.

In this system, the oxidation reaction may be the dissolution of metal, $M \rightarrow M^{+z} + ze^-$, and the reduction reaction may be symbolized as $R^{n+} + ne^- \rightarrow R$. In an aerated neutral or basic aqueous solution, the reduction reaction could be $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, whereas in a deaerated acid, the reduction reaction could be $2H^+ + 2e^- \rightarrow H_2$.
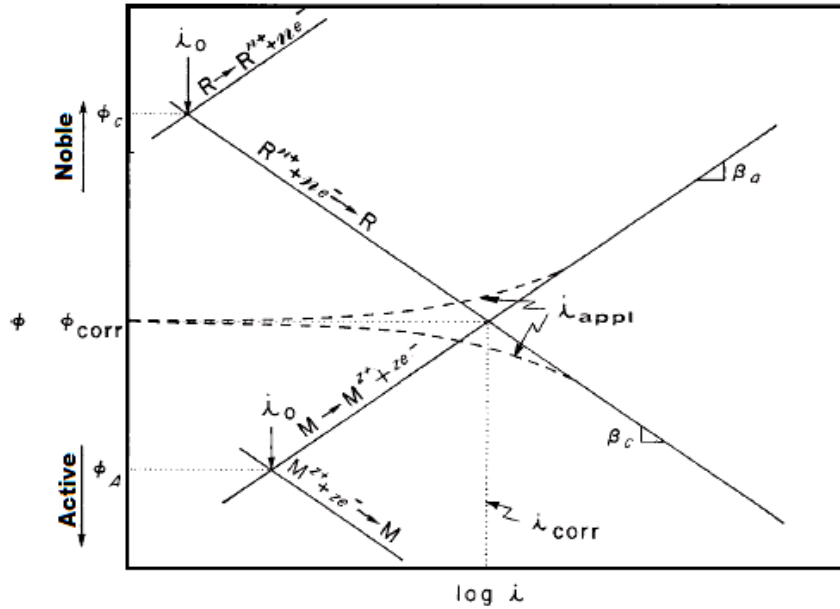
Figure: 1.4: Evans diagram

Corrosion control processes are classified into three types by the patterns of anodic and cathodic polarization curves: anodic, cathodic and mixed controls, as shown in Figure 1.5.
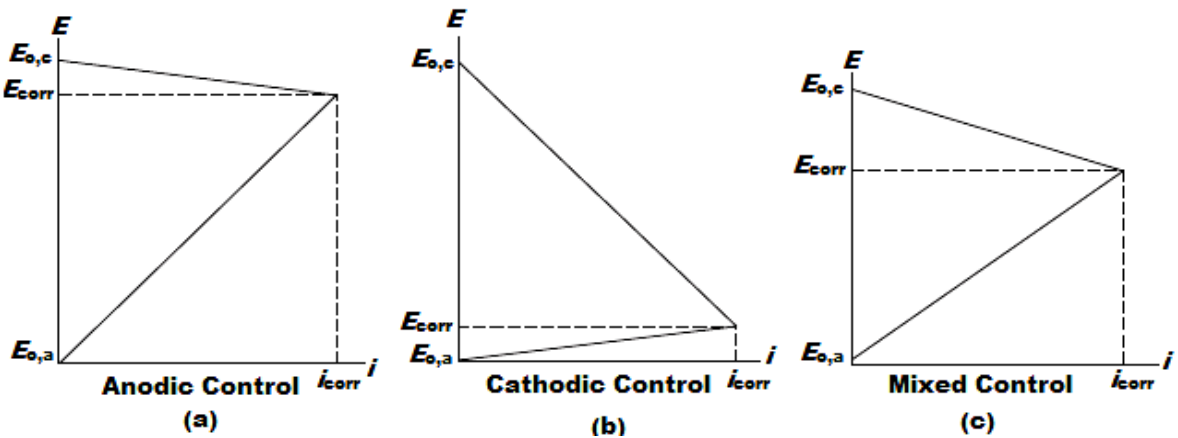

Figure: 1.5: (a) Anodic control (b) cathodic control, (c) mixed control

1.10.2. Mixed Potential Theory

Mixed potential theory can be explained by considering the two metals iron and zinc in an acid solution. The two factors to be considered are the anodic polarization line of the metal and the exchange current density for hydrogen evolution on the metal. Although zinc is expected to corrode according to its position in the galvanic series, it is

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the iron that corrodes in this system because the exchange current density for hydrogen evolution is higher on iron than on zinc. A mixed potential diagram for the iron, zinc system is shown in Figure 1.6. The lines "a" and "b", refer to zinc alone and "a" and "b" are those of iron corroding in an isolated condition. The lines "a" and "b" represent the mixed electrode system of iron and zinc [Tretheway and Chamberlain (1995)].
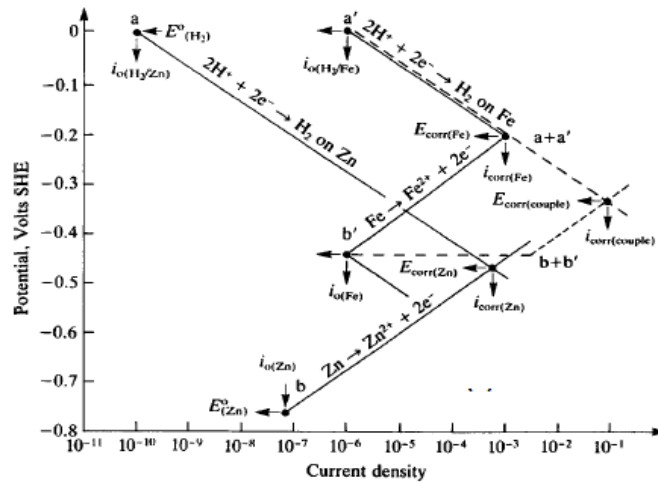
Figure: 1.6: A mixed potential plot for bimetallic couple of iron and zinc

1.10.3. Tafel Extrapolation Method

This technique is based on anodic and cathodic polarization measurements. Figure 1.7 represents the hydrogen evolution as anodic polarization curve and metal dissolution as cathodic polarization curve, which are superimposed as dotted lines. At relatively high-applied current density the corresponding hydrogen evolution become virtually identical. The corrosion rate from these polarization curves were calculated by extrapolating the Tafel region upto the corrosion potential (Figure 1.7). At this corrosion potential, the rate of hydrogen evolution is equal to the rate of metal dissolution and the corresponding current at this point is expressed in terms of current density. The anodic and cathodic Tafel constants were calculated from the anodic and cathodic branches of the Tafel Plot respectively.
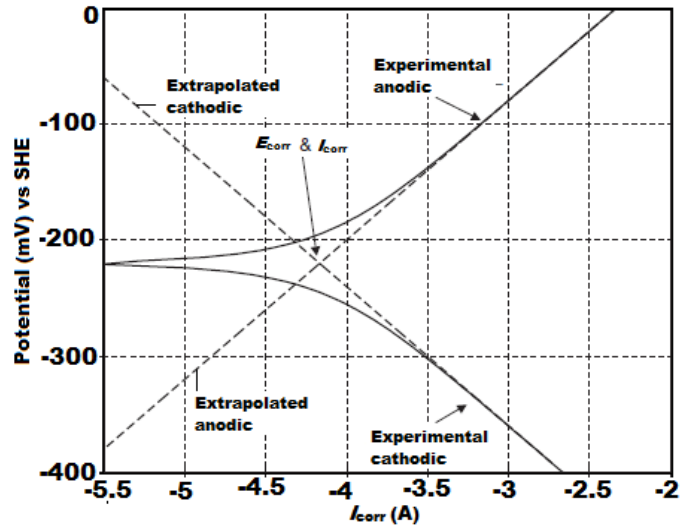
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Figure: 1.7: Extrapolated Tafel curves

1.10.4. Linear Polarization Resistance

It is also called as LPR in short. The polarization resistance of a material is defined as the $\Delta E/\Delta i$ slope of a potential-current density curve at the free corrosion potential (Figure 1.8), yielding the polarization resistance R_p that can be itself related to the corrosion current (i_{corr}) with the help of the Stern-Geary approximation in Eq. (1.45) [Grauer *et al.* (1982)].

$$R_P = \frac{B}{i_{corr}} = \frac{(\Delta E)}{(\Delta i)_{\Delta E \to 0}} \tag{1.45}$$

where, R_p is the polarization resistance, i_{corr} is the corrosion current, B is an empirical polarization resistance constant that can be related to the anodic (b_a) and cathodic (b_c) Tafel slopes with Eq. (1.46).

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$$B = \frac{b_a \times b_c}{2.3(b_a + b_c)} \qquad (1.46)$$
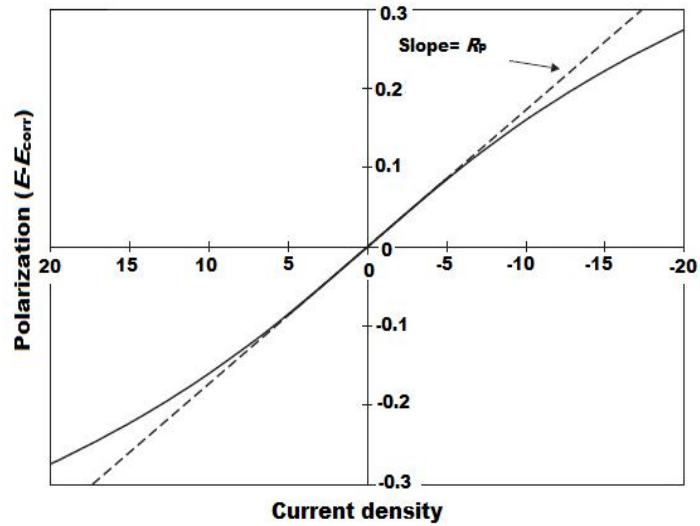
Figure: 1.8: Hypothetical linear polarization plot

1.11. Electrochemical Impedance Spectroscopy

Impedance technique has been widely used for the measurement of corrosion rate, due to the main advantage that the double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) can be determined. The term resistance and impedance both imply a restriction to the current flow. When dealing with direct current (D.C.), only resistors produces this effect. But in the case of alternate current (A.C.), both inductors and capacitors influence electron flow. The cell impedance is resolved into two parts i.e.

Real part $\left|Z^{'}\right| = \left|Z\cos\theta\right|$

Imaginary part $\left|Z^{''}\right| = \left|Z\sin\theta\right|$

The impedance Z is the total resistance to the alternating current and is given by,

$Z = Z' - Z''$

where,

$$Z' = R_s + \frac{R_{ct}}{1 + \omega^2 C_{dl} R_{ct}^{\,2}} \qquad (1.47)$$

$$Z'' = \frac{\omega C_{dl} R_{ct}^{\,2}}{1 + \omega C_{dl}^{\,2} R_{ct}^{\,2}} \qquad (1.48)$$

From equations, the plot Z' against Z'' for various frequencies results in a semicircle which cuts the real axis at higher and lower frequencies. At higher frequency end, the intercept corresponds to R_s and at lower frequency end; the intercept corresponds to $R_s + R_{ct}$. The difference between these two values gives R_{ct} and from the values, the corrosion rate can be calculated. The double layer capacitance is obtained from the frequency at which Z' is maximum.

$$\omega(Z''_{\text{max}}) = \frac{1}{C_{dl} \times R_{ct}} \qquad (1.49)$$

In impedance measurements an A.C. potential of 10 mV was super imposed on the steady open circuit potential. A plot of real part (Z') and imaginary part (Z'') were made and R_{ct} and C_{dl} were calculated. Inhibition efficiency by using impedance measurements were carried out by using the formula:

$$\eta\% = \frac{R_{ct(inh)} - R_{ct(blank)}}{R_{ct(inh)}} \times 100 \qquad (1.50)$$

where, $R_{ct(inh)}$ = Charge transfer resistance with inhibitor

$R_{ct\ (blank)}$ = Charge transfer resistance without inhibitor.

A general impedance measurements curve is shown in Figure 1.9.
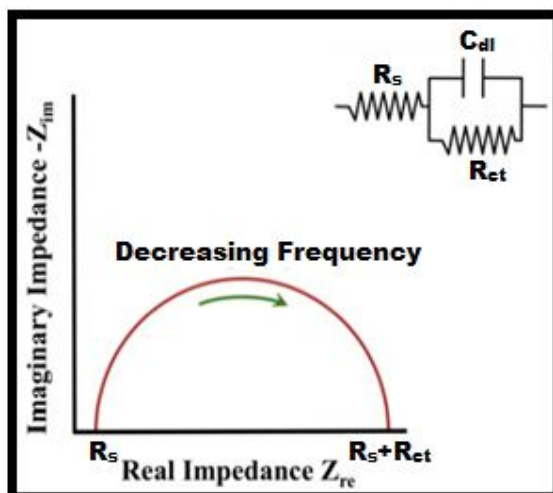
Figure: 1.9: A general impedance measurements curve

Advantages:

EIS Methods offer many advantages:

➢ Data on several cell parameters are obtained quickly and simultaneously.

➢ High electrolyte resistance is not a problem.

➢ Applicable to low conductivity systems also.

➢ Provides mechanistic information.

➢ No reaction products build up because there is no net current flow (if the D.C. component is made zero). This results in the least possible disturbance of cell.

➢ The method is very sensitive. Even small changes in the specimen can alter the impedance plot.

1.12. Corrosion Inhibitors

1.12.1. Definition of Inhibitor

National association of corrosion engineers (NACE) defines corrosion inhibitor as a substance which when added in suitable quantity to corrosive environment lower the corrosion rate [NACE (1965)]. They reduce corrosion by either acting as a barrier by forming an adsorbed layer or retarding the cathodic and/or anodic process [Sastri (1998)].

Any corrosion retardation process or the reduction in the oxidation rate of the metal by addition of a chemical compound to the system is caused by corrosion inhibitors [Hackermann and Hurd (1962)].

Inhibitors are often easy to apply and offer the advantage of in-situ application [Raja and Sethuraman (2008)] without causing any significant disruption to the process.

1.12.2. Classification of Inhibitors

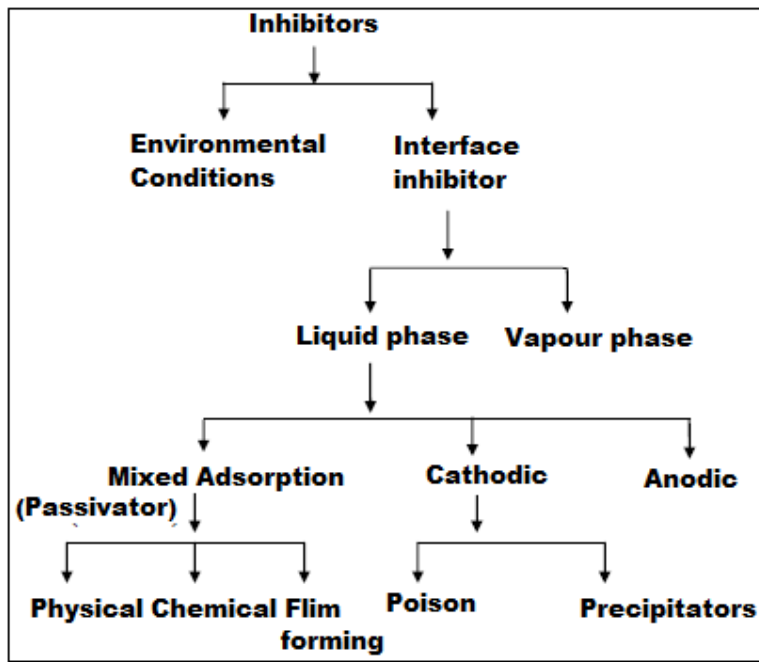Classification of inhibitors is presented below (Figure 1.10) [Revie (2000)].

Figure: 1.10: Classifications of Inhibitors

1.12.3. Environmental Conditions

Corrosion can be controlled by removing the corrosive species from the medium. Inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called environmental conditioners or scavengers [Fanum (2014)]. In near-neutral and alkaline solutions, reduction of oxygen is a common cathodic reaction. In such situations, corrosion can be controlled by decreasing the oxygen content using suitable scavengers.

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1.12.4. Interface inhibitors

(a) Anodic Inhibitors

Anodic inhibitors are used in near neutral solution where oxide, hydroxides or salts are formed as corrosion products. Anodic inhibitors are also called as passive inhibitor because they cause the formation of passive films over the metal surface which inhibits the metal dissolution.

Anodic inhibitor accelerates the corrosion process below the critical concentration. In presence of anodic inhibitor, corrosion potential shifts towards positive direction by increasing the anodic polarization e.g. orthophosphates etc. But some anodic inhibitor at low concentration causes pitting. So, the use of anodic inhibitors is not desirable.

(b) Cathodic Inhibitors

The basic mechanism of cathodic inhibitors is either by acting as cathodic poison i.e. reducing the reduction rate or acting as cathodic precipitators i.e. selectively precipitating on the cathodic areas. There inhibition action occurs either reducing the cathodic area by forming a layer or by adsorbing over the metal surface. In near-neutral and alkaline solutions, these inhibitors inhibit the corrosion by forming a protective films which decrease the cathodic reaction rate by limiting the diffusion of oxygen towards the metal surface [Revie (2000)].

In acid solution, cathodic inhibitor causes hydrogen blisters and hydrogen embrittlement due to hydrogen evolution. The hydrogen gas instead of leaving the surface diffuses into steel causing hydrogen damage such as hydrogen-induced cracking, sulfide stress cracking etc. The cathodic precipitators increase the alkalinity at cathodic sites and precipitate insoluble compounds on the metal surface. The most widely used cathodic precipitators are the carbonates of calcium and magnesium [Revie (2011)]. This type of

inhibitor shifts the corrosion potential in the negative direction. Here cations migrate towards cathode surface, where they are precipitated chemically or electrochemically and thus block the surfaces. For example, the action of As^{3+} and Sb^{3+} on dissolution of iron in acids.

(c) Mixed Inhibitor

The protection power of mixed inhibitors can be divided into three types namely, physical adsorption, chemical adsorption and film formation [Revie (2000)]. The inhibition action of mixed inhibitor depends on the extent at which they are adsorbing at the metal surface and this adsorption mainly depends upon the type of electrolyte used, charge on the metal surface and the structural properties of inhibitor. This type of inhibitors can retard both the anodic metal oxidation and cathodic metal reduction reactions. These inhibitors dominate the other inhibitors because they can control both the anodic and cathodic corrosion reactions and thus are much safer to apply. These inhibitors are classified into acid, base and neutral depending on the environmental conditions, which may be further classified into;

(i) Inorganic inhibitors and (ii) Organic inhibitors

(i) Inorganic inhibitors

To improve the inhibition, one of the methods is to add salts of metals in the corrosive medium. In this case, the protection is due to the reduction of electropositive ions and deposition on the metal surface thus lowering the over voltage of main cathodic depolarization reaction [Tamashov and Cheenova (1967)].

In neutral solutions, inorganic inhibitors interact with the oxide layer which is covering the metal surface and prevent the reduction of oxygen at the cathodic sites. These inhibitors protect the oxide layer of metal from aggressive electrolyte solution. The first step of inhibition mechanism is displacing the pre-adsorbed water molecules, which

is followed by electrochemical and chemical reactions over the metal surface. Thus, inhibitors which can reduce the cathodic oxygen reduction are said to be cathodic inhibitors e.g., phosphates, silicates, borates etc and inhibitors which form the passive oxide layer and prevents the anodic metal dissolution are called as anodic inhibitors e.g., chromates and nitrites. A high surface coverage was observed in presence of benzoate anions, favoring the establishment of passive state [Azambuja *et al.* (1999)].

(ii) Organic inhibitors

Organic compounds having oxygen, nitrogen, sulphur and multiple bonds have been reported as good corrosion inhibitors [Moretti *et al.* (2013), Murulana *et al.* (2015), Pournazari *et al.* (2013), Torres *et al.* (2014)]. Organic inhibitors can be classified as anodic, cathodic or mixed type depending upon their reactions at the metal surface and shift of potential. The effectiveness of these inhibitors depends upon aromaticity, molecular size, length of carbon chain, nature of bonding atoms and conjugation [Schmitt and Bedbur (1985)].

In alkaline solution, metals which are forming amphoteric oxide layer are very susceptible towards corrosion. The inhibitors used in basic medium are tannin, gelatins, agar-agar etc. Also another class of compounds like thiourea, naphthol β-diketone, and substituted phenols has been tested as effective inhibitors in basic solutions and their action of inhibition is due to forming the metal complexes.

1.12.5. Vapor phase inhibitors

A vapor phase inhibitor is an individual chemical or combination of chemicals having a high vapor pressure that can prevent atmospheric corrosion of metallic materials. (e.g., dicyclohexylammonium nitrate, benzotriazole, phenylthiourea etc.). They get readily vaporized and form a protective layer on the metal surface. They are capable of

establishing a stable bond with the metal surface in a given environment of a certain range of acidity and pressure.

1.13. Inhibiting action of inhibitor

Inhibitors decrease or prevent the reaction of the metal with corrosive media by using following ways:

1. Adsorption of ions/ molecules onto metal surface

2. Decreasing the anodic and/or cathodic reaction

3. Decreasing the diffusion rate for reactants to the surface of the metal and

4. Increasing the electrical resistance of the metal surface.

Organic compounds having heteroatom like O, N, and S are found to have higher basicity and electron density and thus act as corrosion inhibitors. O, N and S are the active centers for the process of adsorption on the metal surface and their inhibiting efficiency follows the order O<N<S<P. The inhibitor gets adsorbed on the metal surface by displacing water molecules and forming a compact barrier. Availability of non-bonded electrons (lone pair) and π-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. The electron density in the metal at the point of attachment changes resulting in the retardation of the cathodic or anodic reactions [Shukla *et al.* (2008)]. The physisorption/ chemisorptions strength of the inhibitors depends upon the polarizability of the group and the electron density over the donor atom of functional group.

Inhibition increases with increase in number of carbon in the chain upto 10 carbons, but with higher members little increase or decrease in the inhibiting ability has been noticed. This is attributed to the decreasing solubility in aqueous solution with increasing length of the hydrocarbon chain. However, the presence of hydrophilic functional groups in the molecule would increase the solubility of the inhibitors. The

other factors that contribute to the action of inhibitor are size of the molecule, aromatic ring, conjugation and cross linking ability.

1.14. Theories of inhibition

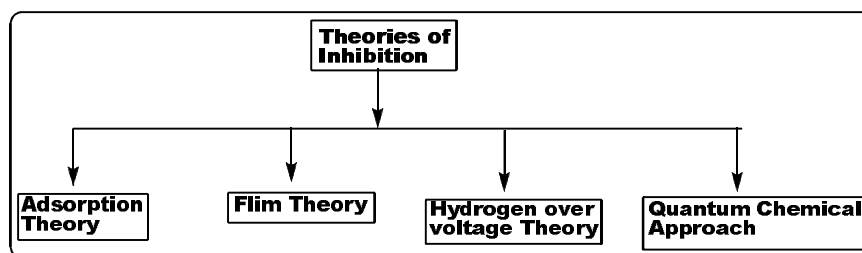There are different types of theories related to inhibition and are given below (Figure 1.11):

Figure: 1.11: Theories of inhibition

1.14.1. Adsorption Theory

According to adsorption theory, inhibitors are adsorbed on the metal surface forming a protective layer. The mode of adsorption leads to its classification as physical and chemical adsorption [Tushar (2004)]. Organic inhibitors have the ability to absorb and impede either anodic or cathodic reaction or both at the metal-electrolyte interface. The different types of adsorptions associated with organic inhibitors are: Electrostatic adsorption or electrosorption, Physical or Van der Waals type adsorption and Chemisorption or π-electron adsorption.

(a) Adsorption Isotherms

An adsorption isotherm is a mathematical equation, which is used to relate the bulk concentration of an adsorbing molecule to its surface concentration at a constant temperature. It is a relationship which can be expressed in terms of the surface coverage of an adsorbing species at the interface with that of the concentration of the species in solution. Various adsorption isotherms have been formulated [Wranglen (1972)]. The

experimental data can be fitted to any one of the adsorption isotherms and the free energy of adsorption can be obtained [Hackermann (1948)].

Various types of adsorption isotherms

S. No.	Isotherms	Equations
1.	Freundlisch	$\beta C_{inh} = \theta$
2.	Langmuir	$\beta C_{inh} = \dfrac{\theta}{1-\theta}$
3.	Frumkin	$\beta C_{inh} = \dfrac{\theta}{1-\theta}\exp(-2a\theta)$
4.	Temkin	$\beta C_{inh} = \dfrac{\exp(a\theta)-1}{1-\exp[-a(1-\theta)]}$
5.	Parsons	$\beta C_{inh} = \dfrac{\theta}{1-\theta}\exp\dfrac{2-\theta}{(1-\theta)^2}\exp(-2a\theta)$
6.	Bockris, Devanathan and Muller	$\log C_{inh} + \log\dfrac{\theta}{1-\theta} = C_{inh} + p\theta^{3/2}$

β = adsorption constant = $1/55.5\ (\exp-(\Delta G^{\circ}_{ads}/RT)$
ΔG°_{ads}= free energy of adsorption
θ = surface coverage
C_{inh}= concentration of inhibitor
 A = molecular interaction constant
a $> 0 = >$ attraction and a $< 0 = >$ repulsion
p and q = constants expressed in terms of dipole moments

(b) Adsorption of Inhibitor in acidic solution

(i) The heteroatom present in the inhibitor molecules would get protonated in acidic solution. As the metal is immersed in the acid solution anionic part of the solution will get adsorbed over it and will facilitate the adsorption of protonated inhibitor molecules over the metal surface through electrostatic interaction (physical adsorption).

(ii) In the acid solution the protonated inhibitor molecules start competing with the H^+ ions for electrons which are present on metal surface. The protonated inhibitor molecule,

upon accepting electron, releases H_2 gas and will become neutral. These neutral inhibitor molecules have free lone pair electrons on the heteroatoms and promote chemical adsorption [Shukla *et al.* (2008)].

1.14.2. Film Theory

This theory reveals that the effective protection of metals by inhibitors is due to the formation of a layer of insoluble or slightly soluble corrosion products on the metal surface [Putilova *et al.* (1960), Husler (1985)].

1.14.3. Hydrogen Overvoltage

This theory postulates that the inhibitors which are adsorbed on the metal, retard either anodic or cathodic or in some case both the reactions. This leads to rapid polarization of anodic or cathodic sites and thus overall corrosion rate is retarded.

1.14.4. Quantum Chemical Approach

Direct interaction between surface metal atoms and the outer most electrons of the organic molecules sometimes lead to chemisorptions phenomenon and thereby causing inhibition. Chemisorptions of organic inhibitors may be taken as a linear combination of the participating wave function of inhibitor molecule as well as of surface metal atoms. The binding energy of the metal inhibitor adduct, may thus be correlated to the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the metal atoms and the inhibitor molecule respectively.

1.15. Effect of inhibitors on corrosion processes

Electrochemical studies have shown that inhibitors in acid solution may affect corrosion reactions of metal in the following ways.

(a) Formation of diffusion layer

The adsorbed inhibitors may form a surface film, which acts as a physical barrier to restrict the diffusion of ions, or molecules to or from the metal surface and so retard the corrosion reactions. This effect occurs particularly when the inhibitor species are large molecules e.g. proteins such as gelatins, agar-agar etc. Similar effect also occurs when the inhibitor can undergo reaction to form a multi molecular surface film e.g. acetylene compounds and sulphoxides.

(b) Blocking of reaction sites

The interaction of adsorbed inhibitors with surface metal atoms may prevent these metal atoms from participating in either anodic or cathodic reactions of corrosion. The simple blocking effect decreases number of surface metal atoms at which these reactions can occur. The mechanism of reactions is not affected and Tafel slope of polarization curve remains unchanged. Behavior of this type has been observed for iron in sulphuric acid solutions containing 2, 6-dimethyl quinoline, β-naphthaquinoline or aliphatic sulphides.

(c) Precipitation in the electrode reactions

The electrode reactions of corrosion involve the formation of adsorbed intermediate species with surface metal atoms e.g. adsorbed hydrogen atoms in the hydrogen evolution reaction and adsorbed (FeOH) in the anodic dissolution of iron. The presence of adsorbed inhibitors would interfere with formation of these adsorbed intermediates but electrode process may then proceed via alternative paths through intermediates containing inhibitor. In this process inhibitor species act in a catalytic manner and remain unchanged, since participation by inhibitor is generally characterized by a change in Tafel slope observed for the process.

1.16. Organic Compounds as Corrosion Inhibitors: Literature survey

The use of corrosion inhibitors is considered as the most effective and economic method to mitigate corrosion in acidic media. Most acid-pickling inhibitors consist of a hydrocarbon part attached to a polar group. They are organic compounds containing heteroatoms (P, S, O, and N), unsaturated compounds containing double and triple bonds in conjugation, aromatic rings, etc. Nitrogen, Oxygen or Sulfur containing compounds have been traditionally used as corrosion inhibitors for metals in acid media [Fouda *et al.* (2015), Bai *et al.* (2015), Nooshabadi *et al.* (2015)]. The available literature on the use of N, S and O containing heterocyclic compounds as corrosion inhibitors in acid media has been surveyed and tabulated as below:

Inhibitor/ Metal-Alloy/Medium	Remark	Reference
Pyridinecarboxaldehyde thiosemicarbazone/ Mild steel/HCl	Potentiodynamic polarization curves show that the inhibitors are mixed type and obey the Langmuir adsorption isotherm.	Xu *et al.* (2014)
5-(4-Dimethylaminobenzylidene) rhodanine/mild steel/H_2SO_4	Corrosion inhibition was investigated by electrochemical and SEM techniques. Inhibitor is mixed type but predominantly cathodic type.	Solmaz (2014)
Acenaphtho quinoxaline (AQ)/ Mild steel /H_2SO_4	Inhibition efficiency increased with increasing concentration of AQ. Langmuir isotherm was used for adsorption behavior.	Obot *et al.* (2010)
N-Aminorhodanine (N-AR)/ mild steel / H_2SO_4	The corrosion study includes immersion time, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), linear polarization resistance	Doner and Kardas (2011)

	(LPR), and chronoamperometry and hydrogen gas evolution. The inhibition efficiency in all methods is nearly 98%.	
Vanillin derivative/ carbon steel/ HCl	The inhibition efficiencies of these inhibitors depend on their concentration and the chemical structures. Tafel curves showed that these inhibitors are mixed type and hence inhibit both cathodic and anodic parts.	Negm *et al.* (2012)
Schiff bases/ carbon steel/ HCl	Weight loss, polarization and electrochemical impedance spectroscopy experiments showed that the Schiff base (S2) is the best inhibitor used. Difference in inhibition efficiency is correlated with their chemical structures.	Hegazy *et al.* (2012)
Cetylpyridinium chloride (CPC)/ Mild steel/ H_2SO_4	The synergistic study of CPC and different halides was investigated using electrochemical methods and SEM. Inhibitor was absorbed with the help of co-operative action of both halide ions and CPC.	Khamis *et al.* (2013)
Benzimidazole derivatives/ Mild steel/ HCl	Benzimidazole derivatives inhibit by adsorption on steel surface and form insoluble complex with ferrous species. Protection efficiency of the inhibitors depends on concentration and temperature.	Tang *et al.* (2013)

Isatin derivatives/mild steel/ HCl	Corrosion study was done by using EIS, weight loss and quantum chemical calculation methods. Inhibitors are mixed type and obeyed Langmuir adsorption isotherm. Inhibition efficiency is 96.2% at 300 ppm.	Ahamad *et al*. (2010)
Schiff base compounds /mild steel/HCl	It was found that maximum R_{ct} value at optimum 1 molar concentration is 811.9 Ω cm^2 and maximum inhibition efficiency is 96.1%.	Behpour *et al.* (2010)
Substituted amino acids/N80 steel/ HCl	Corrosion inhibition study was performed on N80 in 15%HCl using weight loss, electrochemical polarization, ac impedance, Fourier transform infrared spectroscopy and SEM	Yadav *et al*. (2013 a)
Oleylimidazoline/N80 steel/HCl	Surface studies were performed by using FTIR spectra and SEM. Both the inhibitors, AEOI and OAEOI at 150 ppm concentration show maximum efficiency 90.26% and 96.23%, respectively at 298 K in 15% HCl solution	Yadav *et al*. (2012)
Thiadiazole derivatives/ N80 steel/HCl	Inhibition efficiency follows the order AMPT > APT > ACPT. There adsorption was confirmed using SEM and FT-IR spectra.	Yadav *et al*. (2013 b)
Benzodiazepine /N80 steel/HCl	Corrosion inhibition efficiency of 95.6 and 93.4% were obtained with 200 ppm of BMBD and BPBD, respectively at 303 K. The	S. Kumar *et al.* (2013)

	mechanism of the inhibition process was discussed via quantum chemical calculations.	
Pyridine derivatives/N80 steel/HCl	Inhibition efficiency increases and decreases with increase in concentration and temperature. SEM and AFM images reveal inhibitor adsorption on metal.	Yadav and Kumar (2014)
Schiff Bases of Isatin/mild steel/HCl	The effect of molecular planarity on inhibition efficiency is observed. Inhibitor obeyed Frumkin adsorption isotherm.	Singh and Quraishi (2012)
Isatin Derivative/ carbon steel/ CO_2-saturated solution	EIS consists of both capacitive and inductive loops. Tafel data reveals that inhibitor is mixed type.	Silva *et al.* (2013)
Pyridine derivatives/ carbon steel/ HCl	Inhibition efficiency increases with concentration. Results obtained from both potentiodynamic and weight loss techniques reveal that these compounds are good inhibitors.	Maksud and Fouda (2005)
Some Azine and Thiazine Dyes/ mild steel/HCl	Inhibition efficiency increased with increase in concentration of all the studied dyes within the concentration range 100-500 ppm. Potentiodynamic studies revealed that all the inhibitors are of mixed type. QSAR approach was also used to correlate the quantum chemical parameters with the experimentally determined inhibition efficiencies	Ebenso *et al.* (2012)

Quinoxaline and its Derivatives/mild steel/HCl	Tafel polarization curves show that inhibitor actions are mixed-type. The efficiency order obtained by experimental results was verified by theoretical calculations.	Fu *et al.* (2012)
1-Benzoyl-3,3-disubstituted Thiourea derivatives/ Mild steel/HCl	The Tafel polarization revealed the mixed-mode inhibition with predominant control of the anodic reaction. The crystallinity of the inhibitors adsorbed onto the mild steel surface was indicated by wide-angle X-ray diffraction (WAXD) analysis. ΔG^{o}_{ads} reveals both physical and chemical adsorption.	Gopiraman *et al.* (2012)
Schiff Base surfactants /mild steel/ HCl, H_2SO_4	The maximum corrosion inhibition was found at 200 ppm for all the synthesized inhibitors in both HCl and H_2SO_4 solutions. Corrosion in HCl is less than H_2SO_4.	Aiad and Negm (2009)
Sodium gluconate (SG)/ mild steel/ NaCl	The inhibition efficiency became more important with increasing temperature at great concentration (10^{-2} and 10^{-3} M). Adsorption occurs by competition or by co-operation adsorption.	Touir *et al.* (2011)
Poly(vinylalcohol-leucine) composite (PVAL)/ Mild steel/ HCl	PVAL showed more than 95% inhibition efficiency at optimum concentration. It inhibits mild steel corrosion by blocking the active sites of the metal.	Sabirneeza *et al.* (2013)

Alanine/Nickel/ H_2SO_4	At maximum concentration (0.05 molar) 65% inhibition efficiency was obtained. The activation energy is higher in the presence of alanine than in its absence.	Hamed *et al.* (2012)
2-butyl-hexahydropyrrolo[1,2-b][1,2]oxazole/mild steel/HCl	IE was assessed for 2 h and 48 h immersion time tests, through potentiodynamic, EIS and weight loss measurements. The ΔG^o_{ads} values are from -30 to -34 kJ/mol).	Moretti *et al.* (2013)
Itraconazole and Fluconazole/API 5L-B carbon steel/CO_2-saturated 3.5% NaCl solutions	Both the inhibitors are mixed-type and surface analyses confirm the formation of iron nitrides	Ibraheem *et al.* (2012)
Ethoxy-(5-methyl-benzotriazol-1-yl)/X-65 carbon steel/CO_2 saturated oil well produced water	Potentiodynamic polarization and electrochemical impedance techniques indicated that the inhibitor is mixed type. SEM technique confirmed formation of protective film on metal surface.	Migahed *et al.* (2015)

1.17. The scope and importance of corrosion inhibition technology

Organic compounds are widely used in various industries as corrosion inhibitors for preventing corrosion in acidic environments. The major industries using corrosion inhibitors are oil and gas exploration and production industry, petroleum refining industry, chemical industry, heavy industrial manufacturing industry, water treatment industry and additive product industry. Corrosion inhibitors are also used in many systems including cleaning pads, cooling systems, pipelines, chemical operations, steam generators, ballast tanks and many products that are marketed to the general public. One of the salient features of the corrosion inhibitor is non-disruption of the process. Inhibitors

are mainly used for their effectiveness in protecting the specific metal or combination of metals in a closed or recirculation system.

1.18. Objectives of present study

The objectives of the present work are as follows:

1. Synthesis of organic corrosion inhibitors.

2. The evaluation of the inhibition effects of the synthesized compounds on corrosion of N80 steel, J55 steel and mild steel in 15% HCl, 3.5% NaCl saturated with CO_2 and 20% H_2SO_4 solution respectively by using weight loss measurements, electrochemical impedance spectroscopy, potentiodynamic polarization and contact angle measurement.

3. Analysis of surface morphology of uninhibited and inhibited steel samples by SEM, EDX and SECM techniques.

4. Quantum chemical calculations using density functional theory (DFT) and molecular dynamic simulation to correlate the experimental data.

5. Study of the mechanism of corrosion inhibition on the basis of the above studies.