CHAPTER-1

INTRODUCTION

1.1. General introduction

Corrosion is a naturally occurring event defined by ISO 8044 as: “Physicochemical interaction between a metal and its environment that results in change in the properties of the metal, and which may lead to significant impairment of the function of the metal, the environment, or the technical system, of which these form a part” [ISO 8044 (1999; 2015)]. With only a few exceptions, all metals and alloys undergo corrosion because of chemical or electrochemical reaction with their environment which causes safety and economic problems. Corrosion is a result of the inherent property of metals and alloys to convert to their comparatively more stable compounds known as ores. Corrosion is the most common electrochemical phenomenon experience in the daily life which causes loss of metals or their properties. Most of the metals are thermodynamic unstable, generally attacked by water, moist air, acids, bases, oils and gaseous materials such as free acid vapors, formaldehyde, ammonia and sulfur in vapor state along with other solid and liquid chemicals.

Corrosion is a destructive process and exerts adverse economic and environmental impact on the many sectors of nation. Corrosion affects nation economy on daily basis, resulting into destruction and damage to household appliances, airplanes, automobiles, highway bridges, buildings, chemical processing, water and wastewater systems and energy production and distribution system and many more. According to NACE International Gateway India Section (NIGIS), in 1998 the total cost of corrosion in U. S. was around $ US 276 billion which constitutes approximately 3.1% of the nation’s Gross Domestic Product (GDP) [NACE (2002)]. A comprehensive study of corrosion in the

India published in 2011 by the 1st Global Corrosion Summit held in New Delhi [1st Global Corrosion Summit (2011)] reported that total cost of corrosion in India was approximately 2 lac crores. The global annual cost of corrosion now has been increased more than $ US 2.5 trillion (approximately 3.3%) of the nation's GDP.

It has been estimated that due to corrosion about 25% of the total products of the metals and alloys go waste. Thus from national economic point of view, it is necessary for scientists and engineers to adopt various ways to minimize these losses. The use of metals and alloys is increasing rapidly due to substantial growth in the field of technology and industry. And therefore, any step in the direction of understanding the nature of corrosion, its mechanism and the way to mitigate it would be of great help to nation's economy.

1.2. Types of corrosion

Corrosion can be categorized on the different basis; however broadly it can be classified into two categories:

(i) Dry corrosion or chemical corrosion

(ii) Wet corrosion or electrochemical corrosion

1.2.1. Dry corrosion or Chemical corrosion

The chemical corrosion results as a direct chemical reaction between gaseous such as oxygen, hydrogen, hydrogen sulphide, sulfur dioxide, nitrogen or anhydrous inorganic acids and the metal surface in moisture free condition. This process is very sensitive to temperature and generally takes place at high temperature. The dry corrosion is a slow process leading to accumulation of solid corrosion products (usually known as rust) on the metallic surfaces which protect metal from further corrosion. The chemical corrosion takes place uniformly on both homogeneous and heterogeneous metallic surfaces. In some cases chemical corrosion involves formation of soluble or volatile corrosion products which removed and open the metallic surface for further corrosion. Further, at few instances, the oxide layer formed over the metallic surface is porous, and thus corrosion can continue deep into the material. This type of corrosion is known as active corrosion. Tarnishing of copper and silver, and formation of surface oxide film are good examples of dry corrosion. The dry corrosion can be further classified into following three main types:

(a) Oxidative dry corrosion: The oxidative dry corrosion is brought about direct atmospheric oxidation of metals in absence of moisture at comparatively low temperature. The oxidative dry corrosion involves following fundamental steps:

$2\mathrm{M} \rightarrow 2\mathrm{M}^{n+} + 2ne^{-}$ (Loss of electrons) (1)

(Metal cations)

$nO_2 + 2ne^{-} \rightarrow 2nO^{2-}$ (Gain of electrons) (2)

(Oxide anions)

The oxide film formed on the surface of Al, Sn, Pb, Cu, Pt., etc are very stable, adhering and impervious in nature which protects these metals from further oxidative corrosion.

(b) Dry corrosion by other gases: This type of corrosion occur by the chemical reaction between metal and the gases other than oxygen such as SO_2, CO_2, Cl_2, H_2S, F_2, etc surrounding the metal. Generally, the extent of these kinds of corrosion mainly influences by the interaction between the metal and gaseous involved in the corrosion process. The corrosion products so formed on the metallic surface act as barrier for further gaseous attack. However, if a soluble or volatile corrosion product is formed, the metal undergoes further attack. For example, chlorine attacks silver metal to form stable, adhering and impervious protective film of silver chloride which acts as barrier for corrosion. However, chlorine attack on tin (Sn) forms highly volatile $SnCl_4$ (which volatilizes immediately) leading to fresh metal surface for further attack.

$2\,Ag + Cl_2 \longrightarrow 2\,AgCl$ (Stable and impervious corrosion product)

$Sn + 2Cl_2 \longrightarrow SnCl_4$ (Volatile and porous corrosion product)

(c) Liquid metal corrosion: In several industries molten metals such as Hg, Zn, Sn, Pb, Cd etc. passes through metallic pipes made up of Al and stainless steel and causes brittle failure due to internal penetration. Generally, liquid metal corrosion occurs at high temperature and mainly found in devices used for nuclear power. These molten metal atoms penetrate the grain boundaries and fracture the metal lattice. The liquid metal corrosion is example of physical form of attack on the metal surface rather than a chemical attack. The liquid metal corrosion may occur by following types:

(i) Diffusion of liquid into solid metal

(ii) Solution of structural metal

(iii) Intermetallic compounds formation

(iv) Mass transfer

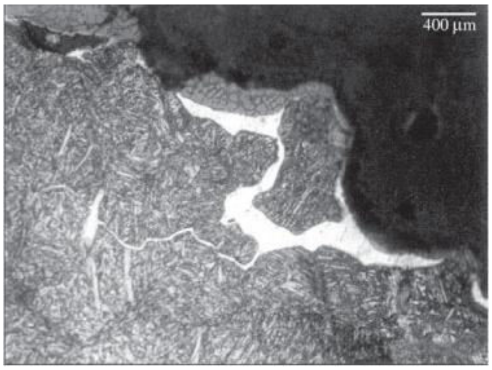


Figure 1.1: liquid metal corrosion of mild steel surface by molten Copper at 1100^0C (MP: 1085^0C)

1.2.2. Wet corrosion or electrochemical corrosion: Most of the corrosion reactions, particularly in aqueous solution or other polar media are electrochemical in nature.

According to Cushman [Cushman (1907)], the overall corrosion process involves formation of anodic and cathodic areas on the metal surface in which highly aerated part of the metal surface act as anode at which dissolution of metal takes place through its oxidation. The anodic reaction can be represented as follows:

$$\mathrm{M} \rightarrow \mathrm{M}^{2+} + 2e^{-} \qquad \text{(Anodic reaction)} \qquad (3)$$

For every oxidation reaction there must be a corresponding reduction reaction which involves consumption of electrons formed by anodic reactions. Although nature and mechanism of cathodic reactions are more difficult to predict, however in aqueous solution depending upon the environment various cathodic (reduction) reactions are possible. Some common possible reduction reactions are:

(i) Reduction of hydrogen ion in acidic solution and evolution of hydrogen gas:

$$2\mathrm{H}^{+} + 2e^{-} \rightarrow \mathrm{H}_2 \uparrow \qquad \text{(Hydrogen evolution)} \qquad (4)$$

(ii) Reduction of oxygen in weakly acidic solution and formation of water:

$$\mathrm{O}_2 + 4\mathrm{H}^{+} + 2e^{-} \rightarrow 2\mathrm{H}_2\mathrm{O} \qquad (5)$$

(Reduction of oxygen in acid solution)

(iii) Reduction of oxygen in neutral solution:

$$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4e^{-} \rightarrow 4\mathrm{OH}^{-} \qquad (6)$$

(Reduction of oxygen in neutral solution)

(iv) Reduction of metal ions from high oxidation state low oxidation state:

$$\mathrm{M}^{3+} + e^{-} \rightarrow \mathrm{M}^{2+} \qquad (7)$$

(Reduction of metal ions)

(v) Deposition of metal:

$$\mathrm{M}^{2+} + 2e^{-} \rightarrow \mathrm{M} \qquad (8)$$

(Metal deposition)

Based on the relative area of the cathode and anode formed on the metallic surface, wet or electrochemical corrosion can be divided into:

(a) Separable anode /cathode type (Sep. A/C): In this type of corrosion distinct areas of metal predominantly act as cathodic or anodic. Although distance between these areas are very small but can be identified by experimental methods. There is a macroscopic flow of charge through the metal.

(b) Interfacial anode/cathode type (interfacial A/C): In this type of corrosion charge is transported through the film of corrosion product accumulated on the metal surface. This type of corrosion generally considered as dry reactions where the uniform formation and growth of film resulted due to accumulation of corrosion product are observed. The reaction of metals with high temperature water and the reaction of copper with sulfur dioxide in carbon dioxide are typical examples of this type of corrosion.

(c) Inseparable anode/ cathode type wet corrosion (Insep. A/C): The uniform dissolution of metal in fused non-aqueous solution; acid, alkaline or neutral solutions like zinc in hydrochloric acid or caustic soda are typical examples of this type of corrosion. In this type of corrosion anode and cathode cannot be identified by experimental means, although their theoretical existences are postulated. It can be postulated that anodic and cathodic sites are interchangeable. The corrosion current of stainless steel in aqueous solution is a typical example of mobile anodic sites, although the corrosion rate is very low.

1.3. Forms of corrosion

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the visual appearance of the corroded metal [Evans

(1976)]. In majority of cases the visualization of forms of corrosion by necked eye is sufficient; however in some cases magnification is required. Several forms of corrosion have been identified; however all of them are more or less interrelated. The common characteristics, mechanism involved in corrosion and their preventive measures of important forms of corrosion are:

(a) Uniform corrosion: This is the most common form of corrosion and commonly known as general corrosion which is characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed metallic surface or over a large area. The uniform corrosion causes the greatest destruction of metal on the tonnage basis which is attributed due to continuous thinning of the metal. The corrosion of a piece of zinc and stainless steel in hydrochloric acid is a typical example of uniform corrosion. The polished metal sheet exposed to open atmosphere also corrode uniformly however, the generation of dulling of metal caused by its exposure to atmosphere at elevated temperature is not to be considered as uniform corrosion. The uniform corrosion can be prevented or reduced by using chemical resistant protective coating or more resistance material.

(b) Galvanic corrosion or two metals corrosion: Galvanic corrosion is also known as dissimilar metal corrosion which refers an electrochemical reaction of two different metals in presence of an electrolyte and electron conductive path known as salt bridge. The natural difference in the metal potentials causes galvanic difference. When galvanic couple is forms, one of the metals in the couple becomes the anode and corrodes faster while other becomes cathode and corrodes with slower rate. In that situation, if the electrical contact made between these metals in the presence of electrolyte, current must flow between them. Typically, due to galvanic corrosion the less resistance material corroded more rapidly and more résistance material corroded less rapidly, as compared with the behaviour of these metals when they are not in galvanic couple.

(c) Crevice or contact corrosion: Crevice or contact corrosion is a localized form of corrosion which is generally produced at the region of contact of metal with metal or metal with nonmetal. Crevice corrosion which is initiated by changes in local chemistry within the crevice; mainly occur at washers, gaskets, fastener heads, surface deposits, disbanded coatings, threads, lap joints and clamps. Crevice corrosion can be monitored by cleanliness, the proper use of sealants and protective coatings.

Table 1.1: ASM classifications of corrosion types.

General Corrosion	**Localized Corrosion**	**Metallurgically Influenced Corrosion**	**Mechanically Assisted Degradation**	**Environmentally Induced Cracking**
Corrosive attack dominated by uniform thinning 1. Atmospheric corrosion 2. Galvanic corrosion 3. Stray-current corrosion 4. General biological corrosion 5. Molten salt corrosion 6. Corrosion in liquid metals 7. High – temperature corrosion	High rates of metal penetration at specific sites 1. Crevice corrosion 2. Filiform corrosion 3. Pitting corrosion 4. Localized biological corrosion	Affected by alloy chemistry & heat treatment 1. Intergranular corrosion 2. Dealloying corrosion	Corrosion with a mechanical component 1. Erosion corrosion 2. Fretting corrosion 3. Cavitation and water drop impingement 4. Corrosion fatigue	Cracking produced by corrosion, in the presence of stress 1. Stress – Corrosion Cracking (SCC) 2. Hydrogen Damage 3. Liquid metal embrittlement 4. Solid metal induced embrittlement

(d) Pitting corrosion: Pitting corrosion is localized form of corrosion which produces cavities or holes in the passive metals such as stainless steel those resist in corrosive media and perform well over long period of times. Pitting corrosion is also known as under deposit corrosion and is considered to be more dangerous than uniform corrosion because pitting corrosion more difficult to detect because corrosion products often cover the pits and a small narrow pit with minimal overall metal loss can lead to the failure of entire engineering system. In majority of cases pitting is extended to throughout the entire metal surface, producing a very rough and irregular metallic surface. However, in few other cases pitting is concentrated mainly in some specific areas, leaving rest of the metal surface unaffected. Pitting most commonly occur in presence of chloride ions, combined with such depolarizes as oxygen or oxidizing salts and where there is incomplete chemical protective film form on metallic surface. The maintaining clean metallic surface, application of uniform protective coating, and use of inhibitors or cathodic protection for immersion service are few common methods that can be used to control pitting corrosion.

(e) Intergranular corrosion: Intergranular corrosion is localized attack on or adjacent to the grain boundaries of a metal or alloy, while the bulk of the grains remain greatly unaffected. The intergranular corrosion is generally associated with chemical segregation effects (impurities have a tendency to be enriched at grain boundaries) or specific phases precipitated on the grain boundaries. Such precipitation can produce zones of reduced corrosion resistance in the immediate vicinity.

(f) Selective Leaching: The selective leaching also known as deploying, demetalification, parting, and selective corrosion which is refers to the selective removal of one element from the alloy by corrosion reactions. A common example is the dezincification of unstabilized brass, whereby a weakened, porous copper structure is produced. Two mechanisms have been described for selective leaching: (1) two metals in an alloy are dissolved and one redeposit on the surface; and (2) one metal is selectively dissolved; leaving other metal behind. The dezincification of brass occurs by the first mechanism while the loss of molybdenum from nickel alloys in the molten sodium hydroxide occurs by second mechanism.

(g) Erosion corrosion: Erosion corrosion is acceleration in the rate degradation of material surface due to mechanical action, particularly by impinging liquid, abrasion by slurry, particles suspended in the fast flowing liquid or gas, bubbles or droplets, cavitation, etc. The increased turbulence caused by pitting on the internal surfaces of a tube can result in rapidly increasing erosion rates and eventually a leak. Erosion corrosion is the combined effect that occurs due to corrosion and erosion and may proceeds by:

(a) Mechanical erosion of the material or protective oxide layer on its surface

(b) Enhanced corrosion of the material, if the corrosion of material depends upon the thickness of the oxide layer.

Mostly, erosion corrosion metal is removed as dissolved ions, or it forms solid corrosion products, which as mechanically washed away from the metal surface. The erosion corrosion can be reduced by: reduce the turbulence of the fluid in the tube by streamlining the piping, control the velocity of the fluid to reduce high-flow velocities, use corrosion-resistant materials, use corrosion inhibitors and cathodic protection, ensure that the entire piping system has been de-burred, replace sharp angles in the piping system with gentler angles to avoid constrictions, reduce the amount of oxygen dissolved in the fluid, adjust the pH value of the fluid, and change the metal alloy.

(h) Stress Corrosion Cracking: The stress corrosion cracking (SCC) occurs when high internal tensile stresses induced in the metal during manufacture are allow to remain i.e. the metal is not properly stress relived. The impact of SCC on a material usually falls between dry cracking and the fatigue threshold of that material. The stresses in the material may be due to applied loads, residual stresses from the manufacturing process, or a combination of both. A general scheme for the classification of corrosion processes given by ASM [Sully *et al.* (1987)] is presented in Table 1.1.

1.4. Basic concept of corrosion

The basic process of metallic corrosion in aqueous medium involves anodic metal dissolution and cathodic reduction of oxidant present in the medium. The anodic oxidative metal dissolution can be represented as follows:

$$\mathrm{M_m} \rightarrow \mathrm{M^{2+}_{aq}} + 2e^-_{\mathrm{m}} \tag{9}$$

Where, Mm is the metal in state of metallic bonding, $\mathrm{M^{2+}}_{\mathrm{aq}}$ is the hydrated metal ion in aqueous solution, and e^-_{m} is the electron lost from the metal. While, the cathodic reduction reaction can be represented as:

$$2\mathrm{Ox_{aq}} + 2e^-_{\mathrm{m}} \rightarrow 2\mathrm{Red}(e^-_{\mathrm{aq}}) \tag{10}$$

Where, Ox_{aq} is an oxidant and Red (e^-_{aq}) is a reductant. There, the overall corrosion reaction can be written as:

$$\mathrm{M_m} + 2\mathrm{Ox_{aq}} \rightarrow \mathrm{M^{2+}_{aq}} + 2\mathrm{Red}(e^-_{\mathrm{aq}}) \tag{11}$$

For general metallic corrosion, anodic reaction involves metal dissolution which is an ion transfer process across the interface, whereas the cathodic reactions involve reduction of hydrogen ions and/or reduction of dissolved oxygen molecules in aqueous solution. These are electron transfer reactions that occur across the interface between the metal and the aqueous solution, and therefore these reactions are depend upon the interfacial potential that essentially corresponds to what is called the electrode potential of metals in electrochemistry terms.

1.5. Factors influencing metallic corrosion

Because, extraction of metals from their ores is always required input of energy (endothermic process), a pure metal is always associated with high energy state as compared to its ore from which it is extracted. Therefore, every pure metal tends to convert into a metallic compounds such as an oxide, hydroxide, sulfate, carbonate, etc. by chemical and/or electrochemical with the environments thereby undergoes corrosion [Abd El Aal *et al.* (2009)]. The nature and extent of corrosion largely depend on the metal and environment. The structure features of the metal, nature of environment, and the type of reactions that occur at metal/ environment interface play important role in the corrosion process [Speller *et al.* (1935)]. Some important factors, which influence the corrosion reactions, are:

1.5.1. Nature of metal:

The nature of metal includes the following factors:

1.5.1.1. Position in galvanic series: Metals can be arranged on the basis of their oxidation potential and corrosion behavior in a series which is known as galvanic series. In this series, the higher oxidation potential i.e. higher up position in the galvanic series greater will be tendency to loss the electrons and greater will be corrosion. If two metals having different position in the galvanic series are connected with each other, the metal which is at higher position in galvanic series acts as anode and corroded first. Moreover, greater is the difference in the position of the metals in galvanic series faster is the corrosion.

1.5.1.2. Over voltage: The difference in the potential between the electrode potential (E) and the equilibrium potential, (E_0) is generally known as over voltage (η). The over voltage is a constant for a given reaction, $\eta = E - E_0$. When, cathodic reaction is hydrogen evolution, the metal with lower hydrogen over voltage on its surface will be more susceptible for corrosion. Since at lower hydrogen over voltage, liberation of hydrogen gas is easy. Therefore cathodic reaction will be relatively faster, which in turn makes anodic reaction relatively faster and thereby increased the rate of corrosion.

1.5.1.3. Relative areas of the anodic and cathodic parts: The rate of corrosion also depends upon the ratio of cathodic are and anodic areas and generally increases with increasing this ratio i.e.

$$\text{rate of corrosion1} \propto \frac{\text{Cathodic area}}{\text{Anodic area}}$$

It has been observed that corrosion is more rapid and severe in case of smaller anodic area which is attributed due to much higher current for smaller anodic area. Further, larger cathodic area also associated with more oxygen reduction, and/or other cathodic reaction which ultimately would increase rate of corrosion.

1.5.1.4. Purity of metal: Impurities present in the metals or alloys cause heterogeneity which is responsible for formation of electrochemical cell over metallic surface and therefore corrosion can initiates at the exposed surface. The impurities in metals and alloys form minute electrochemical or galvanic cells under suitable environmental condition and undergo corrosion. For example, zinc metal having Pb or Fe as impurities undergoes corrosion due to the formation of local galvanic cells. The rate and magnitude of the corrosion increases with increasing exposure time and extent of impurities.

1.5.1.5. Physical state of metal: The rate of corrosion is also influenced by physical state of the metal such as grain size, orientation of crystal, stress etc. it has been reported that smaller the grain size of the metal or alloy, greater will be its solubility in the corrosive medium and hence greater will be its corrosion. Moreover areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

1.5.1.6. Nature of surface film: In actual practice it has been found that all metals undergoes oxidative corrosion upto different extent in aerated atmosphere and thereby metals covered by very thin film of corrosion products (oxide layer). The ratio of the volumes of the metal oxide to the metal is known as “specific volume ratio” or “Pilling-Bedworth ratio” which is very important parameter to deciding the rate of corrosion. The corrosion is rapid and severe, if the oxide film is porous and unstable and on the other hand, for stable and nonporous oxide film, the corrosion rate will be relatively slow. The porous or nonporous nature of surface oxide film depends on the specific volume ratio:

$$\text{Specifice volume ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

If the specific volume ratio is greater than one, the oxide film will be nonporous and hence will be of protective nature and vice versa.

1.5.1.7.Volatility of the corrosion products: The more volatile corrosion products expose the metal surface for further attack, and therefore enhance the corrosion rate.

1.5.1.8.Solubility of corrosion products: In electrochemical corrosion, if corrosion product is soluble in the corroding medium then corrosion proceeds at a faster rate and vice versa. This is because due to continuous removal of corrosion product from the surface, the inner layer of metal comes in contact of corroding medium and corrosion of metal takes place rapidly.

1.5.2. Nature of the corroding environment:

The nature of environment includes following factors:

1.5.2.1. Temperature: In general the rate of corrosion increases on increasing temperature, however wet corrosion at higher temperature becomes slower. The decrease in the corrosion rate on increasing temperature in few cases is attributed due to decreased solubility of gases at elevated temperature. There is a rule of thumb that the corrosion rate of metal becomes double for every 10^0C increase in the temperature. The intergranular corrosion takes place only at higher temperature.

1.5.2.2. pH: pH has very marked effect on the corrosion rate. It has been observed that corrosion takes place more rapidly in acidic ($pH < 7$) aqueous solution as compare to neutral or basic aqueous solution ($pH > 7$). Therefore, the rate of metallic corrosion can be reduced by increasing the pH of corroding medium. For example, the corrosion rate of iron in oxygen- free water is slow, until the pH is below 5. However, the corrosion rate of amphoteric metals such as Al, Zn, and Pb increases on increasing the pH because at high pH i.e. high OH^- concentration they form complex ions and pass into solution.

1.5.2.3. Oxygen Concentration: Generally the rate of corrosion increases with increase in the concentration of the oxygen. This is because differential aeration concentration cell is setup due to change in the concentration of oxygen. In the aeration concentration cell, the less oxygenated part acts as anode and more oxygenated part acts as cathode and the corrosion takes place at the anode. For example, pitting corrosion and water line corrosion takes place due to formation of differential concentration cells resulted due to different oxygen concentrations.

1.5.2.4. Fluid velocity: It is observed that corrosion rate increases with increasing the velocity of the fluid. This because at very low velocity, even zero, there are diffusion effect that cause corrosion. As fluid velocities increase from stagnant to moderate values, the corrosion rate increases. Then, as the limit of diffusion at a particular temperature is reached, further increase in velocity has little effect on the corrosion rate. The increased corrosion rate at high fluid velocity is might be attributed either due mechanical erosion or due to continuous removal of corrosion products from the metal surface or due to combined effect of both.

1.5.2.5. Suspended particles in atmosphere: The suspended particles may be of two types: (i) chemically active suspended particles- NaCl, $(NH_4)_2SO_4$ etc. and (ii) chemically inactive suspended particles- charcoal, etc. Both chemically active and chemically inactive suspended particles increase the corrosion rate when they are present in the medium. The chemically active suspended absorb moisture and thus act as strong electrolytes and thereby enhances corrosion rate. While the chemically inactive suspended particles absorb both moisture as well as soluble gases and therefore slowly enhance corrosion rate.

1.5.2.6. Corrosion inhibitors: In general corrosion inhibitors reduced the corrosion rate by becoming adsorbate at the metallic surface which isolates the metal from the corroding medium. Sometimes, corrosion inhibitors incorporate themselves to corrosion product and enhance the capacity of surface film. The corrosion inhibitors containing polar groups are of particular importance because they can more effectively adsorb on the metal surface and thereby reduced the corrosion rate.

1.5.2.7. Conductance of the corroding medium: Rate of the electrochemical corrosion depends upon the conductive nature of the medium. In general, in high conducting medium corrosion rate will be high. For example, the underground or soil corrosion will be greater in presence of salt or moisture in the earth i.e. if the conductance of soil is more the soil corrosion of the metal will be more rapid.

1.5.2.8. Nature of electrolyte: The presence of counter ions such as Cl^-, SO_4^{--} and $^-NH_2$ etc. increases the rate of corrosion. For example, the chloride ions present in the corroding medium destroyed the protective film and metal surface is exposed to further corrosion.

1.6. Corrosion thermodynamics

Most of the pure metals have an inherent tendency to corrode due to their association with high energy. Thermodynamics can use to evaluate the theoretical activity of a given metal or alloy in corrosive environment. In general corrosion reaction for a metallic material occurs when the change in free energy ΔG is associated with negative sign. In an electrochemical cell at equilibrium, no flows and the energy change occurring in a reaction is expressed in equation:

$$\Delta G = -nF\,\Delta E \qquad (12)$$

where ΔE is equivalent to the electromotive force of the reaction considered and commonly referred as potential difference across the electrochemical cell, and n is the number of electrons transferred and F is the Faraday constant. Under standard conditions, the the standard free energy of the cell reaction, ΔG^0 is directly related to the standard potential difference across the cell, E^0:

$$\Delta G^0 = -nF\,\Delta E^0 \qquad (13)$$

The thermodynamic condition of spontaneity of the corrosion process thus becomes:

$$\Delta G^0 < 0 \text{ and } \Delta E^0 > 0 \qquad (14)$$

Thermodynamically, variation of free energy is expressed by the equation:

$$\Delta G = \Delta G^0 + \mathrm{RT} \ln Q_{\mathrm{reaction}} \qquad (15)$$

where, for a generalized equation of the form:

$$\mathrm{aA + bB + \ldots \longrightarrow mM + nN + \ldots} \qquad (16)$$

In the above equation, the capital letters *A, B, M* and *N* represent respectively the reactants and products of a given reaction while the small letters represent the coefficients required to balance the reaction.

$$Q_{\text{reaction}} = \frac{a_M^m \times a_N^n}{a_A^a \times a_B^b}$$

(17)

At equilibrium, $\Delta G^o = 0$ and Q_{reaction} corresponds to the equilibrium constant (K_{eq}) described earlier. In electrochemical reaction, substitution of the relationships $\Delta G = -nFE$ and $\Delta G^0 = -nFE^o$ into the expression of a reaction free energy and division of both sides by $-nF$ gives the Nernst equation for an electrode reaction:

$$E = E^0 - \frac{RT}{nF} \ln Q_{\text{reaction}} \tag{18}$$

Or

$$E = E^0 - \frac{0.059}{n} \log_{10} Q_{\text{reaction}} \tag{19}$$

In the above equation, the electrode potential (E) would be the actual potential difference across a cell containing this electrode as a half-cell and a standard hydrogen electrode as other half cell. Alternatively, the relationship in equation can be used to combine two Nernst equations corresponding to two half-cell reactions into the Nernst equation for a cell reaction:

$$E_{\text{cell}} = (E^0_{\text{cathode}} - E^0_{\text{anode}}) - \frac{RT}{nF} \ln Q_{\text{reaction}} \tag{20}$$

Similarly, by the temperature dependency of standard free energy change (ΔG^0), other thermodynamic parameters such as standard entropy change (ΔS^0) and standard enthalpy change (ΔH^0) can be derived from electrochemical measurements:

$$\Delta S^0 = -\left(\frac{\partial \Delta G^0}{\partial T}\right)_P \tag{21}$$

Alternatively,

$$\Delta S^0 = nF\left(\frac{\partial E^0}{\partial T}\right)_P \tag{22}$$

And

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 = nF\left[T\left(\frac{\partial E^0}{\partial T}\right)_P - E^0\right] \tag{23}$$

The equilibrium constant (K_{eq}) for same reaction can be obtained from following equation:

$$RT \ln K_{eq} = -\Delta G^0 = nFE^0 \tag{24}$$

The thermodynamic prediction of metallic corrosion was illustrated by potential-pH diagrams known as Pourbaix diagrams or Potential-pH diagrams [Pourbaix (1974)]. In Pourbaix diagram plots, the equilibrium potential (E_{eq}) between a metal and its various oxidized species as a function of pH. The Pourbaix diagrams are plotted for various equilibria on normal Cartesian coordinates with potential on vertical axis and pH on the horizontal axis or abscissa. As, it is well known that nature and rate of metallic corrosion in aqueous solution depends not only the electrode potential but also to the acidic and basic nature of the medium, that is the pH of the medium. The general metal dissolution reaction in the aqueous medium can be represented as:

$$M = M^{z+} + ze^{-} \tag{25}$$

The Pourbaix diagram takes account of electrochemical and chemical equilibria of metals in conjunction with water, and since there are several such equilibria for each metal, only one metal can be clearly represented on one diagram. Figure 1.4 shows the *E-pH* diagram of general metal (*M)* dissolution reaction which can be represented by the Nernst equation as:

$$E_{eq}^{M^{z+}/M} = \Delta E_{\circ}^{M^{z+}/M} - \frac{0.0059}{z}\log a_{M^{z+}} \tag{26}$$

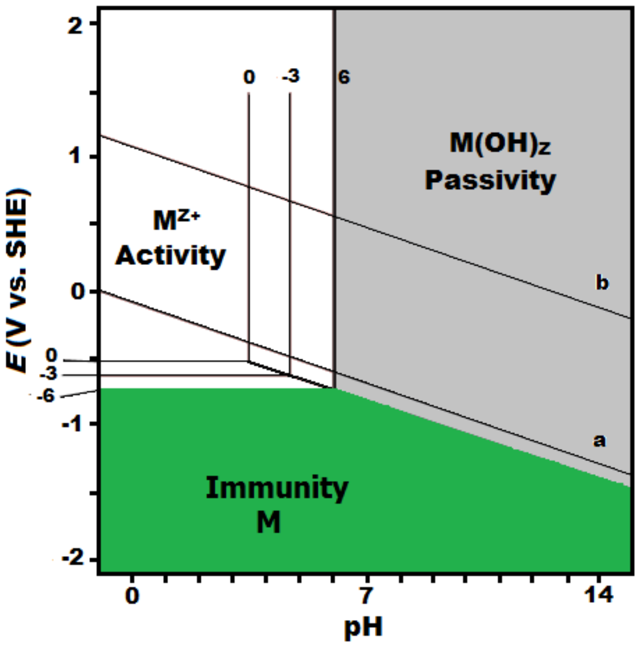


Figure 1.2: *E-pH* diagram for a generic metal M which forms hydroxides.

The line characterized by a value of the parameter corresponding to the concentration of 10^{-6} mol/L divides the plane into two regions: the upper corrosion region for concentrations above this value and the lower thermodynamic stability region of metal

M for lower concentrations, also known as the immunity zone. In Figure, the generic line of equation separates the immunity zone from that of hydroxide formation, also known as the passivity zone. The potential-pH diagram for iron exposed to water has been shown in Figure 1.3. It is necessary to consider the following equilibria before drawing the potential diagram for iron:

$Fe \longrightarrow Fe^{2+} + 2e^-$ (Corrosion reaction) (27)

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ (Oxidation reaction) (28)

$Fe(OH)_3 + 3H^+ + e^- \longrightarrow Fe^{2+} + 3H_2O$ (Precipitation reaction) (29)

$Fe^{2+} + 2H_2O \longrightarrow Fe(OH)^{2+} + 2H^+$ (Hydrolysis reaction) (30)

$2Fe + 3H_2O \longrightarrow Fe_2O_3 + 6H^+ + 6e^-$ (Corrosion reaction) (31)

$Fe + 3H_2O \longrightarrow HFeO_2^- + 3H^+ + 2e^-$ (Corrosion reaction) (32)

$HFeO_2^- + H_2O \longrightarrow Fe(OH)_3 + e^-$ (Precipitation reaction) (33)

$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$ (Precipitation reaction) (34)

In above reactions, reactions 27, 28 and 33 are pH independent, which represented by straight horizontal lines in the Pourbaix diagrams. Whereas, reactions 29, 31 and 32 are pH and potential dependent are represented by the E_H/pH plots by sloping lines. Reaction

30 and 34 are only pH dependent and are represented by vertical lines.

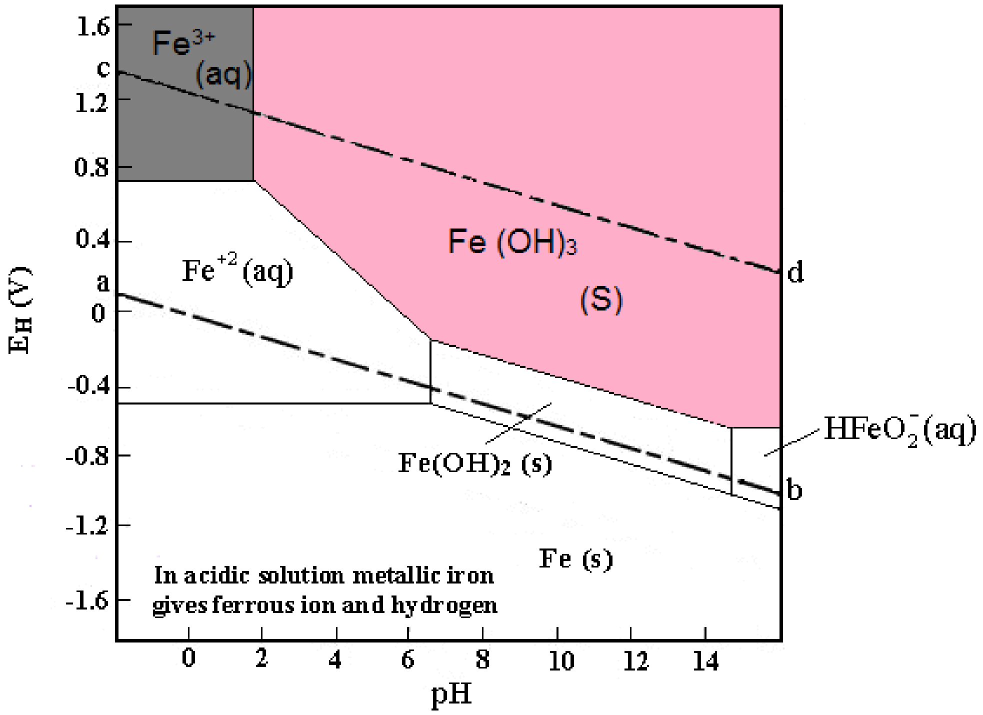


Figure 1.3: Pourbaix diagram for iron/water system at 298 K.

The evolution of oxygen occurs above the ‘cd’ line, below this line no evolution of oxygen occurs. Whereas, evolution of hydrogen occurs below the ‘ab’ line, above this line no evolution of hydrogen takes place. The evolution of oxygen and hydrogen occur as:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad (35)$$

$$H^+ \rightarrow \frac{1}{2}H_2 + e^- \qquad (36)$$

The careful visualization of the Pourbaix diagram it is observed that the hydrogen electrode redox potential (line ‘ab’) lays above immunity region throughout the pH scale. This result suggests that the evolution of hydrogen in aqueous solution by the dissolution of Fe takes place at all pH values. However, in the pH range of 9.4 – 12.5, a passivating layer of $Fe(OH)_2$ is formed . At higher values of pH soluble hypoferrite can form within a restricted active potential range. The passivating layer of $Fe(OH)_3$, or Fe_2O_3:nH_2O, or Fe_2O_3 formed in the corroding medium at higher redox potential. In alkaline solution, soluble ferrate (FeO_4^{-2}) can form at very noble potential, but the stable field is not well defined.

It has been noted that although, Pourbaix potential-pH diagram is very useful in showing at a glance specific conditions of potential and pH under which the metal will corrode, it has several shortcoming regarding their use in the practical corrosion problems.

1.7. Kinetics of corrosion

Thermodynamic principles can help explain a corrosion situation in terms of the stability of chemical species and reactions associated with corrosion processes and can only give information about the reactions that occur, not necessary on the reactions that will occur. Moreover, thermodynamics does not give information on the reaction rate. The rate at which metal is consumed can be controlled by the kinetics of either the anodic or the cathodic reaction (or often both) [Pedeferri (2007)].

1.7.1. The Exchange Current Concept: Kinetics at Equilibrium

The concept of exchange current density implies that rate of dissolution and deposition reactions are equal at equilibrium. When anodic and cathodic reactions are in equilibrium, the rates (equal and opposite) of each of the two reactions are referred to as exchange current density. On expressing reaction rates in the term of corrosion current density we have:

$$\mathrm{M} \rightarrow \mathrm{M}^{Z+} + ze^{-} \tag{37}$$

$$\mathrm{M}^{Z+} + ze^{-} \rightarrow \mathrm{M} \tag{38}$$

Where, first reaction represents the anodic current (i_a) and, second reaction represents the cathodic current (i_c). The sum of these two current densities at equilibrium should be zero:

$$i_a + i_c = 0 \tag{39}$$

$$i_a = -i_c = \mathrm{i}_0 \tag{40}$$

i_o is termed as exchange current density which is the rate of oxidation and reduction at equilibrium. There is no net current under the above conditions even through the concept is a useful method of representing rates at equilibrium.

$$i_{net} = i_a - i_c = 0 \tag{41}$$

For the characterization of electrochemical processes, it is always preferable to normalize the value of the current by the surface area of the electrode and use the current density, often expressed as a small *i*, *i.e.*, $i = I$/surface area.

1.7.2. Kinetics Under Polarization

Whenever more than one complimentary reactions such as oxidation and reduction reactions occur over a metallic surface, the electrode potential of the metal will no longer be at an equilibrium value. The deviation of potential from the equilibrium potential is referred as “polarization”. The magnitude of the polarization is generally measured in terms of overvoltage (η), which is a measure of polarization with respect to the equilibrium potential (E_{eq}) of an electrode. There are three different kinds of polarization, namely activation polarization (η_{act}), concentration polarization (η_{conc}) and ohmic drop (iR) produced in any electrochemical cell. The total polarization across an electrochemical cell will be the summation of the all kinds of polarization as denoted by following equation:

$$\eta_{total} = \eta_{act} + \eta_{conc} + iR \qquad (42)$$

In this equation, activation over potential (η_{act}) describes the kinetics of charge transfer of the electrochemical processes and is predominant at small polarization current or voltage, concentration over potential (η_{conc}) represents the mass transfer limitations associated with electrochemical processes and is predominant at larger polarization current or voltage and ohmic drop (iR) represents the polarization that occur when a current passes through an electrolyte or through any other interface, such as surface film.

1.7.2.1. Activation polarization or activation over potential (η_{act})

When a certain step in an electrochemical half-cell reaction controls the rate of electron flow, the reaction is said to be under activation charge transfer control and activation polarization results. For example, consider the reduction of hydrogen ions (H^+):

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (43)$$

The evolution of hydrogen gas occurs in four major steps:

(a) H^+ is adsorbed at the electrode surface

(b) H^+ reduced to H (atom) by picking electrons on the surface

(c) Two reduced species combine together to form hydrogen molecule

(d) Hydrogen bubbles are formed by the combination of hydrogen molecules

The rate of hydrogen evolution is determined by slowest step. The rate controlling step depends upon the nature of metal, current density and environment. There is a critical activation energy needed to overcome the energy barrier associated with the slowest step. The rate of transformation is controlled by magnitude of energy barrier that an atom or ion must overcome to transform from metal to ion. The energy that must be acquired is the activation energy. A general representation of the polarization of an electrode supporting one redox system is given in the Butler-Volmer equation [Butler (1924)]:

$$i = i_{o}\left(\exp^{(\alpha F\eta/RT)} - \exp^{-((1-\alpha)F\eta/RT)}\right) \tag{44}$$

For multi-electron transfer reactions, the electrons can be transferred in a single step or in multistep process. The Butler-Volmer equation becomes [Bockris *et al.* (1970)]:

$$i = i_{o}\left(\exp^{(\alpha_a F\eta/RT)} - \exp^{-((1-\alpha_c)F\eta/RT)}\right) \tag{45}$$

Where α_a and α_c are transfer coefficients of oxidation and reduction reactions. where *i* is the anodic or cathodic current, *n* is the number of participating electrons, *R* is the gas constant, *T* is the absolute temperature, *F* is the Faraday constant.

when η_{reaction} is anodic, then i_a can be more simply expressed by

$$i_a = i_0 \left\{ \exp\left(\beta_a \frac{nF}{RT} \eta_a \right) \right\} \tag{46}$$

$$\eta_a = b_a \log_{10}\left(\frac{i_a}{i_0} \right) \tag{47}$$

where b_a is the Tafel coefficient that can be obtained from the slope of a plot of η against log i, with the intercept yielding a value for i_0

$$b_a = 2.303\frac{RT}{\beta nF} \tag{48}$$

Similarly, η_{reaction} is cathodic,

$$i_c = i_0\left\{-\exp\left(-(1-\beta_c)\frac{nF}{RT}\eta_c\right)\right\} \tag{49}$$

$$\eta_c = b_c \log_{10}\left(\frac{i_c}{i_0}\right) \tag{50}$$

$$b_c = -2.303\frac{RT}{\beta nF} \tag{51}$$

1.7.2.2. Concentration polarization

When the cathodic reagent at the corroding surface is in short supply, the mass transport of this reagent could become rate controlling. A frequent case of this type of control occurs when the cathodic processes depend on the reduction of dissolved oxygen. Because the rate of the cathodic reaction is proportional to the surface concentration of the reagent, the reaction rate will be limited by a drop in the surface concentration. For a sufficiently fast charge transfer, the surface concentration will fall to zero, and the corrosion process will be totally controlled by mass transport. The region near the metallic surface where the concentration gradient occurs is also called the diffusion layer, δ. Since the concentration gradient ($\delta C/\delta x$) is greatest when the surface concentration of a species is completely depleted at the surface (i.e., $C = 0$), it follows that the cathodic current is limited in that condition, as expressed by:

$$i_c = i_L = -nFD_0 \frac{C_{,bulk}}{\delta} \tag{52}$$

For intermediate cases, η_{conc} can be evaluated using an expression derived from the Nernst equation: $\eta_{conc} = \frac{2.303RT}{nF} \log_{10}\left(1 - \frac{i}{i_L}\right)$

(53)

1.8. Corrosion protection methods

Corrosion is a severe problem which can be control by following ways:

1.8.1. By using pure metals: It has been studied that pure metals have higher corrosion resistance as compare to metal with impurities for example presence of 0.02% iron as impurity decrease its corrosion resistance property.

1.8.2. By selection of materials: Selection of the proper metal depending upon the environment is essential corrosion control. For example, noble metals are most resistance to corrosion and therefore used in surgical instruments and ornaments.

1.8.3. By alloying: Sometime presence of metal impurity in the metal alloys increases the corrosion resistance as well as the mechanical strength of the metal**.** For example, presence of small amount of chromium which forms a protective surface film increases the corrosion resistance property of the stainless steel.

1.8.4. Annealing: While considering metallic corrosion protection measures, the heat treatment such as annealing helps to reduce the internal stresses and therefore reduce the probability of stress corrosion.

1.8.5. By eliminating galvanic action: When to dissimilar metals are in galvanic contact, their selection should be based on the facts that their oxidation potentials are as near as possible. Moreover, the cathodic area should be lower than anodic area in galvanic contacts, for example, use of copper nuts and bolts on large steel plate. The galvanic contact can also be reduced by inserting the insulating materials between two metals.

1.8.6. By cathodic protection: The criterion behind cathodic protection is that metal is induced to behave like cathode. Because in that situation there will be no any anode on the metal surface and therefore corrosion will not occur. The cathodic protection may be of two types:

1.8.6.1. Sacrificial anodic protection: In this method, a metal which is comparatively more susceptible to corrosion is connected with metal structure to be protected and therefore corrosion is mainly localized over more corrosive metal thus protecting the metal structure from corrosion. For example, in sea running vehicles such as ships and boats the sheets of zinc or magnesium are hung near the hull of the ship. These sheets are more prone to corrosion, preferably corrode and protect iron from corrosion. Since sheets of zinc and magnesium are sacrificed in the process of iron corrosion protection, they are called as sacrificial corrosion. After complete consumption of sacrificial anode (Zn, Mg), these anodes should be replaced by new one.

1.8.6.2. Impressed current cathodic protection: In this type of cathodic protection, an impressed current is applied to the corroding metal in opposite direction in order to nullify the corrosion current and converting metal from anode to cathode. Because this method of corrosion protection involves external source to produced impressed current on the system, this is called impressed current method.

1.8.7. By modifying the environment: Since the rate of metallic corrosion mainly depends upon nature of environment, on suitably modifying the environmental condition the rate of corrosion can be reduced. The environment can be modify by following ways:

1.8.7.1. Deaeration: Since presence of oxygen in the corroding environment increases the rate of cathodic reaction, therefore removal of oxygen from the environment decreases the corrosion rate. To remove oxygen from corrosive solution some chemical compounds known as scavenger (eg. Na_2SO_3) being added which remove the dissolved oxygen.

1.8.7.2. Dehumidification: Moisture of the environment can be removed by lowering the relative humidity of the surrounding air which can be achieved by allowing the adsorption of the moisture on the silica gel surface.

1.8.7.3. By application of inhibitors: In this type of corrosion protection technique some chemical compounds known as corrosion inhibitors are added into the corrosive solution in small amount which significantly decreases the corrosion rate. In the oil and extraction industries inhibitors have always been considered to be the first line of defense against corrosion. In general, corrosion inhibitors inhibit metallic corrosion by adsorbing and forming the protective surface film. These inhibitors may be of following types:

(a) Anodic or passivating inhibitors:

Passivating inhibitors are one of the most important inhibitors which slow down the cathodic reactions or relatively precipitate on the anodic areas and shifts the corrosion potential toward more noble direction. The passivating inhibitors lead to the rapid formation of a protective oxide layer over the anodic sites on the metal corroding surface [Rozenfeld (1981); Khan (1993)]. A passivating -type inhibitor functions by producing local-action current which anodically polarizes a metal into the passive potential region and thereby provides the means for obtaining a noble mixed potential. The major factors which determine whether a particular system will exhibit passivity or not are: (a) reversible potential of the redox system created by the oxidizing inhibitor; (b) electrochemical parameters for reduction of the inhibitor on the metal surface (exchange current, Tafel slope, and limiting diffusion current), and (c) critical anodic current and Flade potential of the metal. The anodic inhibitors may be following types:

(1) Oxidizing anions: The anions such as chromate, nitrate and nitrite can passivate metal in absence of oxygen.

(2) Non-oxidizing anions: These anions can passivate metal surface only in presence of oxygen e.g. phosphate, tungstate and molybdate.

(b) Cathodic inhibitors:

Generally, these inhibitors either decrease the rate of cathodic reaction itself or selectively precipitate on the cathodic areas in order to increase the impedance of the metallic surface and thereby limit the diffusion of the reducible species of these areas [Stern (1958)]. The effectiveness of cathodic inhibitors mainly depends upon water quality, flow regime and composition of the electrolytes. The cathodic inhibitors can inhibit metallic corrosion by following three mechanisms:

(1) **Cathodic poison:** During acidic electroplating and pickling, metal can adsorbs hydrogen during cathodic discharge or aqueous corrosion which can cause hydrogen induced cracking of the metal. In order to prevent this undesirable reaction some chemicals such as antimony, arsenic, sulfur, tellurium, selenium and cyanide ions, known as cathodic poison are added into the acid solution during above process. The cathodic poison hinder the hydrogen atoms from forming hydrogen gas and thereby reduces the changes of hydrogen induced metallic cracking.

(2) **Oxygen scavengers:** These cathodic inhibitors act by reacting with the dissolved oxygen for the corrosion reduction and therefore slow down the rate of cathodic reaction. The sulfite and bisulfite are the best examples of the oxygen scavengers.

(3) **Cathodic precipitates:** some species like zinc, cadmium and magnesium precipitated on the surface of the metal to form protective film

(c) Filming inhibitors: The filming inhibitors are also known as precipitation inhibitors because these inhibitors generally precipitate on the metallic surface and form protective surface film. Most common filming inhibitors are silicates and phosphates, for example in aerated hot water systems, sodium silicates protect steel, copper and brass. Further, due to same reason the hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film.

(d) Volatile corrosion inhibitors (VCIs):

The volatile corrosion inhibitors are chemical species which have significantly high vapour pressure and act as efficient inhibitors for corrosion under vapour phase condition even in presence of water vapour in the air. The use of this type of inhibitors is one of the most effective and convenient methods for preventing metallic corrosion and equipments during storage and transportation [Bastidas *et al.* (2005); Vuorinen *et al.* (2004)]. These inhibitors slowly release compounds within the closed airspace that can effectively prevent surface corrosion. A typical application of these inhibitors is to prevent corrosion of stored tools or parts inside the sealed bags, boxes or cupboards. The VCI molecules form a protective invisible film of few molecules thick over the surface and this protective layer will remain on the surface of the metal as long as there is no significant, continuous exchange of air within the enclosure. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH toward less acidic and corrosive values. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine, and hexamethylene amine are used as VCIs.

(e) Inorganic corrosion inhibitors:

Several inorganic anions such as Br^- and I^- and oxides like As_2O_3, Sb_2O_3 possesses substantial corrosion inhibition property in the acid solutions [Halusler (1979)]. These species deposited over metallic surface in form of their oxides and increase the hydrogen over voltage and thereby increases the corrosion resistance [Juttner (1980)]. Moreover, certain heavy metal bivalent cations such as Pb^{2+}, Mn^{2+}, and Cd^{2+} etc. possess the inhibition character for mild steel corrosion in the acid solution. The corrosion inhibition property of these species is attributed due to deposition of cations over the metallic surface [Poling (1967)].

(f) Mixed type inhibitors

Certain chemical species such as gelatin, glue and other high molecular weight compounds inhibit metallic corrosion by interfering with the both cathodic and anodic reactions and so called mixed type inhibitors. Generally, these chemical species inhibit metallic corrosion by forming non-porous surface layer which increases the electrical resistance of the surface layer.

(g) Organic corrosion inhibitors

A large number of organic chemical compounds those contain heteroatoms such as N, O, S, and/ or also contain π and non-bonding electrons have been used as corrosion inhibitors. The organic inhibitors include several classes of the organic compounds like aldehydes, alcohols, murcaptans, urea and Thiourea derivative, etc. [Evans (1948); Zucchini *et al.* (1971)]. Depending upon the mode of their inhibition action and electrode potential, these organic inhibitors may be of anodic, cathodic or mixed type [Thomas *et al.* (1967)]. Organic inhibitors are also known as film forming inhibitors as they generally inhibit metallic corrosion by forming hydrophobic surface film on the surface which separates the metal from corrosive environment. The effectiveness of organic inhibitors depends upon their chemical composition, nature of substituents, environmental temperature, nature of environments and their affinity to the metal surface. Since organic compounds inhibit metallic corrosion by adsorbing on the surface, the presence of heteroatoms like N, O, S, and P along with double and bonds of aliphatic and aromatic rings which can act as adsorption centers and their molecular structures are important parameters that determine their effectiveness [Quraishi *et al.* (1996); Muralidharan and Iyer (1997); Hammouti *et al.* (1997); Monika *et al.* (2005)]. The organic inhibitors may adsorb on the metallic surface in their neutral, cationic or anionic form and their effectiveness depend upon their charge and charge of the metallic surface. Cationic inhibitors such as amines and anionic inhibitors such as sulfonates will adsorb preferably depending on whether the metal surface is positively or negatively charged. The extent of corrosion inhibition by organic inhibitors generally increases with increasing their concentration because the surface coverage value increases along with the concentration. However, after certain concentration when the maximum surface coverage occurs, inhibition efficiency does not increase significantly on further increasing the inhibitors concentrations.

Recently, several authors have investigated the corrosion inhibition property of the several organic classes of compounds such as thiazoles derivatives [Lebrini *et al.* (2007)], sulphonamides [Arslan *et al.* (2009)], thiophene Schiff's bases [Issaadi *et al.* (2011)], semicarbazones and thiocarbazones [Goulart *et al.* (2013)], phenothiazine derivatives [Bostan *et al.* (2012)], dihydroquinazolinone [Ayati *et al.* (2011)], thioamides [Hosseini *et al.* (2010)], thiophene derivatives [Bouklah *et al.* (2004)], pyridinthiourea [Hosseini and Azimi (2009)], phenanthrothiadiazole dioxide [Grillo *et al.* (2009)], Phenyl-substituted amino Thiadiazoles [Tang *et al.* (2009)], pyridine-pyrazole [Tebbji *et al.* (2005)], mercaptothiadiazole derivative [Solmaz *et al.* (2011)], diphenylbenzoquinoxaline [Obot and Obi-Egbedi (2010)], benzoylthiourea derivatives [Li *et al.* (2010)], blue tetrazolium [Doner *et al.* (2011)], aminomercaptothiadiazole [Safak *et al.* (2012)], and phenoxyoxopentanes [Trabanelli and Carassiti (1970)] etc. those exhibited high inhibition efficiency for metals in different aggressive media. These inhibitors should have following properties:

- Ability to protect the metal surface.
- High activity to be used in small quantities (ppm).
- Environmentally Friendly Corrosion Inhibitors
- Low cost compound(s).
- Inert characteristics to avoid altering a process.
- Easy handling and storage.
- Preferably with low toxicity.
- Non-contaminant.
- It should act as an emulsifier.
- It should act as a foaming agent.

1.9. Mechanism of corrosion inhibition in acid solution

The inhibition of metallic corrosion by organic compounds in acid solution is resulted due to their adsorption on the surface. The inhibitor molecules may adsorb on the mild steel surface in acid solution by electrostatic interaction between positively charge inhibitors and already adsorbed counter ions (physisorption), interaction between unshared electron pairs of heteroatoms and vacant d-orbital of surface metal atoms (chemisorption), interaction between π- electrons of aromatic rings and vacant d-orbital of surface Fe atoms(chemisorption) and/or interaction between of d-electron of surface iron atom and vacant antibonding molecular orbitals of the inhibitor molecule (retro donation) [Yadav *et al.* (2010); Machu (1961)].

The presence of the inhibitors in the corrosive environments results into significant decrease in the rate of anodic reaction, the cathodic reaction and/or both the reactions. If the shift in the corrosion potential in presence of inhibitors occur in the positive direction then corrosion inhibition resulted due to retardation of anodic reaction (anodic control), whereas if inhibitors shifted corrosion potential toward negative (noble) direction the corrosion inhibition resulted due to retardation of the cathodic reaction (cathodic control). However, in presence of most of the organic inhibitors did not cause significant change in the corrosion potential indicating that these inhibitors neither act as anodic type nor cathodic type but behave as mixed type. Further, generally the presence of inhibitors did not cause any change in the shape of Tafel slopes indicating that these inhibitor inhibit corrosion by adsorbing over the metallic surface and blocking the active sites present on the surface. in addition, the similar shape of Tafel slopes with and without organic inhibitors further indicate that inhibition mainly occur via adsorption processes without changing the mechanism of corrosion [McCafferty (1979)].

1.10. Adsorptive Mechanism of corrosion inhibition

The adsorption of inhibitor at metal/ electrolyte interfaces is occurs by potential difference between metal corroding electrode and the electrolytic solution which is resulted due to unequal distribution of electric charges at the interfaces. The adsorption of organic inhibitors on metallic surface in aqueous acidic solution is occurs mainly by subsequent replacement of water molecules with inhibitors because due to higher dipole moment of inhibitors as compare to water, metal-inhibitor interaction is stronger as compare to metal-water interaction [Antropov (1967)]. It has demonstrated that adsorption of the organic inhibitors on metallic surface in acid solution firstly occur by electrostatic interaction (physisorption) between appositively charged inhibitors and metallic surface and the chemical adsorption of inhibitor molecules take place by their neutral form through unshared electron pairs of hetero-atoms and π electrons.

1.10.1. Adsorption isotherms

Organic compounds inhibit metallic corrosion in acid solution by adsorbing on their surface. The adsorption of inhibitors at metal/electrolyte interface is a very important topic in corrosion inhibition study because it provides significant insights about the inhibition mechanism. The adsorption of an organic adsorbate at metal/electrolyte interface depends upon the nature of the testing media, the chemical structure of the inhibitor, the charge distribution of the inhibitor, nature and surface charge of the metal. The surface coverage value at different concentrations of the investigated inhibitors was subjected to different adsorption isotherm models in order to find best adsorption isotherm. Various adsorption isotherms have been formulated. Table 1.2 gives a list of isotherms and their corresponding equations:

1.10.2. Factors affecting adsorption of inhibitors on metallic surface

Since the adsorption involves the interaction between metal and inhibitor molecule in the acid solution and therefore following factors may affect their adsorption:

(a) Surface charge of inhibitors

Since adsorption of inhibitors on metallic surface depends upon the intermolecular interaction between them, the sign and magnitude of the metallic surface charge play an important role in the adsorption processes. The effect of organic inhibitor on the electrode reactions must be connected with the modification induced in the structure of the electrochemical double layer because of their adsorption. The metallic charge in solution phase generally expressed in the terms of zeta potential. This potential is totally different from the potential on the hydrogen scale and generally the sign of these potentials are also different [Antropov (1967)]. It has been reported that as the potential become more positive, the anionic adsorption is favored and as the potential become more negative, the cationic adsorption favored.

Table 1.2: Different adsorption isotherms.

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

Where,

β = adsorption constant = 1/55.5 (exp-($\Delta G^\circ_{\text{ads}}/RT$)

$\Delta G^\circ_{\text{ads}}$ = 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) Reaction of the adsorbed inhibitors:

In some cases adsorbed inhibitors molecules react with each other to form some chemical products by a phenomenon of electrochemical reduction that may be of inhibitive nature. The inhibition of metallic corrosion by these products is generally known as secondary inhibition [Horner (1972)]. In such case, the inhibition efficiency may increase or decrease with time depending upon the effectiveness of primary and secondary inhibition.

(c) Interaction of adsorbed inhibitor species

Lateral interactions between adsorbed inhibitor species become significant with increase in surface coverage of the adsorbed species. This lateral interaction may be either attractive or repulsive. Attractive interaction occurs between molecules containing large hydrocarbon components. Repulsive interactions occur between ions or molecules containing dipoles. The repulsive interaction leads to weaker adsorption [Hoar and Khera (1961)].

(d) Interaction of the inhibitors with water molecules:

It has been well established that surface of the metal in aqueous solution is covered by the uniform layer of water molecules, and therefore adsorption of the any inhibitor molecule takes place only by subsequent replacement of water molecules from the metallic surface. The displacement of the water molecules from the metallic surface depends upon the free energy change during adsorption process. It is found to increase with the increase in energy of solvation of the adsorbing species.

(e) Structure of inhibitors and their adsorption:

It has been reported that organic inhibitors inhibit metallic corrosion by adsorbing on the surface which resulted into the formation of adsorption bond between metal and inhibitor molecules. the strength of the bonds mainly depend upon the characteristics of metal as well as inhibitor molecules along with nature of electrolyte. It has been also established that adsorption of the organic compounds on metallic surface occurs by electron transfer from inhibitor to metal surface. And therefore, inhibitor molecule with loosely bounds electrons of the anions and neutral heteroatoms along with the π-electrons and multiple bonds that increases conjugation enhances the extent of adsorption. Moreover, most of the organic inhibitors are heterocyclic compounds that contain at least one polar group of heteroatoms like oxygen, nitrogen and sulfur etc. which can also behave as adsorption center during adsorption process. The adsorption of organic inhibitor may involve chemisorption or physisorption depending upon the nature of substituent of inhibitor molecule. Further, the extent of adsorption also depends upon the electron density over the donor atom or functional groups (adsorption centers). The effectiveness of the electron transfer from inhibitor to metal surface among different heteroatoms follows the following order [Hackerman and Makrides (1954)]:

Selenium > Sulphur > Nitrogen > Oxygen

The availability of electron pairs for the formation of bonds in chemisorption process can thus be altered by regular and systematic variations in the molecular structure.

1.10.3. Factors Influencing the Inhibition Reactions

The corrosion inhibition reactions in acidic solution are influenced by the following factors:

(a) Formation of a diffusion barrier

The adsorption of organic inhibitor molecules on the metallic surface resulted into the formation of protective surface film which separates metal from corrosive environment. This protective inhibitor film acts as barrier for diffusion of ions or molecules from metal surface to the corrosive environment and therefore retards the corrosion process.

(b) Blocking of reaction sites

The adsorption of the organic inhibitors on the metallic surface retards the participation of metal in the anodic as well as cathodic reaction of the corrosion. This type of corrosion inhibition mainly occurs via formation surface film which blocks the active sites present on the surface without changing the mechanism of corrosion which is supported by the unaffected Tafel slopes of the polarization curves. In general, organic inhibitors at low surface coverage or low concentration inhibit the anodic reaction. While the organic inhibitors at high concentration or high surface coverage inhibits anodic as well as cathodic reactions.

(c) Participation in the electrode reactions:

Sometime adsorbed inhibitor molecules involve the formation of intermediate species with the surface metallic atoms that may change the electrode processes. These processes involve change in the rate of corrosion without changing the Tafel slope values [Iofa (1966)]. Inhibitors may retard the rate of hydrogen evolution on metals by affecting the mechanism of the reaction with the increase in Tafel slopes of cathodic polarization curve. This effect has been observed on iron in the presence of inhibitors such as phenylthiourea [Cavallaro *et al.* (1964); Kaesche *et al.* (1966)].

(d) Alteration of the electrical double layer:

The adsorption of ions or species on metal surface change the electrical double layer at the metal solution interface, and this in turn affect the rates of the electrochemical reactions i.e. electrochemical corrosion.

1.11. Inhibition of mild steel corrosion in minerals acids

Iron and its alloys are widely used as construction materials in the petroleum, food, power production, chemical and electrochemical industries because of their high thermal and mechanical stability, ease of fabrication and joining, and low cost [El Adnani *et al.* (2013); Verma *et al.* (2015b)]. The acidic solutions are widely used in acid cleaning, acid descaling, oil well acidification and enhanced oil recovery techniques in petroleum and other industries which causes severe economic and safety problems due to corrosion [Shaban *et al.* (2015); Farag and Ali (2015)]. Commonly used mineral acids are sulfuric acid and hydrochloric acid. One of the most important applications of these acids is in the pickling of steel, to remove rust or iron oxide scale from iron or steel before subsequent processing, such as extrusion, rolling, galvanizing and other techniques. However, during these processes, the metals and alloys become gradually destroyed by corrosion upon exposure to the environment due to chemical or/and electrochemical reactions. And, therefore it is important to add some chemical species known as corrosion inhibitor to acid solution during above processes. The corrosion inhibition of mild steel in acid medium has been reported recently by using several class of organic compounds such as polymers, heterocycles, and heteroatoms containing compounds, natural plant extracts and drugs [Yuce and Kardas (2015); Verma *et al.* (2015b); Olasunkanmi *et al.* (2015)]. These acid inhibitors have excellent wetting property, which facilitates acid penetration. This assists in removing different types of scales without difficulty. With the help of our range, pitting embrittlement is avoided and on the whole metal loss is negligible. Barrier layer formation inhibitors form a layer on the corroding metal surface, modifying the surface to reduce the apparent corrosion rate. They represent the largest class of inhibitive substances. Adsorption-type inhibitors are the most common barrier layer inhibitors. In general, these organic compounds are adsorbed and form a stable bond with the metal surface. The apparent corrosion rate decreases as surface adsorption is completed.

1.12. Graphical representation of kinetic data

Electrode kinetic data are typically presented in a graphical form called Evans diagrams or mixed-potential diagrams. However, the representation of the mixed potential behavior is often associated with Professor Evans who has popularized this representation of corrosion polarization measurements.

1.12.1. Evans diagram

Evans diagram is a kinetic diagram which represents electrode potential in volts verses corrosion current in ampere per unit area. Figure 1.4 represents the Evans diagram for iron corrosion in an acid solution.

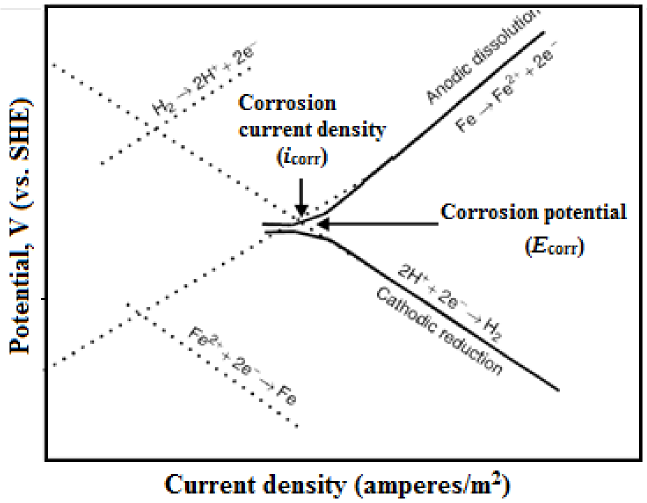


Figure 1.4: Schematic representation of Evans diagram for iron in acid solution.

For this kind of system theoretically four reactions are possible, i.e. oxidation of iron atoms to form ferrous ions (Fe^{+2}), reverse of this process i.e. ferrous ions gain electrons to form iron (Fe), hydrogen ions present in the electrolyte forming hydrogen gas and reverse of this reaction. And therefore, there are four potential (*E*) vs. current (*i*) are possible which are represented in the Evans diagram. For celerity purpose of the thermodynamically feasible reactions are shown in solid lines. The extrapolation these two solid lines give rise to an intercept at the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) for the system.

Generally, Evans diagrams kinetic provide information i.e. rate of corrosion reaction as a function of applied potential. The corrosion potential (E_{corr}) is in effect the line that differentiates the corrosion and immunity regions. In general, if the potential held below E_{corr} in Evans diagram, the rate of anodic reactions i.e. rate of iron dissolution decreases and rate of hydrogen evolution, that is, rate of cathodic reaction increases. While, if the potential held above E_{corr} in Evans diagram, the rate of anodic reactions i.e. metallic dissolution increases and rate of hydrogen evolution, i.e. cathodic reactions increases. And therefore, maintaining the potential below that of E_{corr} is adopted in practice ad is known as cathodic protection.

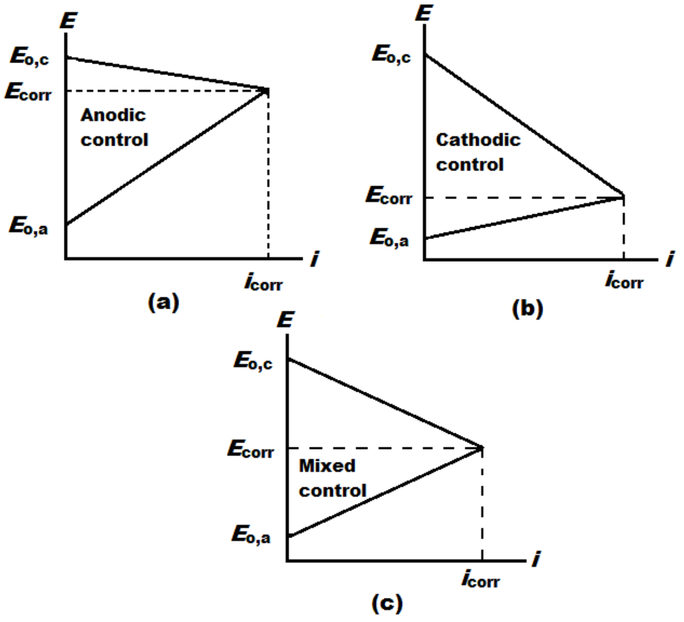


Figure 1.5: (a) Anodic control (b) cathodic control, (c) mixed control of a corrosion process.

Nevertheless, Evans diagrams are a convenient way of viewing electrochemical reactions as shown in Figure 1.5, which tells us the control of electrochemical reaction in either in anodic, cathodic and mixed direction.

1.12.2. Mixed potential theory

The mixed potential theory is simply based on the simple hypothesizes:

(i) Every electrochemical reaction consists of two or more partial oxidation or reduction reactions

(ii) There can be no net accumulation of electric charge during the electrochemical corrosion of metal. This is simply a restatement of the law of conservation of charge.

On this basis it can be concluded that when a metal immersed in an electrolyte it cannot spontaneously accumulate electric charge. And therefore, during corrosion of an electrically isolated metal species, the total rate of oxidation must equal the total rate of reduction.

Corrosion potential and current density

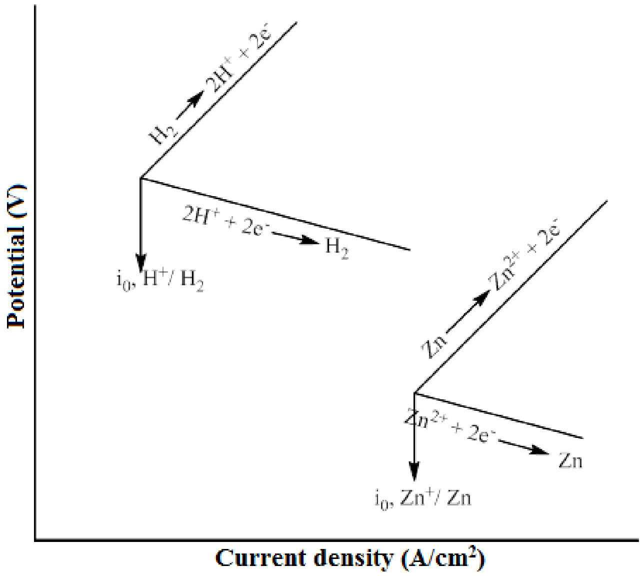


Figure 1.6: anodic and cathodic half-cell reactions present simultaneously on a corroding zinc surface.

To understand what is corrosion potential and corrosion current density, consider the following anodic and cathodic reactions:

$$Zn \longrightarrow Zn^{2+} + 2^{e-} \quad \text{(anodic reaction)} \qquad (54)$$

$$2H^{+} + 2^{e-} \longrightarrow H_2 \quad \text{(cathodic reaction)} \qquad (55)$$

These tow half reactions tales place simultaneously on the metallic surface and each half reaction has its own half-cell electrode potential and exchange current density as shown in Figure 1.6. However, these tow half-cell electrode potential ($E_{Zn2+/Zn}$ and $E_{H+/H2}$) cannot coexist separately on the electro conducting metal surface. And therefore each half cell electrode potential must polarize or change to a common intermediate value which is called as corrosion potential (Ecorr).

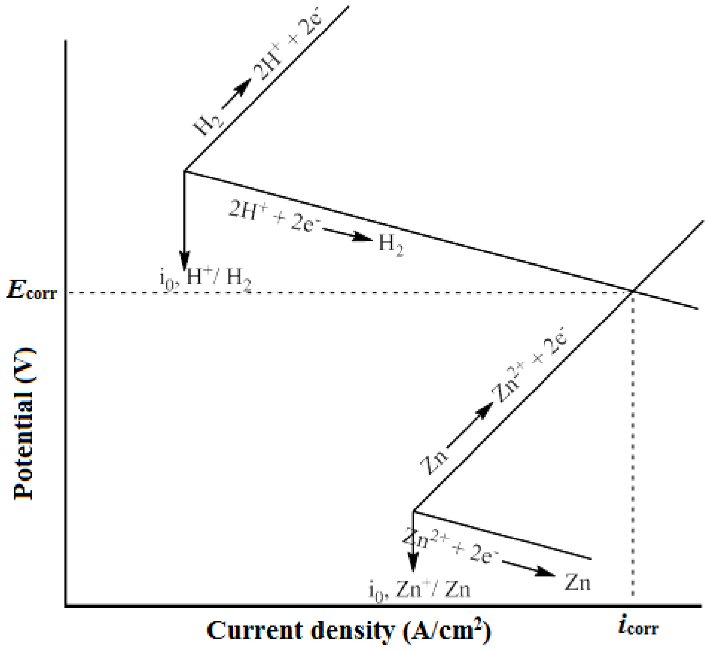


Figure 1.7: Polarization of anodic and cathodic half-cell reactions for zinc in acid solution to give a mixed potential, E_{corr} and a corrosion rate (current density).

The both half-cell reactions polarize on the same metallic surface and during this polarization the half-cell electrode potential changes according to the following relationship until they become equal at E_{corr} as shown in Figure 1.8:

$$\eta_a = \beta_a \log(\frac{i_a}{i_o}) \tag{56}$$

$$\eta_c = \beta_c \log(\frac{i_c}{i_o}) \tag{57}$$

For mild steel corrosion the E vs. i graph is shown in the Figure 1.8. At the point of corrosion potential, the rate of Fe dissolution is equal to the rate of hydrogen evolution expressed in terms of current density.

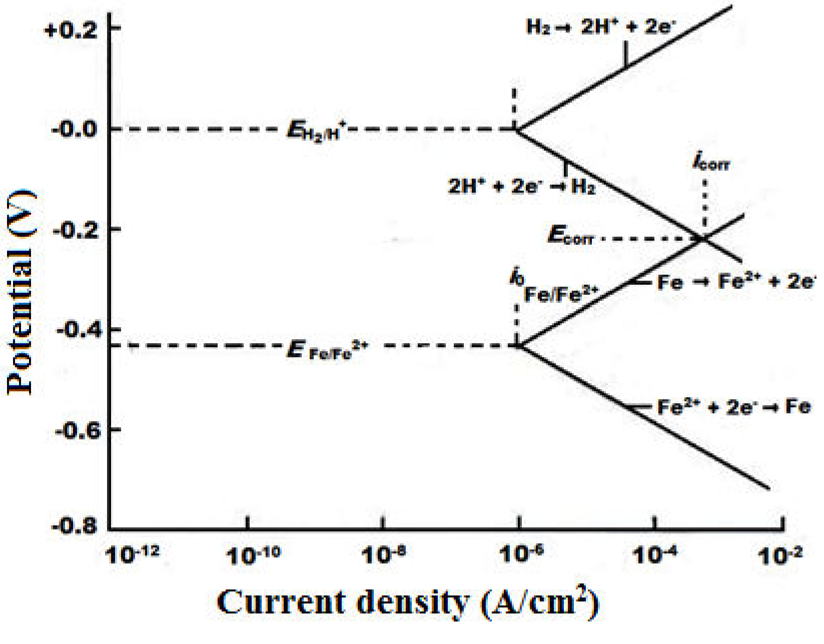


Figure 1.8: "*E vs. i*" for Fe in acid solution.

1.12.3. Tafel extrapolation method

Now it is widely accepted that the rate of general corrosion can be determine by Tafel extrapolation method. The Tafel extrapolation method involves utilization of cathodic and anodic data. Anodic reaction involves the dissolution of mild steel at anode and cathodic reaction involves the hydrogen evolution at cathode and the extrapolation of these two curves gives some important parameters as shown in Figure 1.9. at corrosion potential, the rate of mild steel dissolution, that is anodic reaction will be equal to rate of hydrogen evolution, that is cathodic reaction, and this point corresponds to the corrosion rate of the system expressed in terms of current density. Tafel constants must be calculated from both the anodic and cathodic portions of the Tafel Plot [Shreir *et al.* (1964)]. The Tafel extrapolation method has following advantages:

(a) The Tafel extrapolation method is equal or greater accuracy as compare to convention weight loss method

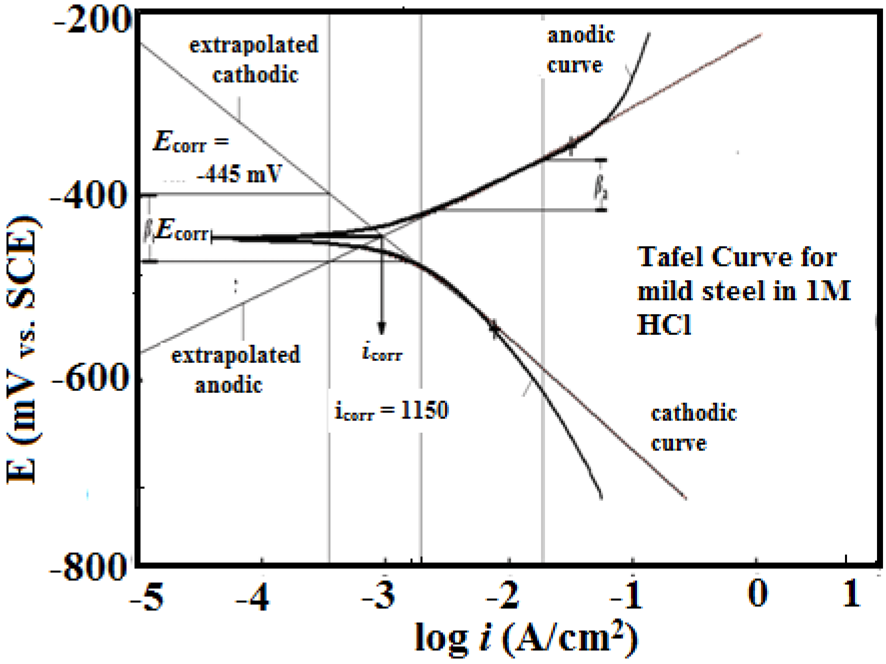


Figure 1.9: Extrapolated Tafel curves.

(b) By employing this method one can continues the monitoring the extremely low corrosion rate of the system

(c) Since the corrosion rate can be measure at extremely low value, the corrosion current can be directly measure using Tafel extrapolation method

(d) The Tafel extrapolation method is a rapid tool and therefore one can quickly study the inhibition evaluation of metal and their alloys.

1.13. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy which is also known as dielectric spectroscopy or impedance spectroscopy, measure the dielectric properties of the medium as a function of frequency. In this technique a small amplitude perturbation is applied to the working electrode at a number of discrete frequencies. Further, the EIS technique measure the impedance of the system over a range of frequencies, and therefore the frequency response of the system including the energy storage and dissipation, is revealed. The main advantages of this technique are:

(a) Applicable to low conductivity system

(b) Provide mechanistic information

(c) Solution resistance is totally eliminated

In EIS technique the electrochemical data expressed graphically in the forms of Nyquist and Bode plots. Impedance is the opposition to the flow of alternating current (AC) in a complex system. Electrochemical impedance is the response of an electrochemical system (cell) to an applied potential. The frequency dependence of this impedance can reveal underlying chemical processes. The response of electrochemical systems is very nonlinear as shown in Figure 1.10.

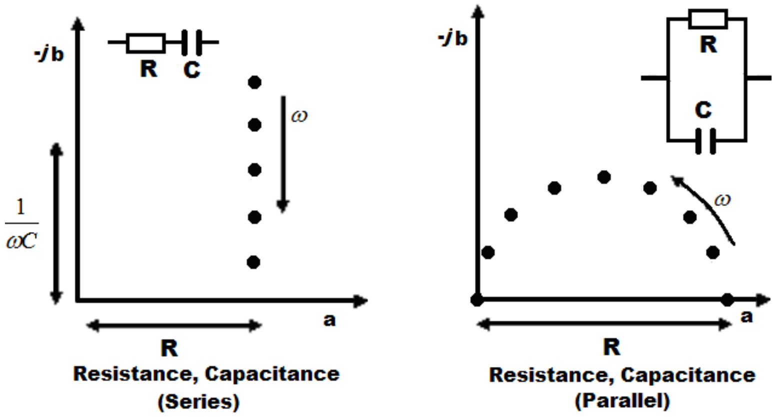


Figure 1.10: Complex plane impedance spectrum.

In present case, we apply small amplitude of ~10 mV) AC ripple on top of the controlled DC polarization potential. The equivalent circuit generally used to explain the complex response of the electrochemical system and display the impedance data in form of Nyquist and bode plots. The Nyquist plots is the most commonly used electrochemical technique which allow easy understanding of the electrochemical behavior of the corroding system. It also offers some easy prediction of the equivalent circuit elements as depicted in the Figure 1.11

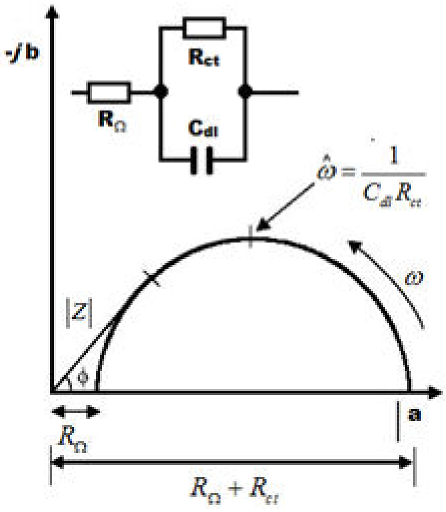


Figure 1.11: Nyquist plot along with constant phase element (CPE).

The response of the electrochemical system as function of small amplitude of perturbation frequency gives information about the internal kinetics of the corroding system. The metal/ electrolyte interface always associate with some capacitance which play very important role while explaining the electrochemical nature of the corroding system. Generally, for a metal corroding in acid solution, the equivalent circuit consists of parallel combination of capacitance and resistance (which represent the corroding interface) in series with the second resistance, as shown in Figure 1.10. The values of various circuit components can be calculated from the series of the equivalent circuit. In the circuit series, the R_{Ω} represents the resistance of the electrolyte caused in the flow of electric charge. The parallel resistance, R_{ct}, which determine the rate of corrosion, is known as charge transfer resistance. The capacitance occurring at metal/electrolyte interface is generally represented by double layer capacitance, C_{dl}. It is well established that in acid solution the metallic surfaces are charged due to excess corrosion of metals which leads to loss of electrons into the electrolyte and accumulation of metals cations on the exterior part of the metals which is balanced by an equal number of the appositively charged particle of the electrolyte. The extent of the force acting between appositively charged species determine the strength of the interface, which in turn determines the magnitude of ion movement (transfer). Generally, the electrochemical impedance spectroscopy measurements are performed after stabilization of the steady state and therefore EIS is a time taking process. The drift in the corroding system being measured is the common cause of problem in EIS measurements.

The electrochemical nature of cell can change through adsorption of the impurities of solution, growth of oxide layers build on metallic surface, formation of corrosion products in solution, coating degradation, and/ or change in temperature are few perturbing factors due to which steady state is difficult to achieve. The EIS data is commonly analyzed by fitting these data in an equivalent circuit model consisting of few common elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most models contain a resistor that models the cell's solution resistance. The aim if EIS analysis is to elucidate the electrode process and to drive its characteristic parameters. It should be noted that the EIS is an important very sensitive technique however does not offer a direct measurement of physical phenomenon [Macdonald (1987)].

1.14. Application of Theoretical Methods in Corrosion Inhibition Studies

1.14.1. Quantum chemical calculations

Recently computational studies using DFT based quantum chemical calculations have gained the substantial advances in determining the molecular structure as well as predicting the electronic structure and reactivity of any given series of compounds. Therefore, it is a common practice to perform quantum chemical calculation in the field of corrosion inhibition. The quantum chemical calculations furnished some important parameters which can be used to predict the reactivity of the inhibitor molecules toward metallic surface and therefore relative affinity of any chemical species can be determine on the basis of these calculations. One’s a series of compounds synthesized, their chemical reactivity can be predicted by simply performing the quantum chemical calculation without doing any experiment and thereby polluting the environment. And thus quantum chemical calculation is a ‘green tool’ which allows the prediction of chemical reactivity of any molecule without performing the experiment [Karelson and Lobanov (1996)].

The quantum chemical calculations give some vital parameters which are derived by employing mathematical equations on the basis of which chemical reactivity of molecule is determined [Bouayed *et al.* (1999)]. Nowadays, the quantum chemical calculation in the field of the corrosion inhibition by organic inhibitors is a very active research. The corrosion inhibition property of the several heterocyclic compounds have been studied by a number of investigators on the basis of quantum chemical calculations which allow the prediction of physiochemical properties of the organic molecules such as presence of functional group, steric effect, electron density of donor atoms and orbital character of donating electrons, and so on towards the metallic surface [Stupnisek-Lisac *et al.* (1994)]. Since, it has been well established that organic inhibitors inhibit metallic corrosion by becoming adsorbate at metals surface; therefore it is essential to correlate their experimental inhibition property with the well-established quantum chemical calculations.

DFT based Quantum Chemical Parameters

The DFT based quantum chemical calculations have been immersed as most powerful theoretical techniques in the last three decades. It not only provides some vital parameters through which chemical reactivity of the molecules are determined but also furnished energetics and structural information of atoms and/or molecules at relatively low cost and high speed. The quantum chemical calculations through DFT method can be successfully applied for atoms, molecules and classical fluids. The DFT based calculation gives the information about properties of ground state of any studding system in which electron density plays an important role. Moreover, DFT method successfully used to study the electronic structures of molecules, ground state of many-body-system with special emphasis of atoms, molecules and the condensed phases. The objective of DFT based calculations is to substitute the wave function of many-body electronic with the electronic density as the basic quantity. For example, the notation BLYP/6-31G* denotes a density functional calculation done with the Becke 1988 exchange functional and the Lee-Yang-Parr correlation functional, with the orbitals expanded in a 6-31G* basis set [Levine (1991)]. Although there is some natural overlap, the derived quantum chemical parameters are fundamentally deferent from the experimentally determined quantities. Unlike experimental measurements, the quantum chemical calculations are devoid of any statistical error. The common quantum chemical parameters which can be used to predict the chemical reactivity of inhibitor molecules are listed bellows:

(a) Atomic charges:

Since adsorption of inhibitor molecules on the metallic surface involves the electrostatic interaction in the first step of adsorption process, the atomic charges in the molecule is important to determine. For this purpose the Mulliken population analysis is mostly used to calculate the charge distribution in a molecule which in turns can be used as descriptor of the molecular polarizability [Murrell *et al.* (1985)].

(b) Molecular orbital energies and related parameters

The E_{HOMO} (energy of highest occupied molecular orbital) and E_{LUMO} (energy of lowest unoccupied molecular orbital) are two most important quantum chemical parameters which can be used to study the interaction between metal and inhibitors. The E_{HOMO} is a measure of the tendency of a molecule to donate its HOMO (highest occupied molecular orbital) electrons to the vacant antibonding molecular orbital of an acceptor molecule during the donor–acceptor interactions. E_{HOMO} generally related with electron donating ability and its high value for any molecule indicates that that particular molecule is susceptible for high electron donation [Murrell *et al.* (1985)]. The E_{LUMO} on the other hand is a measure of the tendency of a molecule to accept electrons into its LUMO (lowest unoccupied molecular orbital) from the appropriate occupied orbital of an electron donor [Fukui (1975)]. The energy gap (E_{LUMO}-E_{HOMO}), ΔE is another index of reactivity of molecules for which a molecule with lower ΔE is usually more reactive and possesses higher inhibition efficiency [Lewis *et al.* (1994)]. Similarly, few other parameters such as global softness (σ), global hardness (η), absolute electronegativity (χ), and fraction of electron transfer (ΔN) can be derive from the values of E_{HOMO} and E_{LUMO}. Generally, corrosion inhibition efficiency of organic molecules increases with increasing the value of global softness and decreases with increasing the value of hardness. The electronegativity is a measure of tendency to trap of electrons from any inhibitor molecule. A higher value of electronegativity for any organic molecule indicates that it has low tendency to donate its electron to the metal surface, while a lower value of electronegativity suggests the strong interaction between metal and inhibitor molecule and therefore exhibit high inhibition performance. The fraction of electron transfer is other important quantum chemical calculation parameter which inform about the extent of electron transfer from inhibitor to metal surface. Generally, the magnitude of inhibition efficiency increases with increasing values of fraction of electron transfer.

(c) Dipole moment

Dipole moment is the most widely used quantity to describe the polarity of molecule. this is measure of polarity of polar covalent bond which can be defined as the product of charge on the atoms and the distance between the bonded atoms. In general on increasing polarity of molecule, the global polarization increases resulting into an increase in the effective surface area. Thus, a molecule with high dipole moment will cover larger metallic surface area and therefore will exhibit high inhibition efficiency. However, the negative trends of inhibition efficiency are also reported by few authors where the increases in the polarity decrease the inhibition performance of the inhibitor molecule [Kikuchi (1987)].

(d) Fukui indices

The Fukui functions f^+ and f^- are local reactivity indices that are often used to analyze the relative susceptibility of the active atomic sites of an inhibitor molecule to electrophilic and nucleophilic attacks respectively [Gomez *et al.* (2006); Yan *et al.* (2013)]. The atom condensed Fukui functions using the Mullikan population analysis (MPA) and the finite difference (FD) approximations approach introduced by Yang and Mortier [Yang and Mortier (1986)] are being used to calculate the Fukui indices. The Fukui indices, f^+ and f^- are calculated to predict the most probable atomic sites for nucleophilic and electrophilic attacks, respectively. The regions of the molecules with higher values of f+ are more susceptible to attack by electron rich species, while the sites of the molecules with higher values of f^- are more disposed to interactions with electron deficient species.

1.14.2. Molecular dynamics simulations

Molecular dynamics (MD) is a computer simulation method for studying the physical movements of atoms and molecules, and is thus a type of N-body simulation. The atoms and molecules are allowed to interact for a fixed period of time, giving a view of the dynamical evolution of the system. In the most common version, the trajectories of atoms and molecules are determined by numerically solving Newton's equations of motion for a system of interacting particles, where forces between the particles and their potential energies are calculated using interatomic potentials or molecular mechanics force fields. The method was originally developed within the field of theoretical physics in the late 1950s [Alder and Wainwright (1959)] but is applied today mostly in chemical physics, materials science and the modeling of biomolecules. The heart of any molecular dynamics scheme is the force model used to analytically describe the atomistic interactions. Regardless of the merits of the other algorithms in the simulation code (integrators, pressure and temperature controls etc.), whether or not the simulation produces realistic results depends ultimately on the force model [Alder and Wainwright (1957)].

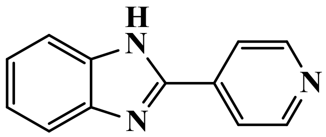
Molecular dynamics simulations help in finding the most stable adsorption sites on metal surfaces through finding the low energy adsorption sites on both periodic and non-periodic substrates or to investigate the preferential adsorption of mixtures of adsorbate components. After minimizing the Fe (111) surface and the inhibitor molecules, the corrosion system will be built by layer builder to place the inhibitor molecules on the Fe (111) surface, and the behaviors of these molecules on the Fe (111) surface were simulated using the COMPASS (condensed phase optimized molecular potentials for atomistic simulation studies) force field. The adsorption locator module in Materials Studio 6.0 [Khaled and Abdel-Shafi (2011)] has been used to model the adsorption of the inhibitor molecules onto the Fe (111) surface and therefore provides access to the energy of the adsorption and its effects on the inhibition efficiencies of the studied amino acid. The binding energy between the asparagine inhibitor and the Fe (111) surface were calculated using the following equation [Khaled (2008)]:

$$E_{\text{binding}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhibitor}}) \qquad (58)$$

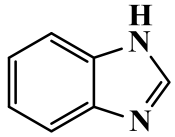
Where, E_{total} is the total energy of the surface and inhibitor, E_{surface} is the energy of the surface without the inhibitor, and $E_{\text{inhibitor}}$ is the energy of the inhibitor without the surface.

1.15. Heterocyclic compounds as corrosion inhibitors: literature survey with particular emphasis of quantum chemical calculations and molecular dynamics simulations

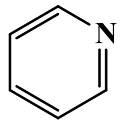
Zhang et al. [Zhang *et al.* (2012)] described the inhibition performance of 2-(4-pyridyl)-benzimidazole (PBI) on mild steel corrosion using weight loss, electrochemical and computational methods in 1M HCl. Results showed that PBI exhibited maximum inhibition efficiency of 94.5% at 2mM concentration and their adsorption on mild steel surface obeyed Langmuir adsorption isotherm.



2-(4-pyridyl)-benzimidazole (PBI)



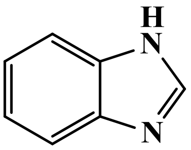
Benzimidazole (BI)

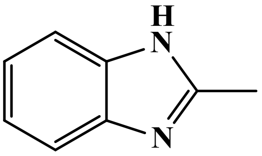


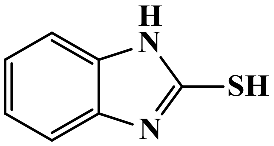
Pyridine (Py)

Quantum chemical calculations based on DFT and molecular dynamics simulations study revealed that the PBI adsorb over mild steel surface by means of coordinate bonds between PBI molecule and iron surface and the binding energy between PBI molecule and iron surfaces highest among the three studied molecules.

Obot and Obi-Egbedi [Obot and Obi-Egbedi (2010)] experimentally as theoretically studied the corrosion inhibition property of benzimidazole (BI) and its two derivatives namely 2-methylbenzimidazole (2-CH_3BI) and 2-mercaptobenzimidazole (2-SHBI). Experimental results showed that the 2-SHBI show the maximum inhibition efficiency among the studied compounds. The quantum chemical calculation based on DFT was performed for neutral as well as protonated form of three inhibitors. The parameters calculated are E_{HOMO}, E_{LUMO}, energy gap (ΔE), dipole moment (μ), electronegativity (χ), global hardness (η) and the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN). The theoretical results are in agreement with the experimental data.





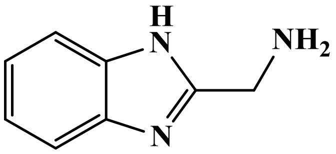


Benzimidazole (BI) 2-methylbenzimidazole (2-CH_3BI) 2-mercaptobenzimidazole (2-SHBI)

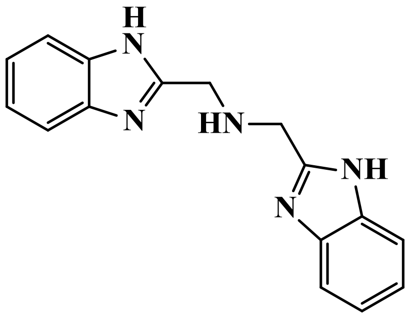
The adsorption tendency of three inhibitors namely imidazole, benzimidazole and 2- mercaptobenzimidazole on copper (111) surface was studied by Sun *et.al.* [Sun *et al.* (2012)] using DFT theory. Results showed that studied neutral molecules can weakly chemisorb perpendicularly on the metallic surface through N-Cu and S-Cu bonds. Further, the neutral form of benzimidazole and 2-mercaptobenzimidazole physically adsorb on copper surface by parallel orientation. While, dehydrogenated form of molecules can strongly chemisorb on the metallic surface with perpendicular and tilt orientations and their chemisorption strength order is consistent with the experimental results of inhibiting efficiency.

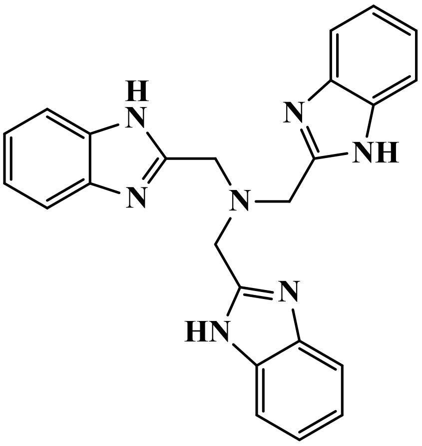
Cao *et. al.* [Cao *et al.* (2014)] described the adsorption behavior of three benzimidazole derivatives namely, 2-aminomethyl benzimidazole (ABI), bis(2-benzimidazolylmethyl) amine (BBIA) and tri-(2-benzimidazolylmethyl) amine (TBIA) on the surface of mild steel using quantum chemical calculations and molecular dynamics simulations. Quantum chemical calculations results showed that studied molecules show the similar tendency to donate the electrons while the difference in the inhibition performance is mainly attributed due to the difference in the electron accepting tendency.

Molecular dynamics simulations study showed that the adsorptive configuration of the molecules on Fe (100) surface was significantly affected by benzimidazole segments of the inhibitor molecules.



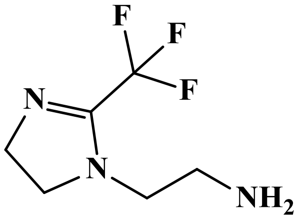
(ABI)



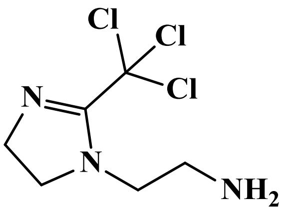


(BBIA) (TBIA)

The corrosion inhibition performance of two novel imidazoline derivatives namely 2-(2-trifluoromethyl-4,5-dihydro-imidazol-1-yl)-ethylamine (1-IM) and 2-(2-trichloromethyl-4,5-dihydro-imidazol-1-yl)-ethylamine (2-IM) on mild steel corrosion in 0.5 M HCl was have been described by Zhang *et.al.* [Zhang *et al.* (2015)] using weight loss, electrochemical, scanning electron microscopy, quantum chemical calculations and molecular dynamics simulations methods. Quantum chemical calculations and molecular dynamics simulation studies revealed that chloro-substituted compound shows better inhibitive property than the fluoride substituted one.



(1-IM)

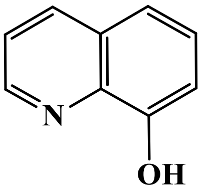


(2-IM)

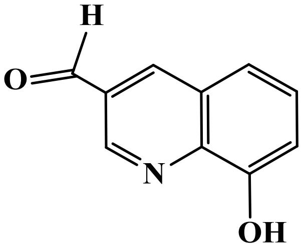
Kovacevic and Kokalj [Kovacevic and Kokalj (2011)] showed the effect of methyl, phenyl and murcapto substituents on the electronic structure of imidazole type inhibitors namely, Imidazole I, 1-Methylimidazole 1-MI, 4-Methylimidazole 4-MI, 2-Mercaptoimidazole 2-SHI, 1-Methyl-2-mercaptoimidazole 1-M-2-SHI, 1-Phenyl-4-methylimidazole 4-MPhI, 1-(p-Tolyl)-4-methylimidazole 4-MTI, Benzimidazole BI, 6-Methylbenzimidazole 6-MBI, 2-Mercaptobenzimidazole 2-SHBI, 6-Methyl-2-mercaptobenzimidazole and 6-Methyl-2-mercaptobenzimidazole 6-M-2-SHBI using density-functional-theory calculations. Results showed that presence of methyl and murcapto groups increases the softness of the inhibitor molecules which offer better binding between them. However, presence of phenyl moiety increases the harness of the inhibitor which offers hard binding between inhibitor and metallic surface.

A series of methyl pyridines have been tested as corrosion inhibitors in acid solution by Sastri *et. al.* [Sastri and Perumareddi (1997)] and observed that inhibition efficiency decreases with increasing the value of ΔE (ELUMO-EHOMO). They also calculated the number of transferred electron (ΔN) and made a qualitative conclusion according to which inhibition efficiency increases with increasing electron donating ability.

Achary *et. al.* [Achary *et al.* (2008)] described the inhibition effect of 8-hydroxy quinoline (HQ) and 3-formyl 8-hydroxy quinoline (FQ) on mild steel corrosion in hydrochloric acid solution using weight loss and electrochemical techniques. They were found that corrosion inhibition efficiency and extent of surface coverage were increased with increase in inhibitor concentration and decreased with increase in temperature and acid concentration. The inhibitors follow Langmuir adsorption isotherm. The compound FQ showed more corrosion inhibition efficiency than HQ.

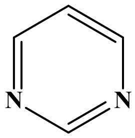


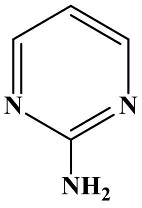
8-hydroxy quinoline (HQ)

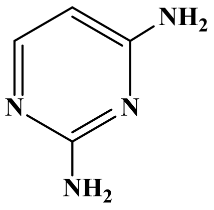


3-formyl 8-hydroxy quinoline (FQ)

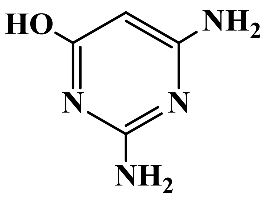
Masoud *et.al.* [Masoud *et al.* (2010)] have studied the inhibition performance of 2-aminopyrimidine (APr), 2,4-diaminopyrimidine (dAPr), 2,4-diamino- 6-hydroxy-pyrimidine (dAHPr) and 2,4,6-triaminopyrimidine (tAPr) during the acidic corrosion of steel surface was investigated using three methods, MP2, ab initio Hartree–Fock and density functional theory (DFT). Quantum chemical parameters such as the highest occupied molecular orbital energy (EHOMO), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (l), sum of the total negative charge (TNC), molecular volume (MV), electronegativity (χ), chemical potential (Pi), global hardness (ρ), softness (σ) and the fraction of electrons transferred (ΔN), were calculated. Furthermore, the interaction energies of the inhibitors with the iron surface were studied. A good correlation was found between the theoretical data and the experimental results.

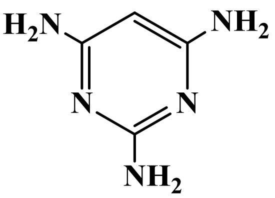






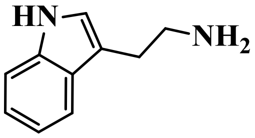
Pyrimidine (Py) 2-aminopyrimidine (APr) 2,4-diaminopyrimidine (dAPr)





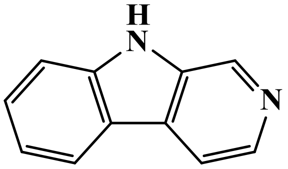
2,4-diamino- 6-hydroxy-pyrimidine (dAHPr) 2,4,6-triaminopyrimidine (tAPr)

The inhibitor effect of tryptamine on the corrosion of mild steel in 0.5 M hydrochloric acid was investigated by Lowmunkhong *et al.* [Lowmunkhong *et al.* (2010)] at 30^0C using linear polarization, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Tryptamine showed the maximum inhibition efficiency of 97% at 500 ppm concentration. They showed that adsorption of Tryptamine on mild steel surface obeyed the Langmuir adsorption isotherm. Polarization study revealed that the tryptamine inhibits both cathodic and anidic reactions and behaves as mixed type inhibitors.

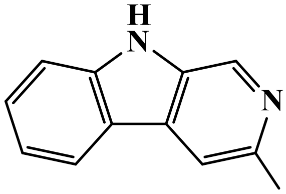


Tryptamine

Lebrini *et. al.* [Lebrini *et al.* (2010)] described the inhibition performance of two indole derivatives namely, 9H-pyrido[3,4-b]indole (norharmane) and 1-methyl-9H-pyrido[3,4-b]indole (harmane) on C38 corrosion in 1M HCl using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. Polarization curves i.e. cathodic and anodic curves show that norharmane and harmane acted as mixed-type inhibitors. Adsorption of both the inhibitors over C38 surface obeyed the Langmuir adsorption isotherm. The strong adsorption of the indole derivatives on the metallic surface was confirmed by Raman spectroscopy. The electronic properties of indole derivates, obtained using the AM1 semi-empirical quantum chemical approach, were correlated with their experimental efficiencies using the linear resistance model (LR).

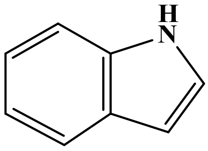


9H-pyrido[3,4-b]indole (norharmane)

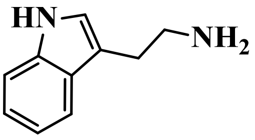


1-methyl-9H-pyrido[3,4-b]indole (harmane)

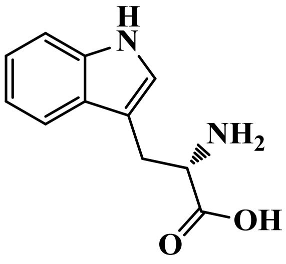
The inhibition ability of indole and its two derivatives namely, tryptamine and tryptophane on pitting corrosion of aluminum was studied by El-Shafei *et. al.* [El-Shafei *et al.* (2004)], using polarization technique. Results showed that the order of inhibition effect of these compounds was found to be tryptamine (II)> tryptophane (III) > indole (I). the current decay measurements conformed the inhibiting characteristics and order of inhibition efficiency of these inhibitors. The inhibition of aluminum pitting corrosion is resulted due to adsorption of these compounds over the metallic surface. The inhibition efficiency was found to be depending upon the number of active centers, molecular size and the mode of adsorption. Finally, their influence on the ethanol oxidation was tested using cyclic voltammetric technique.



Indole

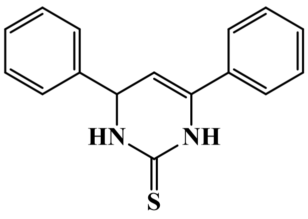


Tryptamine

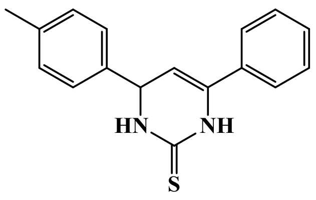


Tryptophane

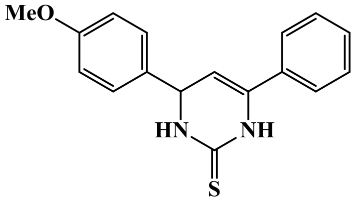
Recently, the inhibition of mild steel in 1M H2SO4 by three pyrimidine-2-thione derivatives namely, 4,6-diphenyl- 3,4-dihydropyrimidine-2(1H)-thione (PTH), 4-(4-methylphenyl)-6-phenyl-3,4-dihydropyrimidine-2(1H)-thione (PTM) and 4-(4-methoxyphenyl)-6-phenyl-3,4-dihydropyrimidine-2(1H)-thione (PTMO)) have been investigated by Soltani *et. al.* [Soltani et al. (2015)].



(PTH)

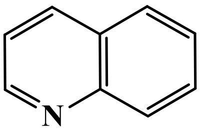


(PTM)

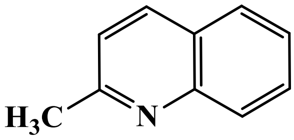


(PTMO)

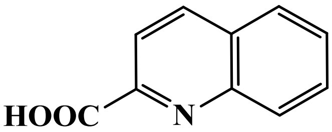
Ebenso *et. al.* [Ebenso *et al.* (2010)] have been described the corrosion inhibition of mild steel in acid solution using Quinoline (QL) and its two derivatives namely quinaldine (QLD) and quinaldic acid (QLDA) at different temperatures. Results showed that inhibition efficiencies of these inhibitors increased with increasing inhibitors concentration and reduced with temperature. The order of inhibition efficiency obeyed the following order: QLDA > QLD > QL. The inhibition of mild steel corrosion in acid solution by these inhibitors is attributed due to adsorption of inhibitors over the metallic surface which follows the Langmuir adsorption isotherm.



Quinoline (QL)

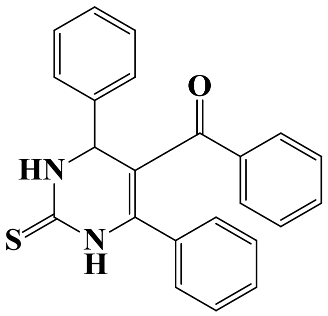


quinaldine (QLD)

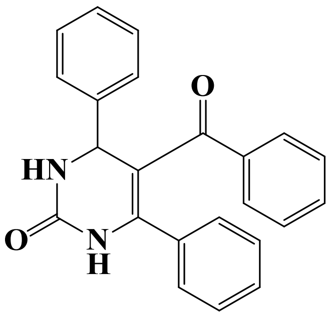


quinaldic acid (QLDA)

The corrosion inhibition of austenitic stainless steel in acidic media have been investigated by Caliskan and Akbas [Caliskan and Akbas (2011)] using two 5-Benzoyl-4-(substitutedphenyl)-6-phenyl-3,4-dihydropyrimidine-2(1H)-(thio)ones (DHPMs) namely, 5-benzoyl-4,6-diphenyl-1,2,3,4- tetrahydro-2-thiopyrimidine (DHPM I) and 5-benzoyl-6-phenyl- 4-p-tolyl-3,4-dihydropyrimidine-2(1H)-one (DHPM II) by electrochemical methods using Tafel plot, linear polarization and electrochemical impedance spectroscopy at 298 K. results showed that inhibition efficiency of both inhibitors increases with increasing their concentrations. The adsorption of the DHPMs onto the stainless steel surface was found to follow Langmuir and Dubinin–Radushkevich adsorption isotherm models. The negative sign of free energy of adsorption suggests that these inhibitors adsorbed spontaneously over the mild steel surface. Results show DHPM I to be the best inhibitor with a mean efficiency of 91% at 2×10^{-3}M additive concentration.

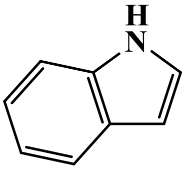


(DHPM I)

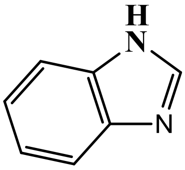


(DHPM II)

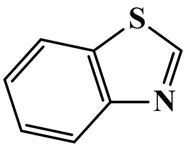
The corrosion inhibition of pure iron in molar hydrochloric acid by four indole derivatives, namely indole (IND), benzotriazole (BTA), benzothiazole (BSA) and benzoimidazole (BIA) have been described by Khaled [Khaled (2008)]. In this study, electrochemical frequency modulation, EFM was used as an effective method for corrosion rate determination in corrosion inhibition studtion study showed that these inhibitors acted as cathodic type inhbitors. ies. Tafel polarizMolecular simulation studies were applied to optimize the adsorption structures of indole derivatives. The inhibitor/iron/solvent interfaces were simulated and the adsorption energies of these inhibitors were calculated. Quantum chemical calculations have been performed and several quantum chemical indices were calculated and correlated with the corresponding inhibition efficiencies.



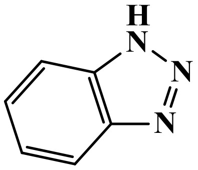
(IND)



(BTA)



(BSA)



(BIA)

Wang *et al.* [Wang *et al.* (1999)] calculated the molecular geometry and chemical adsorption of six imidazolines and Fe atom by MNDO and CNDO/2M methods, and discussed their inhibition performance. They were found good correlation between experimental and computation studies. Similarly, inhibition effect of heterocyclic, benzothiazole derivatives, pyrimidines, amino acids containing an aromatic part, pyridines and quinolines were correlated with quantum chemical indices of the respective molecules by Lukovits *et al.* [Lukovits *et al.* (2001)]. Quantum chemical calculations were made using Huckel molecular orbital (HMO) method. The difference (Δ) between the energy of HOMO and LUMO was related to inhibition efficiency. At values $\Delta < 1.8$ eV mol-1, E increased with increasing Δ values. At values $\Delta > 1.8$ eV mol^{-1}, E tended to decrease with increasing values of Δ. They also reported that Δ and/or E_{HOMO} alone is not sufficient to account for all variation in the experimental inhibition efficiencies.

Objectives:

The specific objectives of the present thesis are:

- To synthesize some heterocyclic compounds (containing N, O, and S) and their characterization by several techniques such as thin layer chromatography (TLC), infra-red (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and melting point (MP) determination.
- To study the corrosion inhibition effect of synthesized heterocyclic compounds on mild steel in hydrochloric acid solution by weight loss, electrochemical, surface and computational methods.
- To investigate the roughness of mild surface using surface using scanning electron microscopy (SEM) and atomic force microscopy (AFM).
- To investigate the elements present on mild steel surface using energy dispersive X-ray spectroscopy (EDX).
- To study the structure-activity relationship of compounds investigated by quantum chemical methods based on density function theory (DFT) using B3LYP with electron basis set 6-31+G(d, p) for all atoms. All the calculations were executed with Gaussian 09, software for windows (Revision D.01).
- To determine the local reactivity indices that are often used to analyze the relative susceptibility of the active atomic sites of an inhibitor molecule towards electrophilic and nucleophilic attacks using Fukui indices.
- To study the optimized adsorption of the heterocyclic compounds, simulation of heterocyclic inhibitors/ iron/ electrolyte interfaces, and the calculation of adsorption energy by molecular dynamics simulations studies using Forcite module in the Material Studio Software 7.0 from BIOVIA Accelrys, USA.