CHAPTER 1

Introduction
1. **INTRODUCTION**

1.1 **Introduction to corrosion**

Human has most likely been trying to understand and control corrosion for as long as they have been using metal objects. The most important periods of recorded history are named for the metals that were used for tools and weapons (Iron Age, Bronze Age). With a few exceptions, metals are unstable in ordinary aqueous environments. Metals are usually extracted from ores through the application of a considerable amount of energy. Certain environments offer opportunities for these metals to combine chemically with elements to form compounds and return to their lower energy levels.

Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals. Metals will also corrode when exposed to gaseous materials like acid vapours, formaldehyde gas, ammonia gas, and sulfur containing gases [1-5].

1.1.1 **Corrosion cost to society**

Corrosion is recognized as one of the most serious problems in our modern society and the resulting losses each year are in the hundreds of billions of dollars. Studies on cost of corrosion have been undertaken by several countries including, the United States, the United Kingdom, Japan, Australia, Kuwait, Germany, Finland, Sweden, India, and China. The studies have ranged from formal and extensive efforts to informal and modest efforts. The common finding of these studies was that the annual corrosion costs ranged from approximately 1 to 5 percent of the Gross National Product (GNP) of each nation [6].
A recent report describes the annual direct and indirect costs of metallic corrosion in the United States and preventive strategies for optimum corrosion management. The total direct cost of corrosion is estimated at $276 billion per year, which is 3.1 percent of the 1998 U.S. gross domestic product (GDP).

The indirect cost of corrosion was conservatively estimated to be equal to the direct cost (i.e., total direct cost plus indirect cost is six percent of the GDP). Evidence of the large indirect corrosion costs are lost time, and thus lost productivity because of outages, delays, failures, and litigations [7-8].

It was found that the sectors of drinking water and sewer systems ($36 billion), motor vehicles ($23.4 billion), and defense ($20 billion) have the largest direct corrosion impact. Within the total cost of corrosion, a total of $121 billion per year is spent on corrosion control methods and services. The study showed that technological changes have provided many new ways to prevent corrosion, and the improved use of available corrosion management techniques.

However, better corrosion management can be achieved using preventive strategies in non-technical and technical areas. These preventive strategies include:

1. Increase awareness of large corrosion costs and potential savings
2. Change the misconception that nothing can be done about corrosion
3. Change policies, regulations, standards, and management practices to increase corrosion savings through sound corrosion management
4. Improve education and training of staff in recognition of corrosion control
5. Advance design practices for better corrosion management
6. Advance life prediction and performance assessment methods
Advance corrosion technology through research, development, and implementation.

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion.

1.1.2 Definition

Scientists have defined the word corrosion in different ways.

According to – **Fontana** - Corrosion is the destruction or deterioration of a material because of its reaction with its environment. In other words it is the destruction of material by some means other than mechanical e.g. deterioration of paint and rubber by sunlight or chemicals [9].

**Verlag** – has defined corrosion as the reaction of the material with its environment causing measurable change in the material and its properties, capable of leading to corrosion damage. It is an electrochemical process but it may be related to chemical and physical processes. Some authors, while defining corrosion directly refer to metals and only refer to the destructive side of corrosion. But not all the corrosion processes are detrimental because some of them give some benefit to metals, as in the case of aluminium, where oxide layer protects the metal from atmospheric corrosion.

**Shrier** defines corrosion as the process where a metal or alloy is transformed from the metallic to combined state by interaction with its environment, He claimed that this definition is a working definition for
corrosion engineers. The definition given by Evans defines corrosion as all the transformations in which a metal passes from elementary to the combined condition, and covers reactions, between metals and gaseous or liquid environments [10-15].

1.1.3 The consequences of corrosion

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarised as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localised zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.

2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).

3. Loss of time in availability of profile-making industrial equipment.

4. Reduced value of goods due to deterioration of appearance.

5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).

6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can
cause expensive damage to carpets and decorations, while corrosive seawater may enter the boilers of a power station if the condenser tubes perforate.

7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.

8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.

9. Added complexity and expense of equipment, which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

1.1.4 Classification of corrosion

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Examination before cleaning is particularly desirable. Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are:

1. Uniform, or general attack,

2. Galvanic, or two-metal corrosion,

3. Crevice corrosion,

4. Pitting
5. Intergranular corrosion,
6. Selective leaching, or parting,
7. Erosion corrosion,
8. Stress corrosion.

1.1.5 Chemistry of corrosion

Common structural metals are obtained from their ores or naturally occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a meta stable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose.

Virtually all corrosion reactions are electrochemical in nature; at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal.

The rates of the anodic and cathodic reactions must be equivalent according to Faraday’s Laws, being determined by the total flow of electrons from anodes to cathodes, which is called the “corrosion current”, Icor. Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which
corrosion cells operate. The corroding piece of metal is described as a “mixed electrode” since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface [16].

The most common and important electrochemical reactions in the corrosion of iron are thus:

**Anodic reaction (corrosion)**

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-
\]

**Cathodic reactions**

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \\
\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2e^- \rightarrow 2\text{OH}^-
\]

Reactions 1a is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction 1b. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2, \text{iron(II) hydroxide}
\]

Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish colour due to partial oxidation in air.

\[
2\text{Fe(OH)}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2\text{Fe(OH)}_3, \text{hydrated iron(III) oxide}
\]

Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements, which are present. Because the rust is precipitated as a result of secondary reactions it is porous and absorbent and tends to act as a sort of harmful poultice, which encourages further corrosion. For other metals or different environments different types of anodic and cathodic reactions may
occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation these may provide a highly protective surface film, which retards further corrosion, the surface is then said to be “passive”. An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidising conditions or elevated temperatures [17].

\[ 2\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \]

### 1.1.6 Corrosion rate

Corrosion takes place with two partial reactions involved: the anodic and cathodic processes. At the anode oxidation of the metal takes place while at the cathode a reduction reaction proceeds. These processes can be represented as

**Oxidation (anodic reaction)**

\[ \text{Me} \rightarrow \text{Me}^{n+} + n\text{e}^- \]

**Reduction (cathodic reaction)**

\[ \text{Ox} + n\text{e}^- \rightarrow \text{Red}^{m-} \]

Where

\( \text{Me} = \) metal, \( \text{Ox} = \) oxidized state, \( \text{Red} = \) reduced state

The rate of reaction, expressed in terms of moles of electrons per second, of reaction is \( r_a \) and for reaction is \( r_c \).

When corrosion of the metal is taking place freely, the rates of both reactions are equal; this is the corrosion rate;

\[ r_{\text{corr}} = r_a - r_c \]
Corrosion rate can be expressed in terms of current, from equation as

\[ I = r \cdot F \]

Where \( F \) now is 96.5x10^3 c.mol\(^{-1}\)

By dividing \( I \) by the surface area, the current density, \( i \), is obtained as

\[ i = \frac{I}{A} = r \cdot \frac{F}{A} \]

Generally, the corrosion rate is measured in terms of current density as a function of over potential (\( \eta \)). Over potential or polarization is the difference between the operating potential (\( E \)) and the equilibrium potential (\( E^0 \)) of a reaction. Current density could be expressed as a function of over potential as:

For anodic reaction

\[ i_a = i_a^0 \cdot \exp \left( \frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot \eta_a \right) \]

\[ \eta_a = E - E_a^0 \]

For cathodic reaction

\[ i_c = i_c^0 \cdot \exp \left( \frac{1 - \alpha \cdot m \cdot F}{R \cdot T} \cdot \eta_c \right) \]

\[ \eta_c = E - E_c^0 \]

Where \( i_a \) and \( i_c \) are the anodic and cathodic current densities at their equilibrium potential \( E_a^0 \) and \( E_c^0 \) respectively, \( \alpha \) is the symmetric factor normally \( \alpha = 0.5 \), \( n \) and \( m \) are the number of electrons involved in the anodic
and cathodic reactions, \( R \) is the universal gas constant = 8.314 J / mol.°K and \( T \) is the absolute temperature (°K).

From these relations, polarization curves can be obtained by plotting \( \log i \) versus the over potential (\( \eta \)) as shown in figure. The intersection point of the anodic and cathodic polarization curves produces the corrosion rate. At this intersection, the anodic and cathodic current density is equal and represents the corrosion rate.

\[
I_{\text{corr}} = I_a - I_c
\]

![Figure 1.1 Polarization curve for anodic and cathodic polarization](image)

1.1.7 Factors effecting corrosion rate

Certain factors can tend to accelerate the action of a corrosion cell. These include:

Establishment of well-defined locations on the surface for the anodic and cathodic reactions. This concentrates the damage on small areas where it
may have more serious effects, this being described as "local cell action". Such effects can occur when metals of differing electrochemical properties are placed in contact, giving a "galvanic couple". Galvanic effects may be predicted by means of a study of the Galvanic Series, which is a list of metals and alloys placed in order of their potentials in the corrosive environment, such as seawater. Metals having a more positive (noble) potential will tend to extract electrons from a metal, which is in a more negative (base) position in the series and hence accelerate its corrosion when in contact with it.

The Galvanic Series should not be confused with the Electrochemical Series, which lists the potentials only of pure metals in equilibrium with standard solutions of their ions. Galvanic effects can occur on metallic surfaces, which contain more than one phase, so that "local cells" are set up on the heterogeneous surface. Localized corrosion cells can also be set up on surfaces where the metal is in a varying condition of stress, where rust, dirt or crevices cause differential access of air, where temperature variations occur, or where fluid flow is not uniform.

(b) Stimulation of the anodic or cathodic reaction. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion. Sodium chloride is encountered in marine conditions and is spread on roads in winter for de-icing. Quite small concentrations of sulphur dioxide released into the atmosphere by the combustion of fuels can dissolve in the invisibly thin surface film of moisture which is usually present on metallic surfaces when the relative humidity is over 60-70%.

The acidic electrolyte that is formed under these conditions seems to be capable of stimulating both the anodic and the cathodic reactions. In practical terms it is not usually possible to eliminate completely all corrosion damage to metals used for
the construction of industrial plant. The rate at which attack is of prime importance is usually expressed in one of two ways:

(1) Weight loss per unit area per unit time, usually mdd (milligrams per square decimetre per day)

(2) A rate of penetration, i.e. the thickness of metal lost. This may be expressed in American units, mpy (mils per year, a mil being a thousandth of an inch) or in metric units, mmpy (millimetres per year).

1.1.8 Corrosion inhibitors

Inhibitors are chemicals that react with a metallic surface, or the environment. This surface is exposed to, giving the surface a certain level of protection. According to Fontana inhibitor is a substance that when added in small concentration to an environment decreases the corrosion rate. Wangles indicated that inhibitors are substances that are added to the corrosive medium to lower the corrosion rate, by retarding the anodic process and the cathode process. Putilova, describes an inhibitor as a corrosion retarder, which is a substance that retards and in some cases, almost completely halts the destruction of metals in corrosive media. These substances may be considered as negative catalyst in respect to corrosion process. This definition is applied only to electrochemical processes.

Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitors slow corrosion processes by either:
- Increasing the anodic or cathodic polarization behavior
- Reducing the movement or diffusion of ions to the metallic surface;
- Increasing the electrical resistance of the metallic surface.

The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. This is partly due to the fact that the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability and environmental friendliness are of considerable importance.

Various authors have classified inhibitors differently. Some authors, for example, prefer to group inhibitors by their chemical functionality. However, by far the most popular organization scheme consists in regrouping corrosion inhibitors in a functionality scheme as follows:

- Passivating inhibitors
- Cathodic inhibitors.
- Organic inhibitors.
- Precipitation inhibitors.
- Volatile corrosion inhibitors.

**Passivating Inhibitors**

Passivating inhibitors (passivators) cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors: Oxidizing anions, such as chromate, nitrite and nitrate, that can passivate steel in the absence of oxygen.
Non oxidizing ions such as phosphate, tungstate and molybdate that require the presence of oxygen to passivate steel.

These inhibitors are the most effective and consequently the most widely used. Chromate based inhibitors are the least expensive inhibitors and were used until recently in a variety of applications, e.g. recirculation-cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers. Sodium chromate, typically in concentrations of 0.04-0.1% was used for these applications.

At higher temperatures or in freshwater with chloride concentrations above 10 ppm higher concentrations are required. If necessary, sodium hydroxide is added to adjust the pH to a range of 7.5-9.5. If the concentration of chromate falls below a concentration of 0.016% corrosion will be accelerated. Therefore it is essential that periodic colorimetric analysis be conducted to prevent this from occurring. In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason it is essential that monitoring of the inhibitor concentration be performed.

**Cathodic inhibitors**

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms as:

- **Cathodic poisons**
- **Cathodic precipitates**
- **Oxygen scavenger**
Some cathodic inhibitors, such as compounds of arsenic and antimony, work by making the recombination and discharge of hydrogen more difficult. Other cathodic inhibitors, ions such as calcium, zinc or magnesium, may be precipitated as oxides to form a protective layer on the metal. Oxygen scavengers help to inhibit corrosion by preventing the cathodic depolarization caused by oxygen. The most commonly used oxygen scavenger at ambient temperature is probably sodium sulfite (Na$_2$SO$_3$).

![Figure 1.2](image-url)  

**Figure 1.2.** Schematic representation of inhibitor action  

a) Anodic inhibition, b) Cathodic inhibition, c) Anodic and cathodic inhibition

**Cathodic poisons**

Cathodic poisons are used advantageously as corrosion inhibitors by stifling the cathodic reduction processes that must balance the anodic corrosion reaction. However cathodic poisons can also increase the susceptibility of a
metal to hydrogen induced cracking since hydrogen can also be absorbed by metal during aqueous corrosion or cathodic charging.

When corrosion occurs in a low-pH solution, some of the reduced hydrogen does not form gaseous hydrogen, but instead, diffuses into the metal as atomic hydrogen. This can happen during pickling and electroplating of metal. Substances such as arsenic, antimony, sulfur, selenium, tellurium, and cyanide ions prevent the hydrogen atoms from forming hydrogen gas, and are called cathodic poisons. Cathodic poisons facilitate contamination by keeping hydrogen in atomic form, in which hydrogen more readily diffuses into the metal. Environments containing hydrogen sulfide, which contains both hydrogen and a cathodic poison (i.e. sulfur), are especially dangerous for alloys and metals. Hydrogen sulfide is often encountered in the petroleum industry during the drilling and completion of oil and gas wells, and during the storage and piping of petroleum products containing hydrogen sulfide.

**Oxygen scavenger**

A chemical that reacts with dissolved oxygen to reduce corrosion, such as sulfite and bisulfite ions that combine with oxygen to form sulfate. This is a redox reaction and requires a nickel or cobalt catalyst. Removal of air from a mud by defoaming and mechanical degassing is an essential first step before a scavenger can lower the dissolved oxygen content.

**Organic Inhibitors**

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors but, as a general rule, organic inhibitors affect
the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually designated as 'film-forming', protect the metal by forming a hydrophobic film on the metal surface.

The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors.

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors.

For any specific inhibitor in any given medium there is an optimal concentration. For example, a concentration of 0.05% sodium benzoate, or 0.2% sodium cinnamate, is effective in water with a pH of 7.5 and containing either 17 ppm sodium chloride or 0.5% by weight of ethyl octanol. The corrosion due to ethylene glycol cooling water systems can be controlled by the use of ethanolamine as an inhibitor.

**Precipitation Inhibitors**

Precipitation inducing inhibitors are film-forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. 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.

The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water. In aerated hot water systems, sodium silicate protects steel, copper and brass. However, protection is not always reliable and depends heavily on pH and a saturation index that depends on water composition and temperature. Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites, however, they are very useful in situations where non-toxic additives are required.

**Volatile corrosion inhibitors**

Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. 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 towards less acidic and corrosive values. In closed vapour spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used.

On contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds; fast action wanting high volatility while enduring protection requires low volatility.

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1.1.9 Inhibitor Efficiency

By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of that inhibitor is thus expressed by a measure of this improvement

**Inhibitor Efficiency (%) = \( 100 \times (CR_{\text{uninhibited}} - CR_{\text{inhibited}}) / CR_{\text{uninhibited}} \)**

where:

- \( CR_{\text{uninhibited}} \) = corrosion rate of the uninhibited system
- \( CR_{\text{inhibited}} \) = corrosion rate of the inhibited system

In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration, e.g. a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%.

Through the years, sophisticated corrosion inhibitor test methods, typically designed to reproduce the most extreme conditions in a system, have been employed to improve inhibitor capabilities. New and better corrosion inhibitors have been developed as a result of their performance in elaborate laboratory apparatus, yet many have not achieved comparable performance in the field. The inability to transfer inhibitor performance from the laboratory to the field remains a challenge today. However, correlation of laboratory and field performance may be possible once key factors involved in inhibitor chemistry and corrosion theory are considered.

1.1.10 Evaluation of corrosion inhibitors

In choosing amongst possible inhibitors, the simplest tests should be done first to screen out unsuitable candidates. The philosophy of initial screening tests
should be that poorly performing candidates are not carried forward. An inhibitor that does poorly in early screening tests might actually do well in the actual system, but the user seldom has the resources to test all possible inhibitors. The inhibitor user must employ test procedures that rigorously exclude inferior inhibitors even though some good inhibitors are excluded.

Inhibitor selection begins with the choice of physical properties. Must the inhibitor be a solid or liquid? Are melting and freezing points of importance? Is degradation with time and temperature critical? Must it be compatible with other system additives? Are specific solubility characteristics required? This list can be extensive, but is important because it defines the domain of possible inhibitors. It must be the first step of the inhibitor evaluation for any new system. These physical measurements are those routinely done as part of minimal quality acceptance testing.

The challenge in inhibitor evaluation is design of experiments that simulate the conditions of the real world system. The variables that must be considered include temperature, pressure, and velocity as well as metal properties and corrosive environment chemistry. System corrosion failures are usually localized and attributed to micro conditions at the failure site. Adequate testing must include the most severe conditions that can occur in the system and not be limited to macro or average conditions. Examples of micro environments are hot spots in heat exchangers and highly turbulent flow at weld beads.

Test specimens should be the same metal as that to be protected; even very small differences in metal chemistry can make major differences in inhibitor performance. Inhibitor performance can vary greatly on different metals and thus inhibitor rankings based on one metal are not universal. Much less obvious are differences between the "same" metal. These nonchemical
differences include grain size and orientation, residual stresses, and surface condition. Surface preparation should, to the extent possible, provide a surface comparable to that in the system that is being modeled. Except in special tests, minimal cleaning includes a solvent wash to degrease the sample. More vigorous cleaning such as bead blasting or acid activation can markedly affect inhibitor response even while improving reproducibility of tests. Many experimenters activate test specimens in acid when doing electrochemical measurements. The purpose is to remove any protective or passive oxide layer so that metal solution equilibrium is reached rapidly.

1.1.11 Transportability of Inhibitor

Corrosion inhibitors are generally described by terms such as oil soluble, water-soluble, oil soluble-water dispersible, etc. Such terms are generalizations, not rigorous descriptions. An oil soluble inhibitor, for example, in reality partitions between the liquid hydrocarbon phase and the water phase as do all other inhibitors: all that can be assumed is that it likely partitions more to the oil phase.

Partitioning of a single compound between two phases is clearly defined. Many commercial corrosion inhibitors, however, are not single compounds but complex mixtures of many compounds, each with its own unique partitioning coefficient. Thus a commercial corrosion inhibitor has no unique partitioning coefficient but rather one for each of the multiple components. Organic inhibitors are generally more soluble in aromatic hydrocarbons than aliphatic ones and more soluble in long chain aliphatics than short chain ones. The result is that partition coefficients must be measured for each "oil" of interest.
1.1.12 Corrosion protection tests

Corrosion rates are most commonly reported as penetration rates. The usual way of reporting protection efficiency is in terms of percent protection. Although this reporting method is useful for comparing inhibitor performance, it obscures the actual number of interest the inhibited corrosion rate.

Film persistency tests are more complex than constant concentration experiments. The test metal is exposed to an inhibited test solution for a fixed period of time, and then the corrosion rate is determined in a similar solution containing no inhibitor. Test variables include inhibitor concentration in the initial filming solution and the number of rinse solution repetitions. A typical experiment might film for one hour with 1000 ppm inhibitor, rinse one time for an hour, and finally measure the corrosion rate in a third solution. Film, rinse, and corrode solution are the same composition except for inhibitor in the filming step.

1.1.13 Metal loss methods

Metal loss can be determined gravimetrically, volumetrically, or radiometrically; all are a direct measures of corrosion. Of these, gravimetric or weight loss methods are mostly used for inhibitor testing. Volumetric methods are associated with inspection or monitoring techniques such as ultrasonic inspection and electric resistance (ER) probe monitoring, although both are sometimes used in long-term inhibitor evaluations. Radiometric methods are used as monitoring methods such as in thin layer activation but could be used for inhibitor evaluation. The corrosion wheel test used to evaluate oilfield inhibitors is an example of weight loss testing.
Planned interval test

Specimens used in the PIT method were polished as described earlier. The variation of metal corrodibility solution corrosiveness and corrosion rates as a function of time was investigated with the PIT (Planned Interval Test) technique. After equilibration with temperature (30°C) three-weighed specimen were introduced into the solution containing 400 ml. of the test solution. The specimens were removed at different exposure times and are referred to as $A_1$, $A_t$, $A_{t+1}$. The fourth specimen was introduced into the cell for the last period (B), the values of $A_1$, B (measure value and Ac) (calculated from $A_t$ and $A_{t+1}$) relate to the same testing period, but under different conditions. This technique is called the "Planned Interval Test" its procedure has been depicted in figure (1) after the experiment, the specimen were planned by washing in water and acetone and then dried and weighed from the weight loss measurements the corrosion rates were calculated. Similar experiments were done separately using different inhibitor.

1.1.14 Electrochemical methods

Electrochemical testing has two major benefits, one major limitation, and one lesser limitation. The benefits are short measurement time and mechanistic information. The severe limitation is the requirement for a conductive corrosive environment. Less troublesome from a testing perspective is the requirement for a corrosion model. Rapidity of measurement makes these techniques useful in characterizing inhibitor performance.

Corrosion rates can be determined electrochemically in minutes while weight loss methods can take days. With the near instantaneousness of electrochemical methods, changes of inhibitor performance with time are
readily measurable. Questions about inhibitor persistence and incubation time are thus experimentally accessible and experiments concerned with velocity effects become less cumbersome.

**Potentiodynamic polarization methods**

- **Linear polarization resistance (LPR)**
- **Electrochemical impedance spectroscopy (EIS)**
- **Electrochemical noise (EN)**

Unlike potentiometry, where the free energy contained within the system generates the analytical signal, electrolytic methods are an area of electroanalytical chemistry in which an external source of energy is supplied to drive an electrochemical reaction, which would not normally occur. The externally applied driving force is either an applied potential or current. When potential is applied, the resultant *current* is the analytical signal; and when current is applied, the resultant potential is the analytical signal. Techniques, which utilize applied potential, are typically referred to as *voltammetric methods* while those with applied current are referred to as *galvanostatic methods*. Applying a potential pulse while observing the variation of the rate, as a function of time constitutes the potentiostatic method. The method, called the potentiodynamic, or potential sweep, method involves observations of the current as a function of the potential, while the latter is varied at a constant, known rate.

The advantages of transient methods over steady-state ones, in which behaviour before the attainment of the steady state is not a part of the observation, are manifold. If observations are made at sufficiently short times,
events can be recorded before the onset of concentration changes, and pure activation values can be found. Hence, Tafel relationships can be obtained over a larger current density range than if one makes measurements over longer times, as is required in the steady-state methods. The structure of the transient states can reveal important information, such as double layer capacitance and surface coverage of the electrode by intermediate species.

Several so-called kinetic parameters, for example, partial derivatives of current density and potential with respect to concentration of chosen reactants, can be extracted from experimental measurements.

**Galvanostatic polarization studies**

At present a number of electrochemical methods are in use for investigation of corrosion and its inhibition. The methods of computing the inhibition efficiencies are numerous; of these galvanostatic polarisation method is most commonly used for the study of action of corrosion inhibition in a wide variety of environments including vapor phase and neutral media. Since the phenomenon of electrochemical corrosion consists of anodic and cathodic processes, examination of inhibitive action may be carried out separately on either of these partial processes by comparing the electrochemical parameters in the presence and absence of an inhibitor in a given environment.

**Voltammetric methods**

Voltammetry refers to the measurement of current that results from the application of potential. Unlike potentiometric measurements, which employ only two electrodes, voltammetric measurements utilize a *three electrode*
electrochemical cell. The use of the three electrodes (working, auxiliary, and reference) along with the potentiostat instrument allow accurate application of potential functions and the measurement of the resultant current. The different voltammetric techniques that are used are distinguished from each other primarily by the potential function that is applied to the working electrode to drive the reaction, and by the material used as the working electrode. Common techniques to be discussed here include:

- Hydrodynamic Voltammetry
- Polarography
- Normal-pulse polarography (NPP)
- Differential-pulse polarography (DPP)
- Cyclic voltammetry
- Anodic-stripping voltammetry

**Time based techniques**

- Chronoamperometry
- Chronocoulometry

**Polarography**

Polarography is a voltammetric measurement whose response is determined by combined diffusion/convection mass transport. Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential to the final potential. As a linear sweep method controlled by convection/diffusion mass transport, the current vs. potential
response of a polarographic experiment has the typical sigmoidal shape. What makes polarography different from other linear sweep voltammetry measurements is that polarography makes use of the dropping mercury electrode (DME).

A plot of the current vs. potential in a polarography experiment shows the current oscillations corresponding to the drops of Hg falling from the capillary. If one connected the maximum current of each drop, a sigmoidal shape would result. The limiting current (the plateau on the sigmoid), called the diffusion current because diffusion is the principal contribution to the flux of electroactive material at this point of the Hg drop life, is related to analyte concentration by the Ilkovic equation:

$$i_d = 706nD^{1/2}m^{1/2}t^{1/6}c$$

Where D is the diffusion coefficient of the analyte in the medium (cm²/s), n is the number of electrons transferred per mole of analyte, m is the mass flow rate of Hg through the capillary (mg/sec), and t is the drop lifetime in seconds, and c is analyte concentration in mol/cm³.

There are a number of limitations to the polarography experiment for quantitative analytical measurements. Because the current is continuously measured during the growth of the Hg drop, there is a substantial contribution from capacitive current. As the Hg flows from the capillary end, there is initially a large increase in the surface area. As a consequence, the initial current is dominated by capacitive effects as charging of the rapidly increasing interface occurs. Toward the end of the drop life, there is little change in the surface area, which diminishes the contribution of capacitance changes to the total current. At the same time, any redox process, which occurs, will result in
faradaic current that decays approximately as the square root of time (due to the increasing dimensions of the Nernst diffusion layer).

The exponential decay of the capacitive current is much more rapid than the decay of the faradaic current; hence, the faradaic current is proportionally larger at the end of the drop life. Unfortunately, this process is complicated by the continuously changing potential that is applied to the working electrode (the Hg drop) throughout the experiment. Because the potential is changing during the drop lifetime (assuming typical experimental parameters of a 2mV/sec scan rate and a 4 sec drop time, the potential can change by 8 mV from the beginning to the end of the drop), the charging of the interface (capacitive current) has a continuous contribution to the total current, even at the end of the drop when the surface area is not rapidly changing. As such, the typical signal to noise of a polarographic experiment allows detection limits of only approximately 10⁻⁸ or 10⁻⁹ M. Better discrimination against the capacitive current can be obtained using the pulse polarographic techniques.

Qualitative information can also be determined from the half-wave potential of the polarogram (the current vs. potential plot in a polarographic experiment). The value of the half-wave potential is related to the standard potential for the redox reaction being studied.

**Normal-pulse polarography (NPP)**

Pulse polarographic techniques are voltammetric measurements which are variants of the polarographic measurement which try to minimize the background capacitive contribution to the current by eliminating the continuously varying potential ramp, and replacing it with a series of potential
steps of short duration. In Normal-pulse polarography (NPP), each potential step begins at the same value (a potential at which no faradaic electrochemistry occurs), and the amplitude of each subsequent step increases in small increments. When the Hg drop is dislodged from the capillary (by a drop knocker at accurately timed intervals), the potential is returned to the initial value in preparation for a new step.

For this experiment, the polarogram is obtained by plotting the measured current vs. the potential to which the step occurs. As a result, the current is not followed during Hg drop growth, and normal pulse polarogram has the typical shape of a sigmoid. By using discrete potential steps at the end of the drop lifetime (usually during the last 50-100 ms of the drop life which is typically 2-4 s), the experiment has a constant potential applied to an electrode with nearly constant surface area. After the initial potential step, the capacitive current decays exponentially while the faradaic current decays as the square root of time.

The diffusion current is measured just before the drop is dislodged, allowing excellent discrimination against the background capacitive current. In many respects, this experiment is like conducting a series of chronocoulometry experiments in sequence on the same analyte solution. The normal pulse polarography method increases the analytical sensitivity by 1 - 3 orders of magnitude (limits of detection $10^{-9}$ to $10^{-7}$ M, relative to normal dc polarography.

**Differential pulse polarography**

Differential Pulse Polarography is a polarographic technique that uses a series of discrete potential steps rather than a linear potential ramp to obtain the experimental polarogram. Many of the experimental parameters for differential pulse polarography are the same as with normal pulse polarography (for
example accurately timed drop lifetimes, potential step duration of 50 - 100 ms at the end of the drop lifetime. Unlike Normal Pulse Polarography, however, each potential step has the same amplitude, and the return potential after each pulse is slightly negative of the potential prior to the step.

In this manner, the total waveform applied to the DME is very much like a combination of a linear ramp with a superimposed square wave. The differential pulse polarogram is obtained by measuring the current immediately before the potential step, and then again just before the end of the drop lifetime. The analytical current in this case is the difference between the current at the end of the step and the current before the step (the differential current). This differential current is then plotted vs. the average potential (average of the potential before the step and the step potential) to obtain the differential pulse polarogram. Because this is a differential current, the polarogram in many respects is like the differential of the sigmoidal normal pulse polarogram. As a result, the differential pulse polarogram is peak shaped.

Differential pulse polarography has even better ability to discriminate against capacitive current because it measures a difference current (helping to subtract any residual capacitive current that remains prior to each step). Limits of detection with Differential Pulse Polarography are $10^{-6}$ - $10^{-7}$ M.

**Anodic stripping voltammetry**

Anodic stripping voltammetry is an electrolytic method in which a mercury electrode is held at a negative potential to reduce metal ions in solution and form an amalgam with the electrode. The solution is stirred to carry as much of the analyte metal(s) to the electrode as possible for concentration into the amalgam.
After reducing and accumulating the analyte for some period of time, the potential on the electrode is increased to reoxidize the analyte and generate a current signal. The ramped potential usually uses a step function, such as in normal-pulse polarography (NPP) or differential-pulse polarography (DPP). The concentration of the analyte in the Hg electrode, \( C_{\text{Hg}} \), is given by:

\[
C_{\text{Hg}} = \frac{i_l t_d}{n F V_{\text{Hg}}}
\]

where \( i_l \) is the limiting current during reduction of the metal, \( t_d \) is the duration of accumulation, \( n \) is the number of moles of electrons transferred in the half reaction, \( F \) is the Faraday constant (96,487 coulombs/mole of \( e^- \)), and \( V_{\text{Hg}} \) is the volume of the electrode.

The expression for current produced by anodic stripping depends on the particular type of Hg electrode, but is directly proportional to the concentration of analyte concentrated into the electrode. The main advantage of stripping analysis is the preconcentration of the analyte into the electrode before making the actual current measurement. Anodic stripping can achieve detection of concentrations as low as \( 10^{-10} \) M.

**Cyclic voltammetry (CV)**

Cyclic voltammetry (CV) is an electrolytic method that uses microelectrodes and an unstirred solution so that the measured current is limited by analyte diffusion at the electrode surface. The electrode potential is ramped linearly to a more negative potential, and then ramped in reverse back to the starting voltage. The forward scan produces a current peak for any analytes that can be reduced through the range of the potential scan. The
current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. As the applied potential is reversed, it will reach a potential that will reoxidize the product formed in the first reduction reaction, and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak. The peak current, $i_p$, is described by the Randles-Sevick equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2}$$

Where $n$ is the number of moles of electrons transferred in the reaction, $A$ is the area of the electrode, $C$ is the analyte concentration (in moles cm$^{-3}$), $D$ is the diffusion coefficient, and $v$ is the scan rate of the applied potential. The potential difference between the reduction and oxidation peaks is theoretically 59 mV for a reversible reaction. In practice, the difference is typically 70-100 mV. Larger differences, or nonsymmetric reduction and oxidation peaks are an indication of a nonreversible reaction. These parameters of cyclic voltammograms make CV most suitable for characterization and mechanistic studies of redox reactions at electrodes.
1.2 SCOPE OF THE WORK

Total annual cost of floods, hurricanes, tornadoes, fires, lightning, and earthquakes are less than the costs of corrosion. Cost of corrosion will escalate substantially during the next decade because of worldwide shortages of construction materials, higher energy cost, aggressive corrosion environments in coal conversion processes, large increases in numbers and scope of plants, and other factors.

In fact our economy would be drastically changed if there were no corrosion. For example automobiles, ships, underground pipelines, and household appliance would not require coating.

The stainless steel industry would essentially disappear and copper would be used only for electrical purpose. Most metallic plants, as well as consumer products, would be made of steel or cast iron.

Investigation in the field of corrosion inhibition has to visualize following objectives:

- To detect inhibition.
- To determine the effects of inhibition.
- To investigates the course of inhibition and its mode.

The rate of corrosion reaction in solution are governed by numerous factors viz. the reversible M/M⁺ potential, the pH of the medium, dissolved oxygen concentration, kinetics of hydrogen evolution reactions at the surface of the metal and temperature etc. Therefore all these factors have been kept constant throughout the investigation as far as possible and practicable. The inhibition of metallic corrosion in acidic solutions was studied using organic
and inorganic compounds by many scientists. Unfortunately, many common corrosion inhibitors are health hazards. To solve this problem, I have investigated the inhibition effect of amino acids on corrosion of metals.

The focus of this study is to investigate the inhibition properties of amino acids on aluminium, brass and carbon steel corrosion in various media with linear polarization and weight loss measurements methods.

Most of the methods prevalent in the field of corrosion rate determination furnish an average value for a long time interval. However, looking at sensitivity and minimum detection limits of voltammetric procedure, I have decided to develop voltammetric method as a short time corrosion rate determination procedures.
1.3 LITERATURE SURVEY

Organic compounds cannot be designed especially as anodic or cathodic inhibitors. They are mixed inhibitors that inhibit both anodic and the cathodic reactions. The effectiveness of organic inhibitors is related to the extent to which they adsorb and cover the metal oxide surface. The adsorption depends on the structure of the compounds, the surface charge on the metal, and on the type of the electrolyte [18]. Heterocyclic organic compounds containing nitrogen, sulphur or oxygen atoms are often used to protect metals form corrosion. Thus, azoles have been intensively investigated as effective corrosion inhibitors [19-24].

The influence of various aliphatic and aromatic quaternary ammonium salts on the corrosion of mild steel in acid solutions has been extensively studied [25-31]. It is well known that the heterocyclic systems, bearing quaternized nitrogen atom, have better corrosion inhibition than the alkyl substituted quaternary ammonium compounds [29]. Little work [32-36] appears to have been done on the inhibition of mild steel in phosphoric acid solutions. It was found that the corrosion of steel in $H_3PO_4$ is strongly inhibited at temperature up to $90^\circ C$ [32] by the addition of benzylquinolininium thiocyanate.

However, it has been reported [37] that the inhibitors which are useful in hydrochloric acid solutions are generally also effective in $H_3PO_4$ solutions. The effect of some N-containing heterocyclic compounds in the salt form on the rate of mild steel dissolution in $H_3PO_4$ solutions was examined by using chemical and polarization techniques [38]. In recent years there has been a considerable advance
in the understanding of the propagation of filiform corrosion on a range of aluminium alloys [39-57].

The basic approach to making electrochemical measurements under atmospheric conditions is to locate electrically isolated coplanar electrodes in close proximity in order to minimize the signal loss between electrodes. As early as 1960, Sereda reported an atmospheric sensor comprised of platinum foil electrodes arranged on a metal panel substrate (either steel or zinc) [58, 59], where the electrode was determined to be active (wet) when a minimum current flowed through the couple. Later, Kucera constructed a more sophisticated device consisting of parallel plates of metal (e.g., steel, zinc or copper) separated with polycarbonate film [60].

A two-electrode linear polarization experiment was performed by applying a constant potential bias and measuring the resulting current flow. Mansfield followed a similar design philosophy in construction of his atmospheric corrosion monitor (ACM), in which interdigitated electrodes were used to maximize surface area and reduce spacing [61-65].

Gonzalez modified the basic design of Kucera such that multiple counter and reference electrode pairs were located on either side of a central reference electrode, allowing three electrode polarization resistance measurements to be made [66]. Much of this information was reviewed by Mansfield in the early 1980's [67, 68]. Recently, more advanced techniques such as electrochemical impedance spectroscopy (EIS) [69-74] and novel means of electrode construction such as screen-printing [75,76] and pindisk arrangements [77] have been used in
efforts to characterize atmospheric corrosion. These studies have allowed measurements of electrolyte conductivity as well as interfacial processes, though most of these measurements have been made under relatively humid conditions. The effect of polyethylene glycol (PEG) polymer as corrosion inhibitor in acidic medium has been studied using the weight loss method by Shukla et al [78,79]. Voltammetric method was adopted to determine the corrosion rate of brass in acidic medium [80-82].

The corrosion rate of iron and carbon steel in sulphuric acid increases with increasing concentration of the acid, reaching a maximum; with further increase in concentration the rate falls sharply [83]. It is suggested that 1,12-bis (1,2,4-triazolyl)dodecane (dTC12) is an excellent corrosion inhibitor for carbon steel in HCl solution. In this work electrochemical and analytical techniques were used to study the inhibition of corrosion on carbon steel in acidic medium, by Chikh et al [84]. Current voltage measurements were performed for corrosion characteristics. The electrosynthesized films have also been studied in the presence of inhibitor by Pathak and Sankwa [85].

References


