Chapter 1
INTRODUCTION
1. INTRODUCTION

Metal and alloys are used as construction and fabrication materials in engineering. Mild steel is the most versatile, less expensive and widely used engineering material, which has found extensive applications in various industries, mining, construction as well as metal processing equipment\(^1\).

Iron is not as strong and hard as needed for construction, building and other purposes\(^2\). So, about 98% of the raw iron is alloyed with a variety of elements such as, tungsten (W), manganese (Mn), nickel (Ni), vanadium (V) and chromium (Cr) to strengthen and harden it, making useful steel - one of the greatest inventions and the most useful materials ever created for construction, automobiles and other forms of transportation such as trucks, train and train tracks\(^3\). If the metal or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of metals and alloys to undergo destruction by the act of the environment is known as corrosion. However, the corrosion resistance of mild steel is relatively limited. This arises many corrosion problems in the related industries. Corrosion has been known to man since the earliest metallurgical times and has been a constant drain on his productive activities, therefore purposeful attention has been focused on the problem both by scientists and engineers.

1.1 General view of corrosion

The corrosion of metals is a worldwide scientific problem as it affects the metallurgical, chemical and oil industries\(^4\). Corrosion control is an outstanding solution for the preservation of the integrity of industrial systems in the world. It is clear that in the oil industry facilities, where there are equipments susceptible to the phenomenon of corrosion, economic losses are very high, as well there is decrease in production, deployment of personnel for the control of corrosion, etc. Therefore, if the phenomenon is not controlled, it can lead to very significant economic, human and social losses\(^5\).

Therefore, there is a need to investigate the corrosion resistance of metallic materials found in the industry. The use of corrosive environments for laboratory evaluations of materials which are used in the oil industry is proposed in the document NACE
1D196 from which, one can establish if a metallic material is effective or not for use in the industrial environment.

1.2 Definition of corrosion
Corrosion can be defined as the slow deterioration and surface wastage of a metal due to its reaction with its surroundings. According to the ASTM terminology (G15), corrosion is defined as, "the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties".

It is the disintegration of an engineered material [metal alloy] into its constituent atoms due to chemical reactions within its surrounding environment. Mild steel (MS) is the most versatile engineering material, which is used in mining, construction, petroleum, power production, food, chemical and electrochemical industries as its price is relatively low. It provides certain material properties that are acceptable for many applications. But, it suffers from severe corrosion in aggressive media.

Acidic solutions have many industrial applications such as acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. Huge amount of $H_2SO_4$ and $HCl$ are used in the chemical industries for the removal of the undesired scales and rust. The use of acid media in the study of corrosion of mild steel has become important because of its industrial applications as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes. Thus corrosion control of metals has technical, economical, environmental and aesthetic importance.

1.2.1 Causes of Corrosion
Corrosion is a key problem which is faced by all types of engineering and household industries and hence requires larger attention. Different identified factors are responsible for corrosion, of which the material properties, nature and aggressiveness of the environment are the main causes.

In nature, most metals are found in a chemically combined state known as an ore. The combined forms of metals represent their thermodynamically stable state (low energy state). The metals are extracted from these ores after supplying a large amount of energy. Metals in the uncombined condition have a higher energy and are in an
unstable state. It is their tendency to go back to the lowest energy state, i.e. combined state by recombining with the elements present in the environment. Metallic compounds are more stable than pure metals and hence, corrosion occurs in metals and alloy. This is the main reason of corrosion.

1.2.2 Effects of Corrosion

- Production loss during a shutdown
- Replacement of corroded equipment
- High maintenance cost such as repainting
- Loss of efficiency
- Contamination of the product

1.2.3 Cost of Corrosion

Corrosion has a negative impact on the economy. In fact, corrosion costs society in three distinct ways.

- It is extremely expensive.
- It is extreme waste of natural resources.
- It causes considerable inconveniences to human beings and sometimes loss of life.

Corrosion has a major impact on the economies of industrialized nations. It has been roughly assessed that the amount of iron wasted due to corrosion is one fourth of the world’s production. It is also estimated that the cost of corrosion in the developed countries such as the U.S.A. and the European Union is about 3-5% of their gross national product.

A large amount of money is wasted each year as a result of metallic corrosion. An estimated loss has the value of 276 USD which is equivalent to 3.1 percent of the United States GDP. It is estimated that with proper corrosion prevention technologies, about 25 to 30% of this loss can be avoided. In India the direct loss due to corrosion amounts to Rs. 200 crore per annum, while the money spent annually in controlling corrosion is of the order of Rs. 50 crore. Corrosion may cause economic losses directly or indirectly. In India, the cost of corrosion per annum is estimated around Rs.80000 crore i.e 6.1% GDP of the nation. The corrosion inhibition is necessary to reduce the unusual economical losses and to prevent the wastage of resources during the industrial applications. Corrosion inhibition is
essential for the extension of the durability of equipments and limiting dissolution of toxic metals from components in the environment\(^4\). It is better to control rather than to prevent corrosion, since it is impossible to eliminate corrosion.

1.2.4 Corrosion measurement units

The corrosion rate may be expressed as an increase in corrosion depth per unit of time (penetration rate, for example, millimeter per year) or weight loss per unit area per unit time, usually \(D\) (gm/cm\(^3\)), or the corrosion current (mA/cm\(^2\)). Though the preferred SI unit of corrosion rate expression is mm/yr, the commonly used and desirable corrosion rate expression is\(^8\)

\[
\text{Corrosion rate (mmpy)} = \frac{87.6 \times W}{D \times A \times T}
\]

where, \(W\) is weight loss (in mg), \(D\) is the density of specimen (in gm/cm\(^3\)), \(A\) is the area of specimen (in cm\(^2\)) and \(T\) is exposure time (in h).

1.3 Theories of corrosion

1.3.1 Dry or Chemical corrosion

The direct chemical action of the environment, atmospheric gases (oxygen, chlorine etc.) or anhydrous inorganic liquid with metal surface is called dry or chemical corrosion. It is classified into three types:

(i) Oxidation corrosion: The direct action of oxygen on metals in the absence of moisture is called oxidation corrosion.

\[
2M \rightarrow 2M^{n+} + 2n e^-
\]

\[
\text{nO}_2 + 2n e^- \rightarrow 2n \text{O}_2^2-.
\]

\[
2M + n\text{O}_2 \rightarrow 2M^{n+} + 2n\text{O}_2^-\text{ or } 2\text{MO}
\]

When oxidation starts, a thin layer of oxide film is formed on the metal surface and the nature of this film decides the further action.

(ii) Corrosion by other Gases: Gases like SO\(_2\), CO\(_2\), Cl\(_2\), H\(_2\)S, etc. attack metal surface and the extent of an attack depends on the film formation on the surface.

a) If the film formed is protective and non-porous (AgCl), the extent of attack decreases, since the film protects the metal from further attack.

b) If the film formed is non-productive and porous like SnCl\(_4\), which is volatile, then fresh metal surface is available for further attack and the corrosion continues.
Atomic hydrogen can easily penetrate into steel and other metals and increase corrosion.

c) Liquid Metal Corrosion: This is due to the chemical action of flowing liquid metal at high temperature on solid metal or alloy. Corrosion occurs by the dissolution of a solid metal into liquid metal or by internal penetration of the liquid metal into the solid metal. This type of corrosion is observed in nuclear power devices.

1.3.2 Wet or Electrochemical corrosion

This type of corrosion is due to two reasons

(i) when a conducting liquid is in contact with metal or

(ii) when two dissimilar metals or alloys are either immersed or dipped partially in a solution. Corrosion occurs due to the formation of separate anodic and cathodic areas and the corrosion current flows through the conducting medium.

- Mechanism

Electrochemical corrosion involves the flow of electrons from anodic area to cathodic area.

At anode: Metal dissolves due to oxidation.

\[ M \rightarrow M^{n+} + ne^- \text{(oxidation)} \]

Hence, corrosion occurs on anode.

At cathode: At cathodic areas where reduction occurs, corrosion depends on the conducting medium.

\[
\begin{align*}
2H^+ + 2e^- & \rightarrow H_2 & \text{(in acid solution)} \\
H_2O + 2e^- & \rightarrow H_2 + 2OH^- & \text{(in alkaline solution)} \\
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O & \text{(in aerated acidic solution)} \\
O_2 + 2H_2O + 4e^- & \rightarrow 4OH^- & \text{(in neutral solution)}
\end{align*}
\]

- Evolution of hydrogen

In acidic medium, H\(^+\) ions are present which accept the electrons and evolution of H\(_2\) gas occur at cathode, e.g. corrosion of iron by industrial waste containing dilute acids.

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- & \text{(at anode)} \\
2H^+ + 2e^- & \rightarrow H_2 & \text{(at cathode)} \\
\text{Fe} + 2H^+ & \rightarrow \text{Fe}^{2+} + H_2&
\end{align*}
\]
Hence, the metals above hydrogen in electrochemical series liberate hydrogen from acidic solution. In this type of corrosion, anode possess large area and cathodes have small area.

- **Absorption of oxygen**

In aerated and alkaline mediums, the present oxygen absorbs the electrons and form hydroxide ions, e.g. rusting of iron.

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(at anode)} \\
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- & \rightarrow 2\text{OH}^- \quad \text{(at cathode)} \\
\text{Fe} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{Fe} (\text{OH})_2
\end{align*}
\]

If sufficient oxygen is present, ferrous hydroxide is oxidized to ferric hydroxide (rust). Hydroxide ions diffuse slowly than ferrous ions and hence, rust occurs near the cathode. In this type of corrosion, cathodic surface area is larger than that of anodic area.

1.4 **Types of corrosion**

The following are the different types of corrosion:

- **Galvanic corrosion:** Galvanic corrosion is a type of electrochemical corrosion in which two different types of metals in contact are jointly exposed to corrosive atmosphere. Here, the metal with more negative electrode potential will become the anode and goes into solution or corrode, e.g. (a) zinc and copper metals and (b) steel pipe connected to copper plumbing. This corrosion can be minimized by (a) avoiding galvanic couples and (b) providing an insulating material between the two metals.

- **Erosion corrosion:** When a corrosive liquid flows very fast through a metal surface, any protective oxide film formed on the metal surface is completely removed due to mechanical abrasion. The underlying metal becomes exposed to the corrosive atmosphere leading to increased corrosion. This is evident by the appearance of grooves and troughs on the metal surface. The erosion corrosion is frequently observed in bends and elbows in pipelines.

- **Pitting corrosion:** Sometimes corrosion may be concentrated at some places while at other places it may be less. Thus, pits or holes are formed at concentrated places. Let us consider a drop of water resting on a metal surface.
The metal surface which is covered by the drop acts as the anode due to low oxygen concentration and offers corrosion. The metal surface which is uncovered acts as the cathode due to high oxygen concentration.

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(at anode)} \\
\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2e^- & \rightarrow 2\text{OH}^- \quad \text{(at cathode)} \\
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2 \downarrow \\
4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{Fe(OH)}_3
\end{align*}
\]

As the anodic area is small as compared to the cathodic area, more and more metal is removed at the same spot. Thus, a small hole is formed on the surface of the metal. This type of intense corrosion is called pitting.

- **Crevice corrosion**: If a crevice between different metallic objects, e.g., bolts, nuts and rivets, is in contact with liquids, the crevice becomes an anodic region and suffers corrosion. This is due to the lack of oxygen in the crevice area. The exposed areas act as the cathode.

### 1.5 Factors influencing corrosion

The rate and extent of corrosion depend mainly on (a) the nature of the metal and (b) the nature of the environment.

#### 1.5.1 Nature of the metal

- **Position in galvanic series**

  Galvanic series gives information about the corrosion behavior of metals and alloys. When two metals are in contact in the presence of electrolyte, the metals positioned higher up in the series undergoes corrosion. The corrosion rate depends on the difference in their positions. If the difference in position is greater, faster is the corrosion.

- **Purity of metal**

  Corrosion resistance increases with the purity of the metal. The presence of impurities in metal creates heterogeneity, which increases corrosion rate due to the formation of a galvanic cell.

- **Physical state of the metal**

  Metal components subjected to unevenly distributed stresses are easily corroded. Even in a pure metal, the areas under stress tend to be anodic and suffer corrosion.
• **Nature of the oxide film**
The oxide film formed by Na, Mg, Ca, Ba has less volume than the volume of the metal. Hence, the film is porous, through which oxygen diffuses and leads to further corrosion, while the metals like Al, Ni, Cr form oxide film with greater volume than that of metal and the film formed is non-porous, protective and prevents further corrosion.

• **Relative areas of the anode and cathode**
The ratio of the anodic and cathodic area also affects corrosion. If anodic area is small, localized and rapid, corrosion occurs because of high current density in a smaller anodic area and the demand for electrons of the large cathodic area can be met by smaller anodic areas by increasing corrosion rate.

1.5.2 **Nature of the environment**

• **Temperature:** The corrosion rate is generally increased with the increase of temperature of the environment by increasing the rate of the reaction.

• **Effect of Moisture:** The presence of moisture in the environment acts as a solvent for the dissolution of oxygen in the air and increases the corrosion rate. Hence, atmospheric corrosion is based on critical humidity.

• **Effect of pH:** The corrosion rate is more in acidic medium than in neutral or alkaline medium.

• **Nature of the electrolyte:** The nature of the electrolyte also affects the rate of corrosion. The presence of chloride ions destroys the protective film formed on the surface of the metal and increases corrosion.

1.6 **Corrosion control**
Corrosion management is a complex science that needs an extensive understanding of corrosion chemistry and of the process or system being assessed\(^\text{15}\). The corrosion process combines the oxidation and reduction reactions to return refined metals to their more stable ore (mineral) states. Corrosion control is a process aimed at decreasing the corrosion rate and increasing the inhibition efficiency in corrosive environment to a tolerable level\(^\text{6}\).

According to the definition it is the chemical or electrochemical reaction between a material and its environment that produces a deterioration of the material and its
properties. So, corrosion control focuses mainly on (i) materials and (ii) environments. In order to control some of the corrosion problems, several preventive measures are taken which are,

1.6.1 Material selection
Selection of the right type of the material is the main factor for corrosion control. Increasing the purity of the metal decreases heterogeneity, which increases corrosion resistance. Pure Mg and Al, provides protective oxide film on the metal surfaces, when they are exposed to the environment. But, corrosion resistance of pure metal depends on the corrosive environment. Some of the most common materials used in construction of variety of facilities, such as steel and steel-reinforced concrete, can be severely affected by corrosion. The corrosion resistance of a metal strongly depends on the environment. For a given corrosion resistance of the material, as the corrosivity of the environment increases, the rate of corrosion increases. For a given corrosivity of the environment, as the corrosion resistance of the material increases, the rate of corrosion decreases. Consideration of corrosion resistance has been often as important in the selection process as the mechanical properties of the alloy. A common solution to a corrosion problem is to substitute the corroded alloy with an alloy having greater corrosion resistance.

1.6.2 Cathodic protection
The base metal to be protected is forced to act as cathode (corrosion does not occur at the cathode). This is called cathodic protection. This is an effective method to control corrosion on structures either buried or immersed in an electrolyte which employs protecting one metal by connecting it to another metal that is more anodic, according to the galvanic series. Cathodic Protection (CP) is a technology that uses direct electrical current to counteract the normal external corrosion of a structure that contains metal, such as an underground petroleum storage tank or natural gas pipeline. On new structures, Cathodic Protection (CP) can help to stop existing corrosion from getting worse.

1.6.3 Proper designing
The corrosion of metals depends on the design of the equipment and structure which are always in contact with any corrosive medium. The material should be designed in such a way that uniform corrosion occurs and does not result in intense and localized
corrosion. The design of a structure should be such that retention of moisture should be as low as possible because corrosion occurs in the presence of moisture.

1.6.4 Protective coatings

The surface of the base metal is protected from corrosion by applying coatings. There are different types of intelligent coatings, such as organic, inorganic, or nanostructured materials which are used for protection of metal as anticorrosive coating at ambient temperatures. These substances are deposited as a strong, coherent film on the metal surface and increase corrosion resistance. This is mainly used to form a physical barrier between the corrosive environments and metal to protect the structure. It is used mainly with metallic elements exposed to the atmosphere.

- **Use of corrosion inhibitors**

Inhibitors are substances that retard chemical reaction and protect the metal surface from its corroding environment. In the closed system, the application of corrosion inhibitors is another prevalent method for controlling corrosion. Organic and inorganic compounds are used as inhibitors, which adsorb on the metal surface and protect the metal from corrosion. This method is mainly applied in the interiors of pipelines, vessels and equipments.

- **Changing the environment**

Environment also provides a versatile means for reducing corrosion. The corrosive environment is modified by removing harmful constituents or by the addition of specific substances, which neutralize the effect of corrosive substances in the environment. For aqueous corrosion, the environment can be made less aggressive by removing constituents or modifying conditions that facilitate corrosion. This can be achieved by decreasing temperature, decreasing velocity, preventing access of water and moisture, removing dissolved oxygen, and increasing pH for steel. However, this method is limited to closed system in which changes in the corrosion medium can be tolerated.

1.7 Corrosion inhibitors

The protection of metals or alloy against corrosion can be achieved by introducing small amounts of special substances into it which are called as corrosion inhibitor. Corrosion inhibitors are chemical substances which are added in small quantities to aggressive environments, in order to reduce the corrosion rate of the metal. These
substances adsorb on the metal surface and form a protective film and decrease the corrosion rate in corrosive environment\textsuperscript{17}. It is well known in surface chemistry that surface reactions are strongly affected by the presence of foreign molecules. Corrosion processes, being surface reactions, can be controlled by compounds known as inhibitors, which adsorb on the reacting metal surface.

Chemical compounds as inhibitors play an important role in the protection and mitigation strategies for retarding corrosion\textsuperscript{18}. The use of inhibitors for metals and alloys which are in contact with aggressive environment is an accepted practice for the control of corrosion\textsuperscript{17}. The use of corrosion inhibitors is the most economical and practical method in reducing corrosive attack on metals. Organic and inorganic compounds, especially those with N, S and O had shown significant inhibition efficiency\textsuperscript{19}. Inhibitors increase inhibition efficiency and decrease the corrosion rate by\textsuperscript{20}

- Adsorption of ions/molecules onto the metal surface
- Increasing or decreasing the anodic and/or cathodic reaction
- Decreasing the diffusion rate for reactants on the surface of the metal
- Decreasing the electrical resistance of the metal surface
- Using inhibitors that are easy to apply and have in situ application advantage.
1.8 Classification of Inhibitors

Selection of inhibitors is on the basis of metal and its environment. A qualitative classification of inhibitors are presented in as follows:

![Classification of inhibitors diagram]

**Figure 1.1: Classification of inhibitors**

1.8.1 Environmental Conditioners (Scavengers)

Corrosion can be controlled by removing the corrosive species from the medium. These are substances which act by removing corrosion reagents from solution. Inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called environmental conditioners or scavengers. In near-neutral and alkaline solutions, oxygen reduction is a common cathodic reaction. In such situations, corrosion can be controlled by decreasing the oxygen content using scavengers (e.g., hydrazine).
The examples of this type of inhibitors are sodium sulphite and hydrazine which removes oxygen from aqueous solutions as follows:
\[
2\text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{Na}_2\text{SO}_4
\]
\[
\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\]
These inhibitors are often called as negative inhibitors because they remove the undesired species.

1.8.2 Interface Inhibitors
Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors can be classified into liquid and vapour-phase inhibitors.

- **Vapour Phase Inhibitors**

Volatile Corrosion Inhibitors (VCI), also called as Vapour Phase Inhibitors (VPI), are compounds which are transported in a closed environment to the site of corrosion by volatilization from a source. Temporary protection against atmospheric corrosion, particularly in closed environments, can be achieved by using vapor-phase inhibitors (VPI). Substances having low, but significant pressure of vapour with inhibiting properties are effective. The vapour phase inhibitors are used by impregnating wrapping paper or by placing them loosely inside a closed container. The slow vaporization of the inhibitor protects against air and moisture. In general, VPIs are more effective for ferrous metals than non-ferrous metals. In boilers, volatile basic compounds such as morpholine or hydrazine are transported with steam to prevent corrosion in a condenser tube by neutralizing acidic carbon dioxide. Both in molecular and in dissociated forms, VPIs adsorb either physically or chemically on the metal surface to inhibit corrosion.

- **Liquid-Phase Inhibitors**

Liquid-phase inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on whether they inhibit the anodic, cathodic, or both electrochemical reactions.

(i) **Anodic inhibitors**
Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. Anodic inhibitors are frequently called passivating inhibitors as they cause a large shift in the corrosion potential. They form,
or facilitate the formation of passivating films that inhibit the anodic metal dissolution reaction. Passivation by inhibitors is more difficult at higher temperatures, higher salt concentration, lower pH, and lower dissolved oxygen concentrations. Anodic inhibitors are usually used in near-neutral solutions where sparingly soluble corrosion products, such as oxides, hydroxides, or salts, are formed. When the concentration of an anodic inhibitor is not sufficient, corrosion may be accelerated, rather than inhibited. The critical concentration above which inhibitors are effective depends on the nature and concentration of the aggressive ions.

(ii) Cathodic inhibitors
Cathodic inhibitors control corrosion by either decreasing the reduction rate (cathodic poisons) or by precipitating selectively on the cathodic areas (cathodic precipitators). The rate of the cathodic reactions can be reduced by the use of cathodic poisons. However, cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by the metal during aqueous corrosion or cathodic charging. The corrosion rate can also be reduced by the use of oxygen scavengers that react with dissolved oxygen. Cathodic precipitators increase the alkalinity at cathodic sites and precipitate insoluble compounds on the metal surface.

The cathodic reaction, hydrogen ions and / or oxygen reduction make the immediate environment adjacent to the cathodes to become alkaline. Therefore, ions such as calcium, zinc, or magnesium may be precipitated as oxides to form a protective layer on the metal. Many natural waters are self inhibiting due to the deposition of a scale on metals by precipitation of naturally occurring ions.

(iii) Mixed inhibitors (Adsorption inhibitors)
Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface, thus, blocking both the anodic and cathodic sites indirectly. The effectiveness of the organic inhibitors is dependent on the extent to which they adsorb and cover the metal surface. Adsorption depends on the structure of the inhibitor, the surface charge of the metal, and the type of electrolyte. Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorption and film formation. Physical (or electrostatic) adsorption is the result of electrostatic attraction between
the inhibitor and the metal surface. Physically adsorbed inhibitors interact rapidly, but they are also easily removed from the surface. Increase in temperature generally facilitates desorption of physically adsorbed inhibitor molecules. Most organic inhibitors contain at least one polar group with hetero atom such as nitrogen, oxygen or sulphur through which they can be adsorbed, usually by chemisorption, into the metal surface and reduce the corrosion rate. The most effective inhibitors are those that adsorb chemically (chemisorb), a process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface. Chemisorption takes place more slowly than physical adsorption. As temperature increases, adsorption and inhibition also increase. Chemisorption is specific and is not completely reversible.

1.8.3 Green corrosion inhibitors

The use of inhibitors for the control of corrosion is one of the most practical method that is used for metals and alloys which are in contact with aggressive environment especially acid solutions. Organic compounds that exert a significant influence on the extent of adsorption on the metal surface can be used as corrosion inhibitors for an acidic environment in various industries. Many organic compounds were studied to investigate their anticorrosion property. All these studies reveal that most of the organic compounds adsorb on the metal surface and thereby reduce the corrosion rate through hetero atoms such as O, N, and S and multiple bonds which are present in their molecules. It has been investigated that adsorption on metal depends mainly on certain physicochemical properties of the inhibitor group, such as functional groups, electron density at the donor atom, \( \pi \)-orbital character and the electronic structure of the molecule. But unfortunately, synthesis of these compounds is very expensive and these inhibitors are toxic and hazardous for human beings and the environment.

Recently, the use of chemical inhibitors has been limited because they pose environmental threats as per environmental regulations. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system, namely, kidneys or liver, or disturb a biochemical process or an enzyme system at some site in the body. The toxicity may appear either during the synthesis of the compounds or during their applications. Most of the organic and synthetic compounds which
showed a good anticorrosive activity are highly toxic to both human and environment. These are known hazardous effects of most of the synthetic corrosion inhibitors. They are the motivators which necessitates the use of some natural products as corrosion inhibitors. Increasingly, there is a need to develop sophisticated new generation coatings for improved performance, especially in the view that Cr(VI) is banned and labeled as a carcinogen. These toxic affections have led to the use of natural products as anticorrosion agents, which are eco-friendly and harmless. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds.

In the 21st century, the research in the field of "green" or "eco-friendly" corrosion inhibitors has been addressed with the goal of using cheap and effective compounds at low or "zero" environmental impact. Thus, the researchers have focused on the use of eco-friendly compounds which are ecologically acceptable, such as extract of common plants because of their biodegradability, eco-friendliness, cost-friendliness and easy availability, and also they are renewable sources of materials.

Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and are renewable sources of materials which are ecologically acceptable. Plant products are organic in nature, and some of the constituents, including tannins, organic compounds, amino acids, alkaloids, and pigments are known to exhibit inhibiting action. Moreover, they can be extracted by simple procedures with low cost. These extracts contain different hydroxy organic compounds, e.g. tannins, pectin, flavonoids, anthraquinones, steroids, saponins and coumarins, in addition to other nitrogen containing compounds.

Extracts of plant materials is a complex mixture of various phytochemical components and contain a wide range of organic compounds. Most of them contain hetero atoms such as P, N, S, O. These atoms coordinate with the corroding metal's atoms (their ions) through their electrons. Hence, protective films are formed on the metal surface and hence, corrosion is prevented.

The inhibition performance of the plant extract is normally ascribed to the presence of the typical composition of complex organic species, including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products. Naturally
occurring plant extracts contain mixtures of compounds which exhibit polar functions with nitrogen, sulfur or oxygen atoms as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures, which act as major adsorption centers.

In 1930, plant extracts, dried stems, leaves, seeds and other plant parts were used in H₂SO₄ acid pickling baths. Animal proteins which are found in the products of meat and milk industries are also used for retarding acid corrosion. The additives used in acid, including flour, bran, yeast, a mixture of molasses and vegetable oil, starch and hydrocarbons (tars and oils) are used as corrosion inhibitors.

Many scientific researches have been dedicated to prevent metallic corrosion and for the use of natural products as a green corrosion inhibitors such as *Medicago sativa*³, *Azadirachta indica*⁷, *Gundelia tournefortii¹¹, Nicotiana tabacum¹¹, Chenopodium ambrosioides³³, *Camellia sinensis*³⁴, *Cuminum cyminum*³⁵, *Sida acuta*³⁶, *Anacyclus pyrethrum* L.⁷ are found to be very efficient corrosion inhibitors for steel in acidic media.
REFERENCES


