CHAPTER 1

INTRODUCTION

Introduction

1. Introduction.

Modern research focuses on protecting metals and alloys from corrosion in acidic solutions because they have many applications in industries such as acid handling and cleaning, oil recovery, petrochemical industries, etc. One of the most difficult challenges in modern science is protecting metals and alloys from corrosion. Metals like carbon steel are essential to the industrial process and are inevitably exposed to different industrial environments. Corrosion of carbon steel pipes and equipment occurs when water and acidic gases like CO_2, H_2S, and CH_3COOH are present. The chemical environment or the surrounding environment can cause carbon steel to corrode on exposure to different chemicals. Corrosion control techniques generally increase the service life of steel. Changing the surrounding environment or modifying the metal surface are the most common methods to reduce corrosion.

Using appropriate inhibitors, steel corrosion is successfully prevented in these cases. Organic compounds containing heteroatoms such as N, S, and O are the most common acid corrosion inhibitors. N and S-containing corrosion inhibitors have been demonstrated to be powerful corrosion inhibitors. Most organic inhibitors work by attaching to metal surfaces [(Lee, Kim, and Kim 2012; Zheng *et al*. 2014; Belayachi *et al*. 2015; Tang *et al*. 2011)].

The creation of an inhibitory layer at the metal/solution interface can drastically modify how metals resist corrosion. This phenomenon of shielding corroding metal and equipment surfaces stops the squandering of resources and wealth. It helps to increase the equipment's

lifespan and decreases the release of harmful metals into the environment. Quaternary ammonium compounds are crucial corrosion inhibitors in sulfuric and hydrochloric acid media.The synergistic impact between the organic cation and the halide anion and its inhibitory influence on metal corrosion is crucial [(Soror and El-Ziady 2003)].

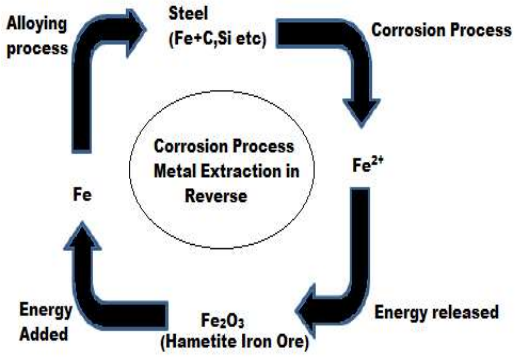

Figure: 1.1: Corrosion process

1.1 Definition of Corrosion.

Corrosion is described as the eating away of metal or the degradation and deterioration of the metal's useful properties as a result of chemical, electrochemical, and biochemical reactions with environmental factors [(Fontana and Greene 1967)] or Metal corrosion is also defined as the spontaneous degradation of metals as a result of chemical, electrochemical, and biological exchanges with the environment. Therefore, it may be argued that it is the inverse of metal extraction from ores. Most metals are found in settings in an unstable or reactive

state, which causes them to transform into more stable compounds through a process known as corrosion.

1.2 Economic losses

According to NACE (National Association of Chemical Engineers) estimates from 2014, the cost of corrosion annually in the United States is in the neighbourhood of $1 trillion, whereas it costs Rs. 1.07 Million crores in India. Direct and indirect losses in the economy can be distinguished.

1.2.1 Direct losses:

- Inability to use otherwise desirable materials.
- Overdesign to accommodate corrosion.
- The price of fixing or replacing the rusted part.
- The price of corrosion-resistant paint or other types of protection.

1.2.2 Indirect losses:

- Product contamination
- The loss of a valuable product as a result of a rusted container.

- Corrosion failure caused damage to surrounding equipment.
- Product loss.
- Safety, for example, a sudden failure of equipment can result in a fire, explosion, or the release of a toxic product.

1.3 General idea of Corrosion

Corrosion is a type of chemical or electrochemical oxidation that involves anodic and cathodic processes. Assume a metal "M" is engrossed in a H_2SO_4 Solution . As a result, Metal oxidation takes place via anodic reaction, and metal reduction takes place by cathodic reaction, as seen below:

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

$$zH^+ + zSO_4^{2-} + ze^- \rightarrow z/2\ H_2SO_4 \qquad \text{(Cathodic = Reduction)} \qquad (1.2)$$

$$M + zH^+ + zSO_4^{2-} \rightarrow M^{+z} + z/2\ H_2SO_4 \qquad \text{(Overall = Redox)} \qquad (1.3)$$

where: M= Metal, H^+ = Hydrogen cation, z= Valence or Oxidation state

M^{+z}= Metal cation, SO_4^{2-}= Sulfate anion

The aforementioned equations include an anodic process, also known as oxidation, in which metal loses electrons, and a cathodic reaction, also known as reduction, in which electrons are accepted or gained in order to reduce relevant ions. Redox reaction, also known as overall reaction, is the result of combining anodic and cathodic reactions.

1.3.1 Corrosion problems in oil/petroleum industry

Corrosion of steel and other metals in the pipeline and storage equipment, as well as in the gas and oil well equipment, is a prevalent issue in the oil and petroleum business. (Sutanto and Semerad 1990; Wu *et al*. 2010).

Corrosion damage is determined to be predominantly caused by chemical causes in the petroleum industry, such as high levels of water mineralization, high concentrations of corrosive gases (CO_2, H_2S, etc.), and the presence of atmospheric oxygen in pipelines, physical factors, such as temperature, pressure, and flow hydrodynamics, and metallurgical factors, such as the properties of the metal.

The primary cause of pipeline corrosion in sweet oil wells is H_2CO_3, which is produced when CO_2 and H_2O react. Due to the high sulphur content, sour wells have more corrosive environments and severely corrode the casing in the top part of the well. CO_2, seawater, H_2S, N_2,O_2, H_2SO_4, NH_3, HCl, NaOH, and some organic chemicals like mercaptan and naphthenic acid at high temperatures are the main inorganic compounds that impact corrosion on the metal surface in refineries.

1.3.2 Acidizing treatment in oil wells

A typical stimulation approach for enhancing crude oil productivity by widening the microscopic flow channels is acidizing an oil well with N80 steel tubing. The acid mixture helps dissolve drilling mud components that restrict oil flow into the producing zone. The treatment fluid is commonly composed of hydrochloric acid and acidic additions, depending

on the subsurface nature of the oil wells. Acid treatments usually involve a range of acid types or mixtures, such as CH_3COOH, HCOOH, HCl, HF, and HBF_4. The uses of various acid types or mixes are determined by the reaction properties of the prepared treatment fluid. Hydrochloric acid is a fundamental component of acidic solutions used in the petroleum industry to clear clogging in bore wells and boost production. Because it is less expensive than other acids, hydrochloric acid is favoured for acidifying carbonate-based reservoirs because the Fe_2Cl_2 generated on the surface is extremely soluble in H_2O [(Jayaperumal *et al*. 2000)]. In the petroleum industry it doesn't produce any soluble reaction products, 15% HCl is frequently used for acidizing. It is commercially accessible and moderately priced. HF combined with other acids is sometimes used to dissolve clays and other silicate minerals. To boost commercial output, the acid is pumped within the well through steel tubing, where it enters the tributary drainage channels and dissolves the exposed limestone surfaces of the rocks. The acid reaction is shown by the equation below.

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2 \quad (1.4)$$

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

1.3.3 Pickling

Pickling is a process that uses a water solution of inorganic acids, such as sulfuric or hydrochloric acid, to chemically remove oxides and scale from the surface. Pickling with hydrochloric acid results in a quicker and cleaner process with less acid intake and waste pickle fluid. Steam use is 40% less since hydrochloric acid pickling uses lower temperatures

[(Kladnig 2008)]. Pickling with hydrochloric acid results in a smoother, pore-free steel surface than pickling with sulfuric acid. Pickling in hydrochloric acid is likewise around 10 times faster at comparable temperatures and acid concentrations. One of the most notable environmental benefits of thermal regeneration plants is their ability to fully recover hydrochloric acid (up to 99% yield). [(Kladnig 2008)]. Hydrochloric acid is also more effective at removing scale and embedding metal particles. Scale breaking and temper rolling, which are sometimes required in a sulphuric acid pickling line, are normally not required for high-speed pickling in hydrochloric acid baths, allowing them to be more adaptable. Pickled surfaces are often cleaned and dried before further processing. Pickling the surface of a metal before galvanizing, coating, or painting it improves bonding and adhesion [W.T. Lankford (1985)].

1.4 Classification of Corrosion

There are many different ways to categorise corrosion., but the most preferred classification is.

(a) Chemical Corrosion or Dry Corrosion

(b) Electrochemical Corrosion or Wet Corrosion

1.4.1 Chemical Corrosion or Dry Corrosion.

This type of corrosion is primarily brought on by the direct chemical reactions between metal and surrounding gases (O_2, halogen, H_2S, SO_2, or anhydrous inorganic liquid). One type of dry corrosion is oxidation corrosion.

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

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

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

1.4.2 Electrochemical Corrosion or Wet Corrosion.

This type of Corrosion occurs:

i) When a conducting liquid comes into contact with a metal. or

ii) when two metals or alloys with different properties are partially immersed in a solution.

Because anodic and cathodic components are distinct from one another and current travels via the conducting solution between them, wet corrosion happens. An oxidation reaction Occures at the anodic location, destroying the anodic components.

$$M \rightarrow M^{n+} + ne^{-} \quad \text{(At anode)} \qquad (1.9)$$

Electronation (reduction process) takes place at the cathodic portion. Since most metals cannot be reduced any further, it has little effect on the cathode. At the cathodic section, the conducting medium's dissolved constituents take the electrons, forming ions (OH^{-},O^{2-}). Between the anode and the cathode, the metallic ions created at each of the anodic and cathodic parts diffuse towards one another across the conducting medium to create a corrosion product.

$$Fe \rightarrow Fe^{2+} 2e^{-} \quad \text{(oxidation)} \qquad (1.10)$$

The electrons liberated pass through the metal from anode to cathode, while the acidic solution's H^+ ions are removed as H_2 gas,

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

The overall reaction is:

$$Fe + 2H^{+} \rightarrow Fe^{2+} + H_2 \qquad (1.12)$$

At anode:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad \text{(Oxidation)} \qquad (1.13)$$

At cathode: The liberated electrons pass through iron metal from anode to cathode.

$$\frac{1}{2} O_2 + H_2O + n2e \rightarrow 2OH^{-} \quad \text{(Reduction)} \qquad (1.14)$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \qquad (1.15)$$

If oxygen is in excess, $Fe_2(OH)_2$ is easily oxidized to $Fe(OH)_2$.

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \qquad (1.16)$$

The product called yellow rust corresponds to $Fe_2O_3.xH$

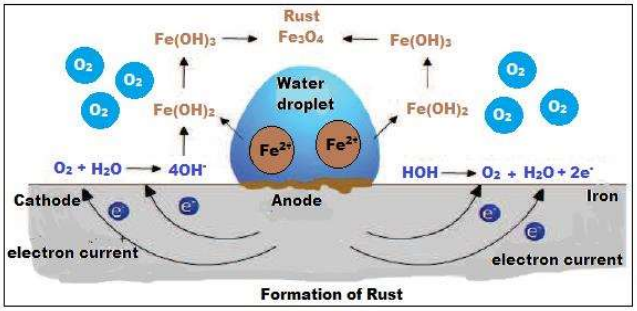

Figure: 1.2: Formation of rust

1.5 Different forms of corrosion.

It is more Suitable to talk about corrosion in terms of the different ways it appears as corroded metal [(Fontana and Greene 1967)]. Visual observations can be used to characterize every form. Most of the time, we can distinguish between different types of corrosion with our naked eyes, but occasionally, magnification is necessary. By carefully examining the corroded test specimens using various approaches, useful information can be gleaned from the resolution of a corrosion problem. These eight corrosion types are somewhat interconnected [(Wranglén *et al*. 1985)]. Several types of corrosion include:

1. Uniform corrosion

2. Galvanic corrosion

3. Crevice corrosion

4. Pitting corrosion

5. Selective leaching

6. Intergranular corrosion

7. Stress corrosion

8. Erosion corrosion

9. Hydrogen damage

The characteristics, mechanisms, and Protective methods of the eight forms of corrosion are detailed here. Hydrogen damage is frequently caused indirectly by corrosive attack. Although it is not a type of corrosion, it is also examined. Figures 1.3 to 2.2 depict eight types of corrosion.

1.5.1 Uniform corrosion

It is the most frequent type of corrosion and is also known as consistent attack. As the name implies, it is typically detected evenly over the entire exposed surface area as a result of a chemical or electrochemical response. Metal thickness decreases equally. A piece of steel, for example, immersed in weak H_2SO_4 will generally dissolve at a uniform rate across its whole surface. The identical corrosion is depicted in Figure. 1.3. Uniform attack, also known as general corrosion, causes the most metal or alloy degradation. However, from a technical standpoint, this type of corrosion is not a major issue because the service life of equipment can be estimated using relatively simple tests.

1.5.2 Galvanic or two metal corrosion.

A potential difference is formed when two different metals are immersed in a corroding or conductive fluid. If these metals come into touch or are electrically linked, electron flow takes place due to a potential difference between them. The metal which is less corrosion-resistant will be more corroded. Here, the less resistant metal serves as the anode, while the more resistant metal serves as the cathode. In this pair, the cathodic metal usually corrodes very little or not at all. Because of the presence of electric currents and different metals, this type of corrosion is known as galvanic or electrochemical corrosion. In designing the heat transfer equipment, galvanic corrosion is considered where two dissimilar metals are present in electrical contact. However, two different metals are present in electrical contact in the cooling water system due to the presence of water. Figure 1.4 represents the Galvanic corrosion.

1.5.3 Crevice Corrosion

It is also an electrochemical attack generated by a differential in corrosion-causing species concentrations between a protected area and its surroundings. This corrosion is common on metal surfaces exposed to corrosive environments, especially in crevices and other shaded areas. Figure 1.5 depicts crevice corrosion. This form of assault typically happens in areas with modest amounts of the stale solution, such as holes, gasket surfaces, surface deposits, and crevices under bolts. As a result, this type of corrosion is often referred to as crevice corrosion, deposit corrosion, or gasket corrosion

Fig.1.3 Uniform corrosion

Fig.1.4 Galvanic corrosion

Fig.1.5 Crevice corrosion

Fig.1.6 Pitting corrosion

Fig.1.7 Selective leaching

Fig.1.8 Intergranular corrosion

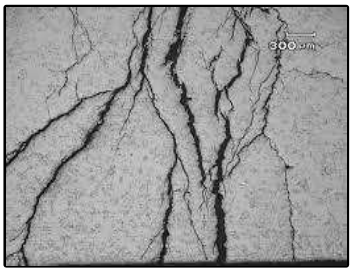

Fig.1.9 Stress corrosion

Fig.1.10 Erosion corrosion

Fig.1.11 Hydrogen damage

1.5.4 Pitting Corrosion.

Pitting is a highly localized form of corrosion that causes holes to emerge in the metal. Although the holes' diameters can vary, they are often quite small in diameter. Due to their

proximity to the viewer, pits might occasionally appear to have a rough surface. Pitting corrosion is depicted in Figure 1.6.

One of the most subdued forms of corrosion is pitting. Perforation caused equipment failure with only a modest percent weight loss of the overall surface produced by this form of corrosion. Because of their small size, pit detection is difficult, and the pits are frequently hidden by corrosion agents. Furthermore, it is difficult to quantify and evaluate the level of pitting because depths and numbers of pits vary under identical conditions. Pitting is also challenging to find in a lab. Sometimes it takes several months for the actual vision to appear. Pitting is particularly dangerous since It is a concentrated and localised form of corrosion., and breakdowns can occur abruptly.

1.5.5 Selective leaching or selective dissolution.

In this kind of corrosion, the corrosive process eliminates one element from a solid alloy. The most typical use is to selectively remove zinc from brass alloys (dezincification).Other alloys that have had Al, Fe, Co, Cr, and other components removed go through the same processes. Figure 1.7 depicts the corrosion type known as selective leaching.

The removal of any metal is generally referred to as selective leaching, which gives birth to phrases like dealuminification, decobaltification, etc.

1.5.6 Intergranular Corrosion.

Intergranular corrosion (IGC) occurs when the material's crystal borders are more susceptible to corrosion than its interior faces.This type of corrosion is frequently accompanied by chemical separation effects, which can lead to the enrichment of contaminants near grain boundaries. Typically, the impact is related with the isolation of specific components or the formation of a complex along the borders. This form of corrosion preferentially affects the grain boundary phase, making the grain boundary zone anodic in comparison to the rest of the material. Because the grain borders have disintegrated completely, the process frequently takes a limited path along the grain boundary, and whole grains may be eliminated. In the vast majority of metal applications or uses, grain boundary effects are not an issue. When a metal corrodes, a homogeneous attack occurs because grain boundaries are often only slightly more reactive than the matrix. However, under some conditions, grain interactions are prone to reactions that result in this type of corrosion. The alloy deteriorates and loses tensile strength. Impurities close to grain borders can lead to intergranular corrosion, alloying element supply, or alloying element dissolving in grain-boundary regions. Small levels of iron in aluminium cause grain boundary segregation, a type of intergranular corrosion. Chromium breakdown at grain boundaries causes stainless steel intergranular corrosion. Intergranular corrosion is depicted in Figure 1.8.

1.5.7 Stress-corrosion cracking.

Stress-corrosion cracking occurs when ductile stress and a certain corroding medium coexist. The majority of a metal or alloy's surface is essentially unaffected by stress-corrosion cracking, while tiny fissures are processed through it. Since it can happen within the range of traditional design stress, this furious phenomenon might have serious consequences. Two examples of SCC are the corrosive embrittlement of steel in riveted steam locomotive boilers and the season cracking of brass in brass cartridge cases as a result of ambient ammonia. Stress cracking can occur in a variety of alloys depending on the corrosive environment. In chloride conditions, stainless steel corrodes. In Figure 1.9, stress corrosion cracking is depicted.

"The two most prevalent types of stress-corrosion cracking are "caustic embrittlement" of steel and "season cracking" of brass. Season cracking describes the stress-corrosion cracking collapse of brass cartridge casings. During heavy rains, usually in the tropics, brass sealed unit cases were discovered to have cracks where the case was folded to the shell. It was previously shown that ammonia, which is produced by the decomposition of organic waste, is a key environmental component that contributes to stress corrosion cracking.

In mechanical metallurgy, stress alone will create creep, fatigue, and tensile failure, and corrosion alone will produce the standard dissolving responses; however, the simultaneous action of both can be quite damaging.

1.5.8 Erosion Corrosion.

It is the acceleration of the assault on the metal surface caused by the relative mobility of the metal surface and a caustic medium. Because of the presence of mechanical abrasion, this movement often occurs quickly. Dissolved ions remove metal from the surface, or less commonly, by solid corrosion products scraped off the metal surface. When a corrosive material is flowing, this sort of corrosion takes place. When a limited assault takes place during a dormant period, the environment might sometimes slow the corrosion process down, but this does not always indicate erosion corrosion because the attack on the metal is not accelerated.

Grooves, gullies, waves, circular holes, and valleys are telltale signs of erosion corrosion and typically follow a directed pattern. Corrosion and erosion are shown in Figure 1.10.

1.5.9 Hydrogen Damage.

Titanium and various other metals, as well as high-strength steels, are susceptible to hydrogen embrittlement. Hydrogen removal from the environment or the usage of resistant alloys can manage it. In Figure1.11, this sort of corrosion is depicted.

1.6 Factors Affecting Corrosion rate.

1.6.1 Primary factors, depending on the metal:

1.6.1.1 Nature of the metal:

The nature of a metal determines its affinity to ensure corrosion. Metals with a low reduction potential corrode easily, whereas metals with a high reduction potential do not. Noble or less reactive metals such as Ag, Au, Pt, and Pd are less prone to corrosion, whereas reactive metals such as Na, K, Mg, and Zn are more vulnerable.

1.6.1.2 Surface state of the metal:

Corrosion is a surface occurrence. As a result, the surface area is directly proportional to corrosion processes. The greater the corrosion, the finer the grain size of the metal. Smooth surfaces are less prone to corrosion than rough surfaces. Due to the existence of ups and downs on the rough surface, A large number of air-concentration cells with anodic and cathodic regions form. As a result, the metal corrodes.

1.6.1.3 Nature of the corrosion product:

Low hydrogen values over the metal's voltage make the metal more corrosive. This is due to the fact that more hydrogen gas may be easily generated in hydrogen evolution cathodic reactions with lower hydrogen overvoltage, which speeds up the cathodic process and

accelerates metal corrosion. Metals exposed to high hydrogen overvoltage undergo a delayed cathodic reaction, which inhibits metal corrosion.

1.6.1.4 Hydrogen overvoltage:

Low values of hydrogen over the metal's voltage make the metal more corrosive. This is because more hydrogen gas can be easily evolved in cathodic reactions of the hydrogen evolution type with lower hydrogen overvoltage, which speeds up the cathodic reaction and accelerates metal corrosion. High hydrogen overvoltage metals experience a slow cathodic reaction, which slows down metal corrosion.

1.6.2 Secondary factors related to the environment:

1.6.2.1 pH of the medium:

In general, the rate of corrosion reported in the acidic pH range is relatively high. If the pH range is greater than 10, then very less possibility of corrosion of iron because of the formation of a protective coating of iron hydrous oxides. If the pH is between 10 and 3, oxygen is required for iron corrosion. Even in the absence of air, significant corrosion occurs when the pH is 3 or lower due to the sequential development of hydrogen gas at the cathode. However, metals like Al, Zn, etc., also show rapid corrosion in the highly alkaline medium.

1.6.2.2 Temperature:

Corrosion accelerates as temperature rises. This is because aqueous medium conductivity increases with temperature. As a result, the rate of diffusion increases. In other words, deceit occurs, and inhibitors do not act correctly.

1.6.2.3 Presence of oxidizing agents:

The metal corrodes more quickly when oxidizing chemicals are present. When oxidizing substances are present, corrosion occurs even to inert metals.

1.6.2.4 Humidity:

In humid air, most metals corrode faster than in dry air. Critical humidity is a specified level of humidity above which the rate of corrosion significantly rises. Humidity provides a conducting medium, which aids in the growth of electrochemical cells on metal surfaces. O_2, CO_2, and SO_2 gases dissolve and contribute to corrosion.

1.6.2.5 Presence of impurities in the atmosphere:

Because acidic conditions are formed by the dissolution of pollutants such as SO_2 and HCl, their presence in the environment increases corrosion. As an example, when SO_2 is present in the atmosphere as an impurity, it mixes with moisture or water droplets to form sulfuric acid. When there is acid in the system, metals such as iron corrode faster.

1.6.2.6 Conductance of the medium:

Corrosion accelerates when conducting species are present in the air. This is because higher medium conductivity allows ions to travel quickly between the anodic and cathodic regions of the corrosion cell, speeding up electron exchange at the electrode surfaces. Corrosion is a considerably bigger problem in salt water than in fresh water.

1.6.2.7 Area effect:

A smaller anodic area and a bigger cathode area cause faster corrosion, while a larger anodic area and a smaller cathode area cause slower corrosion. This is because the anode (which has a smaller anodic area) releases electrons, which the massive cathodic area quickly consumes, increasing the rate of corrosion.

1.6.2.8 Polarization at anodic and cathodic area:

Corrosion is slowed by polarisation of the cathode or anode. Anodic polarization occurs as a result of a reaction, which reduces the metal's proclivity for oxidation and makes metal ions less likely to dissolve in the solution. This is generally caused by an increase in the concentration of ions from dissolved metals in the vicinity of the electrode, but it is also possible that corrosion resistance provided by anodic passivity is to blame. Cathode polarization hinders the combination of cathodic species with electrons because it reduces the cathodic reaction. For corrosion to occur, both anodic and cathodic processes must occur at the same time. Corrosion will be slowed if any of them responds slowly. Depolarizers function by lowering the polarization effect, which slows the corrosion reaction.

1.6.3 Electrochemical Theory of Corrosion.

Electrochemical reactions are responsible for the majority of metal corrosion, particularly in aquatic settings. The whole corrosion process involves two reactions: one is the oxidation of the metal, known as anodic process, and the other is an equivalent reduction reaction, known as cathodic process. The generation of electrons, as seen here, indicates an oxidation reaction:

$$M \longrightarrow M^{n+} + ne- \quad (1.17)$$

The anodic process in which electrons are lost is what causes metals to corrode. A reduction reaction uses electrons in a similar way. For any oxidation process, a matching reduction reaction must exist. Several examples of reduction reactions include:

Hydrogen evolution: $2H^+ + 2e- \; H_2$ (in acidic system) (1.18)

Oxygen reduction: $O_2 + 4H^+ + 4e^- \; 2H_2O$ (in acidic solution)

$O_2 + 2H_2O + 4e- \longrightarrow 4OH^-$ (in neutral and alkaline solution) (1.19)

Metal ion reduction: $M^{n+} + e^- \longrightarrow M^{(n-1)+}$ (1.20)

Metal deposition: $M^{n+} + ne^- \longrightarrow M$ (1.21)

Reduction reactions are referred to as cathodic, while oxidation events, which take place at anodic sites, are known as anodic reactions. Throughout the corrosion process, more than one oxidation and cathodic reduction reaction may occur. The Corrosion of Carbon steel in H_2SO_4 contaminated with ferric ions can be used as an example to explain oxidation-reduction (redox) reactions. The following diagram illustrates the anode reaction:

$$M \longrightarrow M^{n+} + ne^- \quad (1.22)$$

All of the constituent components of Carbon steel, such as Fe, Mn, and others, enter the solution as their appropriate ions.These anodic (oxidation) reactions will consume the electrons produced. In this case, reaction (1.22) is depicted as follows:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ _____ (1.23)

By removing the Fe^{3+} ions, the corrosion rate will be lowered. When a metal or alloy is subjected to a corroding media, multiple potential zones are formed on the surface due to the existence of diverse grain boundaries, segregation, crystallographic distortions, metallic phases, impurities, and so on . As a result of the potential difference, anodic and cathodic areas, where oxidation and reduction occur on the surface of metal, are produced. As a result of these regions, local action cells grow on metal surfaces. Environmental or temperature changes can potentially cause the formation of local action cells. To calculate the electrode potential, the Nernst equation is utilized

$$E = E_0 + \frac{RT}{ZF} \ln \frac{(Ox)}{(red)} \quad \text{_____ (1.24)}$$

Where,

I = Standard electrode potential

R = Gas constant (1.98 Cal/GM. Equivalent)

F = Faraday constant

T = Temperature

z = Number of electrons transferred in the reaction

(ox) = Concentration of oxidized species (mol/L)

(red) = Concentration of reduced species (mol/L)

1.7 Thermodynamic Principles of Corrosion

Metallic state often refers to the higher energy state of metal. In order to return to a lower energy state with subsequent releases of energy, metal has a natural tendency to react with other compounds. All metals' free energy is reduced as a result of environmental reactions (except noble metals, which are found in the native state in nature). When chemical compounds are created from simpler substances, the signs and changes in free energy (G) are used to determine the thermodynamic stability of those molecules. The thermodynamic property known as free energy expresses the substance's resultant enthalpy and its inherent probability. The following are some ways to express free energy at constant temperature:

$\Delta G^{\circ}_{ads} = \Delta H - T\Delta S$ _____ (1.25)

In this equation, ΔG^0 stands for changes in free energy, ΔH for enthalpy, S for entropy, and T for absolute temperature.

When the reaction is at equilibrium, then:

$\Delta G^0 = -RT \ln Keq$ _____ (1.26)

R is the gas constant, ΔG^0 is the standard free energy, and Keq is the equilibrium constant. The free energy (ΔG) of a reaction is proportional to its potential through:

$\Delta G^0 = -nFE^0$ _____ (1.27)

A positive number of ΔG denotes that the reaction has no tendency to advance, whereas a negative value of free energy implies that the reaction is spontaneous. Cell potential of the reaction can be used to quantify the change in free energy associated with an electrochemical or corrosion reaction [(Dean and Von Dem Bussche 1981)]. By using the redox potential, one may determine whether or not a metal will corrode in a specific environment.

1.7.1 Kinetics of Corrosion.

Consider an electrochemical reaction that occurs at the metal-solution interface and is proportional to the current-potential dependence.

Nernst and Caspari proposed voltage (polarization) as the potential change, E-Er, from the equilibrium half-cell electrode potential Er induced by a net surface reaction rate for the half-cell reaction. Tafel established that for a hydrogen evolution reaction, the dependence on current density is =a + b log i. Butler offered a kinetic description of reversible electrodes that used an exponential equation to connect the concepts of partial anodic and cathodic currents.

1.7.2 Activation controlled corrosion.

Slow electrode reaction is the most common cause of activation polarization. To proceed, The reaction at the electrode necessitates the use of activation energy. The hydrogen ion reduction reaction at the cathode is the most well-known activation-controlled corrosion reaction. The use of electrochemical kinetic theory can be used to derive the relationship

between current and potential for a corroding system in which the anodic reaction is metal dissolution and the cathodic reaction is hydrogen evolution.

For the metal dissolution reaction,

$$M \rightarrow M^{+2} + 2e^{-} \tag{1.28}$$

$$i_c = i_c^{o}\left\{\exp\left(\frac{\alpha_c F}{RT}(E - E_c^{r})\right) - \exp\left(\frac{-\beta_c F}{RT}(E - E_c^{r})\right)\right\} \tag{1.29}$$

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

Normally, the corrosion potential (E_{corr}) will be far from the reversible reaction's equilibrium potential. As a result, the contribution from the metal dissolution reaction deposition reaction and the anodic partial reduction process is insignificant. As a result, the net current of the mixed electrode system is as follows:

$$i = i_a - i_c \tag{1.30}$$

$$= i_a^{o}\left\{\exp\left(\frac{\alpha_a F}{RT}(E - E_a^{r})\right) - \exp\left(\frac{-\beta_a F}{RT}(E - E_a^{r})\right)\right\} \tag{1.31}$$

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

$$\text{i.e. } i_{corr} = i_a^{o}\left(\exp\frac{\alpha_a F}{RT}(E_{corr} - E_a^{r})\right) \text{ (for anodic reaction)} \quad (1.32)$$

$$\text{i.e. } i_{corr} = i_c^{o}\left(\exp\frac{\alpha_c F}{RT}(E_{corr} - E_c^{r})\right) \text{ (for cathodic reaction)} \quad (1.33)$$

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

$$i = i_{corr}\left\{\exp\left(\frac{\alpha_a F}{RT}(E - E_{corr})\right) - \exp\left(\frac{-\beta_c F}{RT}(E - E_{corr})\right)\right\} \quad (1.34)$$

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

$$i = i_{corr}\left\{\exp\left(\frac{2.3(E - E_{corr})}{\beta_a}\right) - \exp\left(\frac{-2.3(E - E_{corr})}{\beta_c}\right)\right\} \quad (1.35)$$

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

$$i = i_{corr}\left\{\exp\left(\frac{2.3\eta}{\beta_a}\right) - \exp\left(\frac{-2.3\eta}{\beta_c}\right)\right\} \quad (1.36)$$

The aforementioned expression serves as the foundation for calculating the corrosion rate using the electrochemical approach.

1.7.3 Diffusion controlled reaction.

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

$$i_a = i_{corr}\left(\exp\frac{\alpha_a F}{RT}(E - E_{corr})\right) \tag{1.37}$$

$$i_c = i_d = \frac{\eta F D C_b}{\delta} \tag{1.38}$$

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

$$i = i_a - i_c \tag{1.39}$$

$$i_a = i_{corr}\left(\exp\frac{\alpha_a F}{RT}(E - E_{corr})\right) - i_d \tag{1.40}$$

i_d= limiting diffusion current density

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

As a result, the id is the most critical parameter in the corrosion reaction where the cathodic reaction is diffusion controlled, and every component that increases i_d increases the corrosion rate.

1.7.4 Diagrams associated to Kinetic parameters.

Corrosion polarization diagram, often known as an Evans diagram or a mixed-potential diagram. U. R. Evans of the University of Cambridge in England created the initial polarization diagram.

1.7.4.1 Evans Diagram.

This is a plot that shows potential vs log current or log current density. In addition to the electrode being investigated (the "working" electrode), the conventional electrodes used to generate an Evans diagram are the reference electrode and the inert counter (or auxiliary) electrode, which is commonly made of platinum. Depending on the type of measurements to be performed, a galvanostatic circuit comprised of a power source, resistor, ammeter, and potentiometer can also be used.The current between the working and counter electrodes is controlled, and the potential of the working electrode in respect to the reference electrode is monitored. Figure 1.12 shows a metal M. Evans diagram.

The oxidation reaction in this system might be metal dissolution, $MM^{+z} + ze^-$, while the reduction reaction could be Rn^{++} ne^-R. The reduction reaction in an aerated neutral or basic

aqueous solution could be $O_2 + 2H_2O + 4e^- \; 4OH^-$, whereas in a deaerated acid may be $2H^+ + 2e^- \; H_2$.

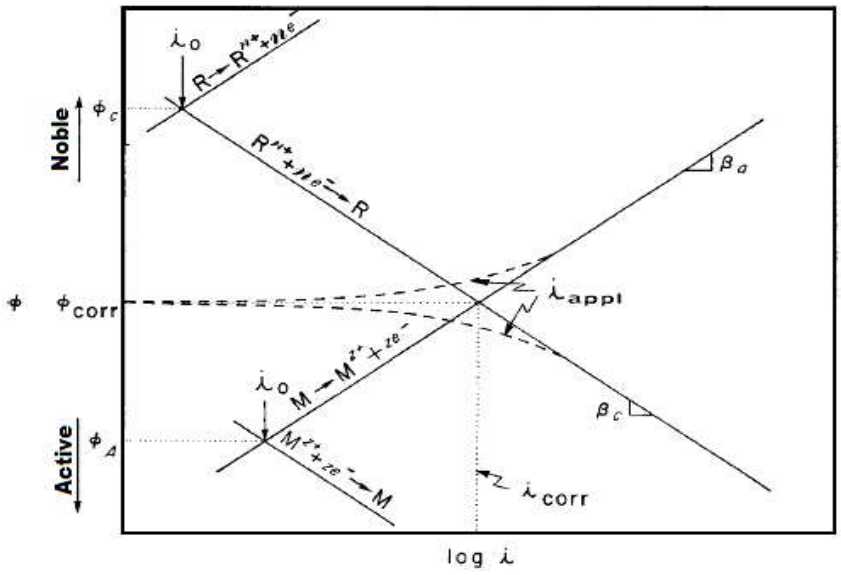

Figure: 1.12: Evans diagram

Corrosion control procedures are categorised into four types based on anodic and cathodic polarization curve patterns, as shown in Figure 1.13: anodic, mixed, and cathodic controls.

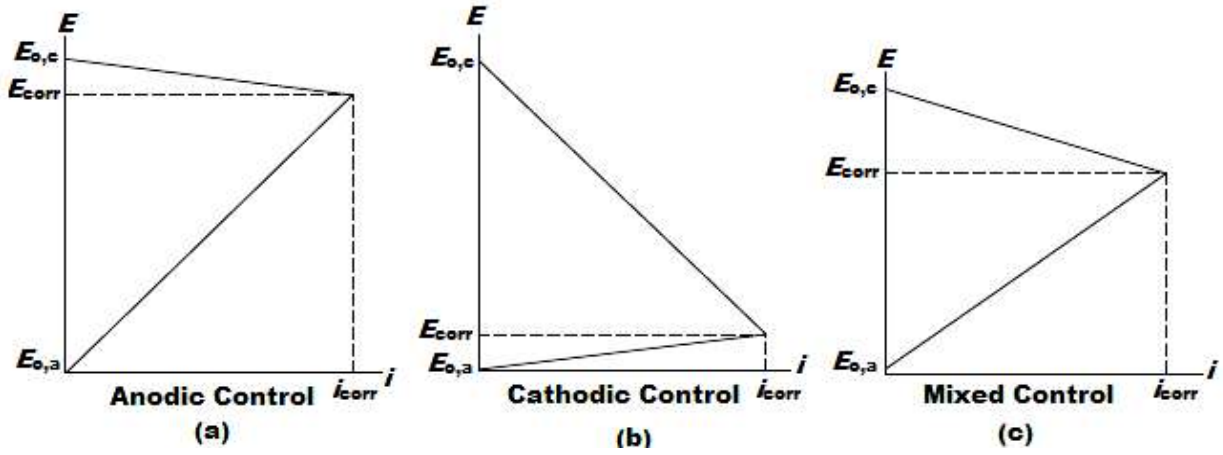

Figure: 1.13: (a) Anodic control **(b)** cathodic control, **(c)** mixed control.

1.7.5 Mixed Potential Theory.

Any electrochemical process can be divided into two or more partial oxidation and reduction steps., according to the mixed potential hypothesis [(Singer, Carosella, and Reed 1981)] During an electrochemical reaction, There can be no net electrical charge accumulation. Consequently, metal submerged in an electrolyte cannot spontaneously accumulate electrical charge. During the corrosion of an electrically separated metal sample, the overall rate of oxidation must equal the total rate of reduction [R.H.]. Using the mixed potential theory, It is possible to show the polarisation curves for corroding metal. If the attack is uniform, the entire surface can function as an anode for metal oxidation reactions and a cathode for corrosive agent reduction reactions. Corrosion is said to be under cathodic control when polarisation occurs at the cathode.The corrosion is said to be under anodic control when polarization occurs at the anode. Polarization happens to some extent at both anodes and

cathodes in the majority of cases, and the corrosion is therefore said to be under mixed control. The degree of polarization is governed not only by the metal and electrolyte but also by the electrode's actual exposed area.

Consider the two metals iron and zinc in an acid solution to demonstrate the mixed potential theory. There are two things to take into account: the metal's anodic polarisation line and the density of the exchange current during hydrogen evolution on the metal. Although zinc should corrode due to its position in the galvanic series, iron corrodes in this system because the exchange current density for hydrogen evolution is greater on iron than on zinc. Figure 1.14 depicts a mixed potential diagram for the iron-zinc system. The lines "a" and "b" represent zinc alone, while "a" and "b" represent iron corroding in isolation. The mixed lines are represented by lines "a" and "b."

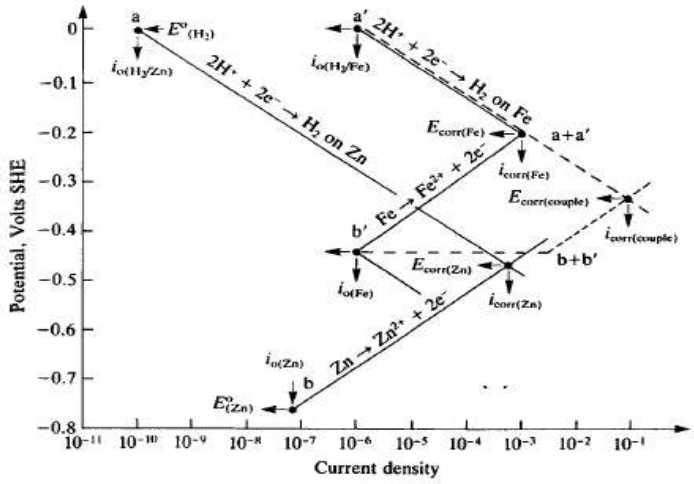

Figure: 1.14: A mixed potential plot for bimetallic couple of iron and zinc.

1.7.6 Tafel Extrapolation Method.

Cathodic and anodic polarisation measurements provide the information used in this technique.The entire anodic and cathodic polarization curves for hydrogen evolution and metal dissolution are superimposed as dotted lines in Figure 1.15. The applied current density and that corresponding to hydrogen evolution are nearly equal for reasonably large applied current densities. The corrosion rate is calculated by extrapolating the Tafel area to the corrosion potential from such polarization observations, as shown in Figure 1.15. At the corrosion potential, the rate of hydrogen evolution is equal to the rate of metal dissolution, and this point corresponds to the system's corrosion rate expressed in terms of current density. The anodic and cathodic potentials must be used to calculate Tafel constants.

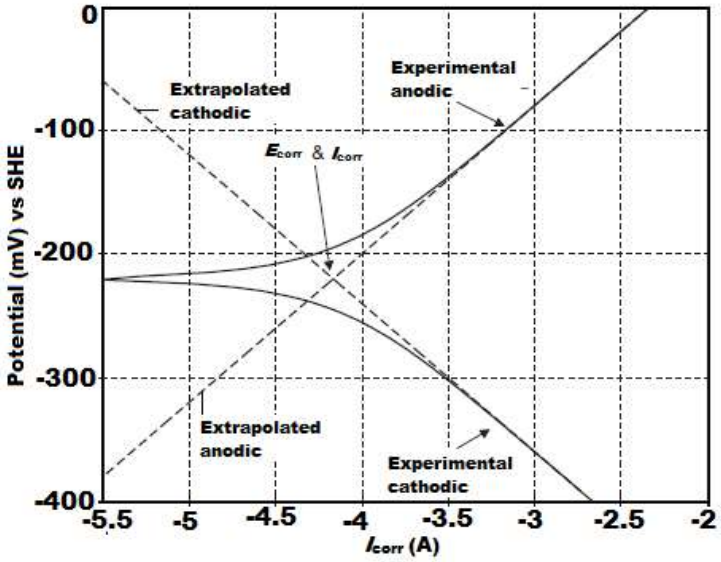

Figure: 1.15: Extrapolated Tafel curves.

1.7.7 Linear Polarization Resistance.

It is also abbreviated as LPR. The polarization resistance (Rp) of a material is defined as the E/i slope of a potential-current density curve at the free corrosion potential (Figure 1.16), which may be connected to the corrosion current (i_{corr}) using the Stern-Geary approximation in Eq. (1.41).

$$R_P = \frac{B}{i_{corr}} = \frac{(\Delta E)}{(\Delta i)_{\Delta E \to 0}} \qquad (1.41)$$

where: R_p is the polarization resistance

i_{corr} is the corrosion current

B is an empirical polarization resistance constant that can be related to the anodic (b_a) and cathodic (b_c) Tafel slopes with Eq. (1.42).

$$B = \frac{b_a \times b_c}{2.3(b_a + b_c)} \qquad (1.42)$$

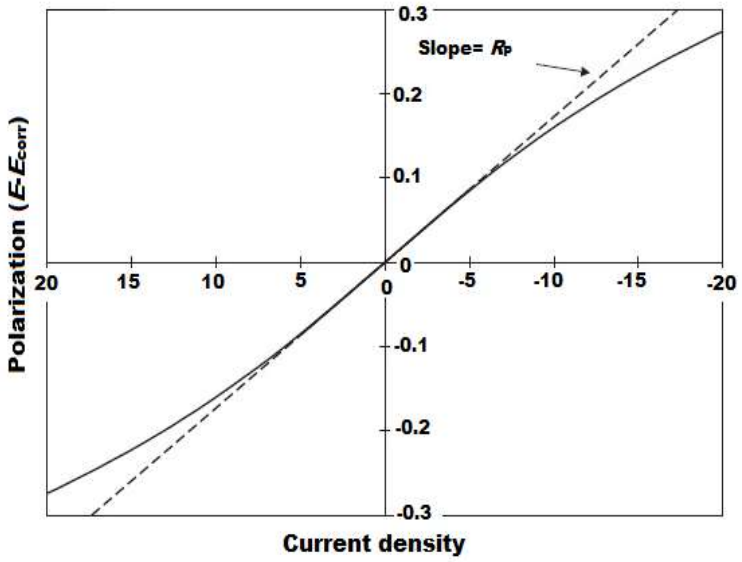

Figure: 1.16: Hypothetical linear polarization plot

1.7.8 Electrochemical Impedance Spectroscopy.

Because the impedance approach can detect double-layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}), it is commonly used for corrosion rate monitoring. Resistance and impedance both refer to current flow restrictions. Only resistors generate this effect when dealing with direct current. In the case of alternating current, however, both inductors and capacitors control electron flow. The cell impedance is separated into two portions, namely

Real part $Z'| = |Z\cos\theta$

Imaginary part $Z''| = |Z\sin\theta$

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

$$Z = Z' - Z''$$

$$\text{Where, } Z' = R_S + \frac{R_{ct}}{1 + \omega^2 C_{dl} R_{ct}^2} \tag{1.43}$$

$$Z'' = \frac{\omega C_{dl} R_{ct}^2}{1 + \omega C_{dl}^2 R_{ct}^2} \tag{1.44}$$

A semicircle that crosses the real axis at higher and lower frequencies is produced by plotting Z' against Z'' at various frequencies. The intercept is Rs at the higher frequency end and $R_s + R_{ct}$ at the lower frequency end. The difference between these two numbers produces R_{ct}, and from these values, the corrosion rate can be computed. The frequency at which Z'' is greatest yields the double-layer capacitance.

$$\omega(Z''_{max}) = \frac{1}{C_{dl} \times R_{ct}} \tag{1.45}$$

Mild steel impedance experiments in acidic media were performed. The cell utilized for impedance measurements was the same one used for potentiodynamic polarization measurements. An AC potential of 10 mV was superimposed on the continuous open circuit potential. R_{ct} and Cdl were determined after plotting the actual part (Z') and the imaginary part (Z''). The formula was used to calculate inhibition efficiency based on impedance measurements:

$$\eta\% = \frac{R_{ct(inh)} - R_{ct(blank)}}{R_{ct(inh)}} \times 100 \qquad (1.46)$$

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

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

A general impedance measurements curve is given in Figure 1.17.

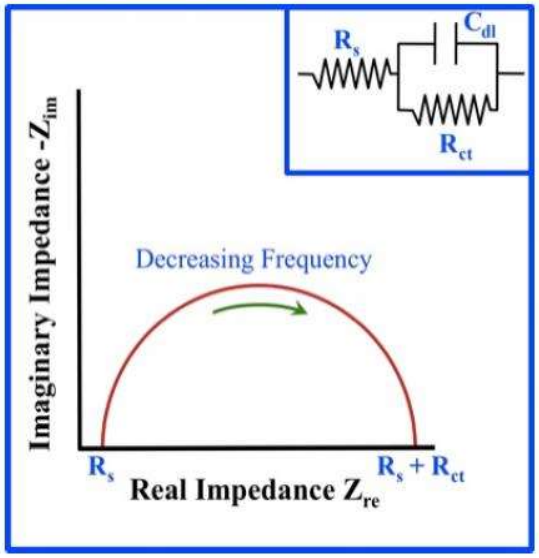

Figure: 1.17: A general impedance measurements curve

Advantages:

EIS Methods offer many advantages:

- Data on multiple cell parameters are collected fast and concurrently.

- High electrolyte resistance is not an issue.
- Low conductivity systems are also affected.
- It gives mechanical information.
- The technique is quite intuitive. Even little changes in the specimen can cause the impedance plot to shift.
- There is no accumulation of reaction products because there is no net current flow (if the DC component is made zero). This leads in the least amount of cell disruption.

1.7.9 Methods of Corrosion Control.

Corrosion can be controlled by a variety of methods. Details on these many corrosion control techniques ways can be found in the wide corrosion control literature. The following is a general classification. Methods of Corrosion Control:

a. By surface modification of metal and alloy.

b. By the use of corrosion inhibitors.

c. Cathodic protection.

d. anodic protection.

1.7.9.1 Surface modification of metal and their alloys.

Surface coatings or bulk alloying are commonly used to defend against corrosion. Surface modification is significantly less expensive than bulk alloying. Surface coatings may cause issues with thermal expansion compatibility, connection, and so on. The ion implantation technique [(Singer, Carosella, and Reed 1981)] and laser treatment [(Moumene *et al*. 2014; Ayers *et al*. 1981)] have improved metal surface

processing by resulting in the production of a single phase surface layer that is homogeneous in nature. This technology has recently been discovered to extend the wear life of iron base tool materials, which can be done with electron beam surface area glazing [(Kear and Strutt 1987)].

1.7.9.2 Cathodic protection.

Both types of protection are important in electrochemical techniques. When we connect to an external DC source, the corrosion rate decreases. To overcome an ultimate cathodic current, a power supply and an auxiliary electrode are utilized. As a result, by using a sufficient cathodic current, it is possible to deposit or reduce the corrosion rate to the desired level. This technology becomes too expensive when applied to massive structures such as pipelines, ships, and so on. In such instances, "sacrificial anodes" are employed to cathodically insulate the metal. Reactive metal, such as in most circumstances, zinc is employed as a sacrificial anode, such as in the corrosion protection of ship and boat hulls, where the anode is in contact with corrodible metal. These two metals in contact create a complete cell, with the terminals shorted. While zinc eventually dissolves, the other metal is cathodically shielded. Another form of anode used for cathodic protection is known as "impressed current anodes." This type of anode does not generate electrical energy. As an alternative, An external direct current source is attached within the structure to be protected, as is the anode. The power source's positive end is always linked to the anodes, while the negative end is always attached to the structure to be protected.

Impressed current anodes include graphite, scrap iron, platinum, and lead-silver alloys. Rectifiers are used as system power sources in this situation. The main benefit of an impressed current system over a galvanic system with a fixed maximum current input is the ability to increase the current by adjusting the applied voltage as needed. Although the impressed current approach is more adaptable, the most important consideration is that the anode lead be adequately insulated, waterproof, and have consistent electrical power supplied.

1.7.9.3 Anodic protection.

Anodic protection indicates that the anode is protected. The anode is built here, and the potential is installed in the inner region. In this scenario, the type of the auxiliary electrode is inconsequential because it is the cathode and is cathodically shielded. Because current density in the inert area is extremely low, the electric power required for anodic protection is significantly lower than that required for cathodic protection. Cathodic protection is chosen because of its benefit. Anodic protection[(Uhlig and Revie 1985)] is used on steel vessels that hold sulfuric and phosphoric acid. This method also has a limitation in that passivation does not occur in the presence of Cl ions in iron and ferrous alloys.

1.7.10 Other measures.

1.7.10.1 Design.

The incorrect design of plant equipment, buildings, and transportation units has been linked to increased corrosion failure. The design should include mechanical and service needs, as well as corrosion.

1.7.10.2 Electroplating.

Electroplating with less reactive metals such as tin, chromium, nickel, and others improves surface finishing and controls metal corrosion.

1.7.10.3 Metallic coatings.

Metallic coating is an important and widely used technology for protecting somewhat corrosive metals such as iron and steel. It is classified as sacrificial or anodic or noble or cathodic. A more electronegative metal than the base metal is applied to the surface during sacrificial coating, but in noble coating, more electronegative metals are coated on the base metal.

1.7.10.4 Organic coatings.

Compared to inorganic coatings, organic coatings are more widely used. In general, these have two applications.

1. To begin, they shield the metal by producing a protective coating or layer on its surface.

2. The second type of design has a pleasing effect on the eye. Paints, enamel, lacquers, and varnishes, among other things, are classified as organic coatings. The following are the four main elements of paints and enamels:

   a. Pigment,

   b. Binding medium

   c. Solvent and

   d. Drier.

   A particle is a solid that cannot be dissolved or tiny powders with the distinguishing features of colour and capacity.

The binding medium refers to the continuous phase in which the pigment is disseminated. Solvents are volatile liquids that are mixed into paints and dyes to make application and penetration easier by lowering the viscosity. Driers are compounds that induce a notable delay in drying time at normal temperatures when present in relatively small concentrations in drying oils or paints. In addition to paints and enamels, lacquers and varnishes are utilized for protective coatings. Lacquers are commonly made by dissolving any cellulose derivatives with plasticizers and pigments in a volatile solvent mixture or mixes of cellulose derivatives in a volatile solvent, such as cellulose nitrate or acetate.