

CHAPTER I

INTRODUCTION

1.1 Metals and alloys

Metals are dominant material in various fields owing to their mechanical strength and they are strong enough to sustain in various environments. Mild steel (**Fig. 1.1a**) has wide applications including construction of bridges, buildings, machine parts, automobiles and industries¹. It is affordable as well as a strong metal and it can be moulded into the required shape. It possesses some properties such as weldability, malleability, ductility etc.,. But it is prone to corrosion under aggressive environments. Steel rebar (**Fig. 1.1b**) also called as reinforcement steel utilised in concrete to hold the concrete and to enhance the quality of bond which in turn strengthen the structures. The damage in steel rebar is due to carbonation, chloride ingress and sulphate attack². Ti-6Al-4V alloy (**Fig. 1.1c**) is the broadly used Ti alloy. It has excellent corrosion resistance and good mechanical properties and it has been applied in biomedical³, marine equipment, aerospace, chemical industries, gas turbines etc.,.

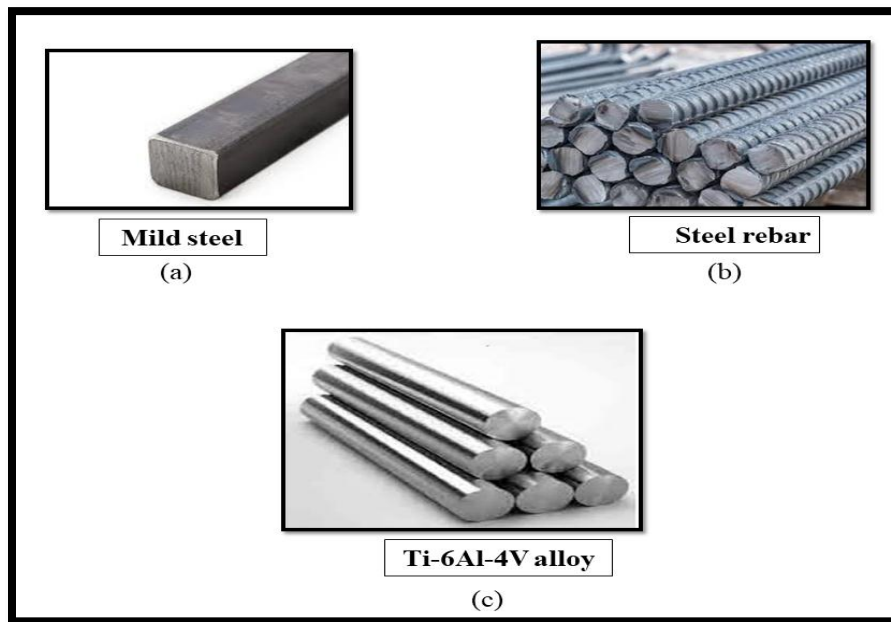


Fig. 1.1: Images of metals and alloys

1.2 Corrosion - metal degradation

Corrosion is the interaction of metals due to the contact with aqueous environment such as air, soil, moisture via electrochemical or chemical reaction triggering a slow, steady and irreversible functional loss of metal⁴. Corrosion is a natural process. Corrosion is an inevitable part due to dependence of living things on water and air. In general, most of the metal exist in a combined form known as ore. The ores represent the thermodynamically stable state i.e. low energy state. The metals are extracted from the ores by applying a large quantity of energy. The extracted form of metals exists in the uncombined condition possessing higher energy state i.e. unstable condition. These metals recombine with the element available in the environment and may revert back to the low energy state and it is the major reason for corrosion⁵. **Fig. 1.2** represents corrosion cycle of steel. According to IUPAC (International Union of Pure and Applied Chemistry), corrosion is an irreversible reaction causing metal degradation⁶. Corrosion is a serious issue leading to environmental danger in terms of economic as well as safety is concerned in various fields such as automobile, constructional activities, metallurgical fields⁷ etc.,.

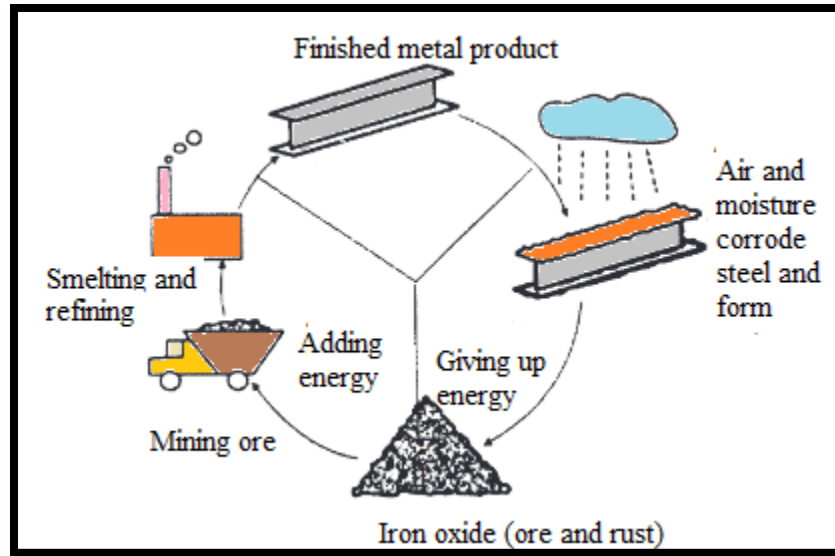


Fig. 1.2: Corrosion cycle of steel

NACE (National Association of Corrosion Engineers 2002) reports, revealed that in 1998 the corrosion cost was US\$276 billion, which constitutes about 3.4 % of world's GDP⁸. In 2011, in United States, the loss due to corrosion was more than US\$2.2 billion.

According to first global corrosion summit in 2011 held in New Delhi, India, loss due to corrosion in India is Rs. 2 lakh crores (US\$45 billion) every year. The recent NACE data about the loss due to corrosion worldwide is about US\$2.5 trillion covering about 3.4% of global GDP⁹. The annual cost due to corrosion in India and South Africa is about US\$100 billion and US\$9.6 billion respectively¹⁰.

1.3 Necessity for corrosion studies

It is essential to focus more attention towards metallic corrosion due to

- rapid industrialization increases the usage of metals
- utilisation of rare and cost effective metals need special care and protection
- pollution of water and air leads to aggressive (corrosive) environment
- health and safety is very important as far as corrosion is concerned

Due to awareness in recent years, researchers are developing new, innovative technologies in order to conserve the world's metal resources as well as to reduce the economic loss due to corrosion. **Fig. 1.3.** depicts the cost of corrosion in different sectors.

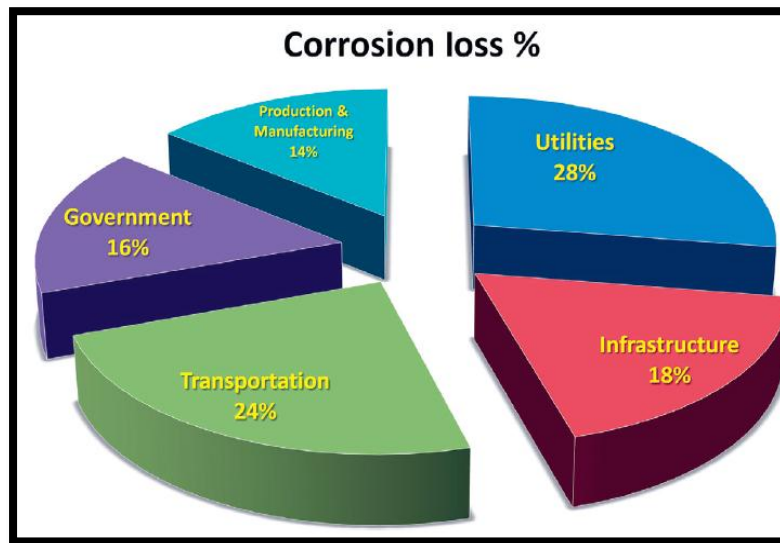


Fig. 1.3: Cost of corrosion in different sectors

1.4 Impact of corrosion

The problem caused due to corrosion are many including the degradation of metal¹¹. Even though a small amount of metal is lost the cost spent for the replacement is more.

The effects of corrosion are,

- Reduction in the thickness of the metal leads to loss of mechanical strength and structural disturbances (or) breakdown.
- Replacement of industrial equipment leads to loss of time and money¹².
- Loss of value of goods due to damage in appearance.
- Liquids preserved in vessels and pipes contaminated due to corrosion.
- Damage to valves, pumps due to corrosion products.
- Industrial equipment may suddenly shutdown due to corrosion.
- The corrosion leads to sudden failure in industries result in fire, explosion, collapse of buildings, release of toxic product.
- Corrosion products causes health hazards to human beings.

Natural resources are depleted including metals and fuels due to utilisation of these materials for manufacturing the equipment.

1.5 Forms of corrosion

Corrosion is a tedious phenomenon. However, based on the distribution of the attack on the metal surface it is classified into different forms,

(a) Uniform corrosion/shallow pitting corrosion

When a metal is exposed to an aggressive environment, this type of corrosion takes place over the entire surface area. It is mainly due to chemical (or) electrochemical reactions resulting in the formation of oxides. These type of corrosion reactions force the metal to reduce thickness over time and can persist until the metal dissolution is complete¹³.

Fig. 1.4 illustrates uniform corrosion.

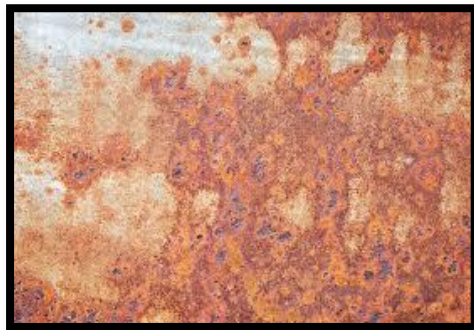


Fig. 1.4: Uniform corrosion

(b) Galvanic/bimetallic corrosion

The contact (direct/indirect) between the two dissimilar metals in presence of an electrolyte results in galvanic corrosion (**Fig. 1.5**). It is based on electrochemical reaction due to the variation in electrode potentials between two metals. In the presence of electrolyte, one of the metal act as anode where as other metal act as cathode¹⁴. The movement of electrons takes place from anode to cathode, thus triggers the oxidation reaction at anode pushing the metal to dissolve.



Fig. 1.5: Galvanic corrosion

(c) Crevice corrosion

Crevice corrosion is a localised corrosion that takes place on crevices of the metal¹⁵. These crevices may result from the connection between two surfaces (or) by an accretion of deposits (dirt, mud, biofouling etc.,). The corrosion process takes place in the crevice area, whereas the area other than crevice gets unaffected. The growth of crevice corrosion is due to the liquid (water) within the crevice, which has a tendency to undergo electrochemical reaction in acidic environment. The acidity in the crevice tend to disrupt the passive layer of the metal and it is prone to corrosion (**Fig. 1.6**).



Fig. 1.6: Crevice corrosion

(d) Pitting corrosion

Pitting corrosion occurs due to the formation of pits or holes at corrosion concentrated places. Consider an example of a drop of water resting on the surface of the metal. The metal area covered by the drop act as anode due to low oxygen concentration and suffers corrosion, and the uncovered metal surface area act as cathode due to high oxygen concentration¹⁶. The anodic area is small compared to cathodic area hence more and more metal is eliminated from the same spot. Thus a small pit is formed on the metal surface leading to pitting corrosion. **Fig. 1.7** represents pitting corrosion

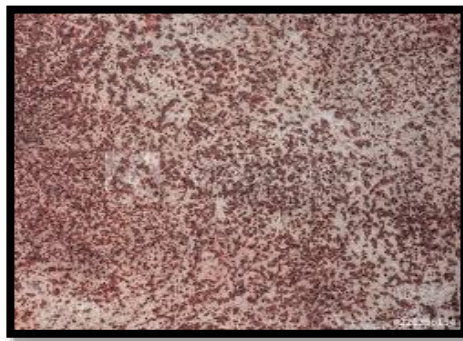


Fig. 1.7: Pitting corrosion

(e) Inter granular corrosion

This type of corrosion occurs due to variation in structures as well as the composition in which the grain boundaries undergo localised anodic corrosion¹⁷. The metal disintegrates due to the rigorousness of corrosion at grain boundaries leading to inter granular corrosion represented in **Fig. 1.8**.

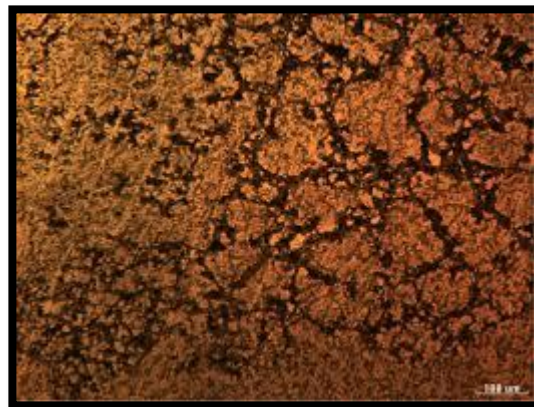


Fig. 1.8: Inter granular corrosion

(f) Stress-corrosion cracking

Simultaneous occurrence of tensile stress in the aggressive environment forms stress - corrosion cracking (SCC). SCC is insidious type of corrosion because it is difficult to identify the damage but it may lead to rapid disastrous failures¹⁸. The impurities have a tendency to weaken the grain boundaries, leading to minute cracks in the microstructure as indicated in **Fig. 1.9**.



Fig. 1.9: Stress-corrosion cracking

(g) Erosion-corrosion

The relative movement between an electrolyte and surface of metal leading to degradation of a metal is called as erosion corrosion (**Fig. 1.10**). The flow of a liquid at high velocity breaks the metal passive layer resulting in the damage of the metal. In this process, the metal may be eliminated as dissolved ions. This type of corrosion can be visualised as grooves, craters and gullies¹⁹.

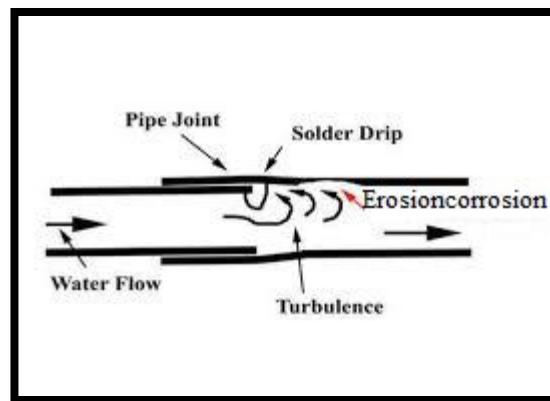


Fig. 1.10: Erosion-corrosion cracking

(h) Microbial corrosion

This type of corrosion is caused by microorganisms usually chemoautotrophs. It is also called as bacterial corrosion, microbially induced corrosion (or) microbiologically influenced corrosion. Certain bacteria have a tendency to sense surfaces. The contact of bacteria on the surface is capable of producing alginate. Metal surfaces are quickly colonised by bacteria due to the influence of natural (or) aquatic environments, giving rise to a strong adherent microbial community called as biofilm²⁰. The build-up of biofilm leads to deterioration (or) degradation of the metal surface (**Fig. 1.11**).

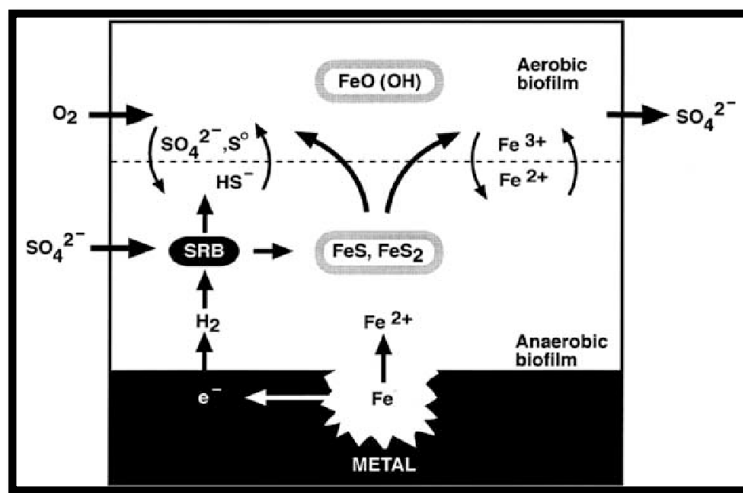


Fig. 1.11: Microbial induced corrosion

(i) Reinforced corrosion

Steel reinforcement gets corroded due to the influence of carbon dioxide and chloride. The high alkalinity in concrete lead to the formation of adherent film, which passivates the reinforced steel and shield the metal from corrosion. But, the presence of pores in concrete easily allows the corrosive agents to diffuse and dissolve in pore solution and finally reaches the metal surface. These corrosive agents have a tendency to remove the protective passive layer and thus initiate corrosion²¹. **Fig. 1.12** represents steel rebar corrosion due to ingress of corrosive agents.

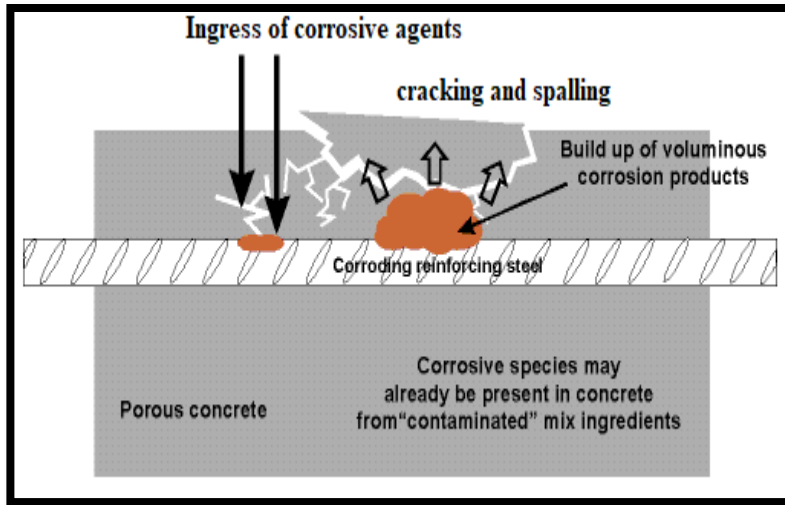
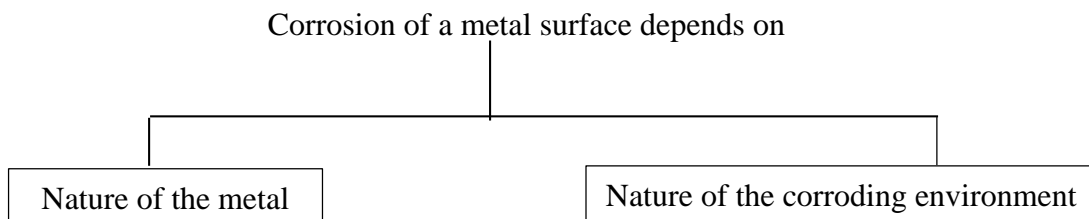


Fig. 1.12: Corrosion in reinforcing steel

1.6 Factors affecting corrosion



1.6.1 Nature of the metal

(a) Position in emf series

When two metals are in electrical contact, the more active metal present in the higher position in the galvanic series possess greater oxidation potential in the presence of electrolyte and constitutes as anode and suffers corrosion. The rate and severity of the corrosion is based on the difference in their position in the galvanic series. Higher the difference, greater is the corrosion of the metal.

(b) Relative areas of anode and cathode

Larger the area of the cathode greater is the rate of corrosion. It is because, as cathodic area is larger there will be greater demand for electrons resulting in the increased dissolution rate of metals at anode. The corrosion of anode is directly proportional to the ratio of the cathodic to anodic area. Severe and extreme corrosion is noticed if the anodic area is small due to heavy current density at the anode.

(c) Purity of metal

The presence of impurities in a metal creates heterogeneity resulting in the formation of local electrochemical cells with distinct anodic and cathodic areas in the metal. The rate of corrosion depends on the percentage of impurity present in a metal, e.g., addition of impurities such as Pb and Fe in Zn leads to the formation of electrochemical cells especially at the exposed part of the impurity, and the corrosion of Zn around the impurity occurs due to local action²².

(d) Physical state of the metal

Metals subjected to irregularly distributed stress are more prone to corrosion. Considering an example, caustic embrittlement corrosion in a metal occurs in stress parts like joints, bends and rivets in boilers.

(e) Passivity (or) passivation

The metal (or) alloy possessing much higher corrosion resistivity than expected based on their position in emf series is called as passivity (or) passivation. A very thin protective as well as invisible film formed around 0.0004 mm thick on the metal surface (or) alloy makes it noble. For e.g., steel containing nickel and chromium. Chromium has a tendency to form a protective layer (Cr_2O_3) on steel, thus steel becomes passive in corrosive environment.

(f) Nature of the corrosion product

The corrosion occurs at a higher rate if the corrosion product is volatile (or) soluble in aggressive medium, whereas the corrosion product insoluble in electrolyte results in the formation of film at the metal surface, this protective layer tends to reduce further corrosion. If the corrosion product is oxide, then the corrosion rate depends on volume ratio, higher the specific volume ratio, lower the oxide corrosion rate.

(g) Nature of the oxide film

Metals like Mg, Ca and Ba forms oxides less than the volume of metals, then the oxide film formed is porous, so that the oxygen diffuses easily and accelerates corrosion²³. On the other hand, metals such as aluminium, chromium, nickel form oxides with volume greater than that of metal, then the oxide film is non-porous thus protecting the metal from corrosion.

1.6.2 Nature of the corroding environment

(a) Effect of temperature

The corrosion rate increases with rise in temperature, since the rate of chemical and electrochemical reactions as well as the rate of ions increases leading to stress and inter granular corrosion. In addition to this, at higher temperature a passive metal may become active.

(b) Dissolved oxygen concentration

With increasing supply of oxygen, the corrosion rate also increases whereas the corrosivity of water reduces with temperature, since dissolved oxygen content reduces with temperature. In general, corrosion occurs under metal washers in pipelines, where oxygen cannot penetrate readily. Similarly, pipelines and cables buried under the soil passing from one type of soil to another undergo corrosion due to differential aeration corrosion. For e.g., part of the lead pipeline passing through clay undergoes corrosion than sand because clay is less aerated than sand.

(c) Nature of the electrolyte

The rate of corrosion also depends on the nature of the electrolyte. If the conductance of the electrolyte is more, it means that corrosion current is easily conducted which in turn increases the rate of corrosion. On the other hand, if silicate ions are present in electrolyte they tend to form insoluble silicates which impede further corrosion.

(d) Presence of corrosive ions

The presence of chlorides and sulphates accelerates corrosion due to destruction of the protective film and thus exposing the metal surface to corrosion.

(e) Flow rate

The corrosion rate increases due to high flow rate and liquid turbulence since they eliminate the oxide film made by the corrosion products exposing the metal to aggressive chemicals.

(f) Humidity

The corrosion rate and extent of corrosion increases with rise in humidity, due to the fact that humidity act as a solvent for oxygen to produce corrosion cell. The atmospheric

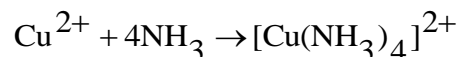
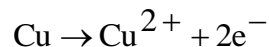
corrosion of iron increases rapidly in moisture environment and it is slow in dry air. When the relative humidity of air rises from 60% to 80% the rusting of iron also increases substantially.

(g) Effect of pH

The corrosion probability with respect to pH of the solution and the electrode potential of the metal can be determined based on Pourbaix diagrams, which obviously indicates the zones of immunity, passivity, potential values and corrosion based pH. By increasing the pH of the solution with the addition of alkali reduces the corrosion rate of iron. Corrosion especially electrochemical corrosion depends on pH of the solution. Thus, the corrosion is more in acidic medium than the alkaline (or) neutral medium. Moreover, by applying the positive potential the corrosion rate of iron is decreased by shifting it into the passivity region.

(h) Presence of impurities in the atmosphere

In atmosphere, variety of suspended particles are present. Certain particles have a tendency to absorb moisture, resulting in the formation of galvanic cells, increasing the corrosion rate rapidly. These particles are called as active particles, e.g., sodium chloride, sulphates, nitrates, $(\text{NH}_4)_2\text{SO}_4$ etc.,. The corrosion rate of copper is increased in the presence of ammonia.



An important parameter causing metal corrosion is acid rain which is mainly due to the combustion of fuels. During combustion, gases like SO_x and NO_x liberated into the atmosphere readily combines with water vapour and moisture producing sulphuric and nitric acid, which mixes with rain and fall down the earth, corroding the metals and historical artifacts.

1.7 Inhibitors

Inhibitors are added chemical compounds capable of reacting with metal surface (or) the environment at which the metal is exposed, thus protecting the surface to a certain level. The function of the inhibitor is to adsorb on the metal surface thus shielding the metal

surface by forming a protective layer. In general, inhibitors spread from a solution (or) by dispersion. The corrosion processes are slowed down by inhibitors by,

- increasing anodic (or) cathodic polarisation behaviour (Tafel slopes)
- decreasing the mobility (or) diffusion of ions to the metal surface
- increasing the electrical resistivity of the metal surface

The classification of the inhibitors is differently presented by various authors. Some authors prefer to group inhibitors based on their chemical functionality as follows²⁴,

(a) Inorganic inhibitors

Crystalline salts such as sodium chromate, phosphate (or) molybdate are inorganic inhibitors. In these compounds, the negative anions are involved in mitigating corrosion process. In a special case, when zinc is used in the place of sodium, zinc cation can add some beneficial effect. These zinc added compounds are called mixed charge ion.

(b) Organic anionic inhibitors

These type of inhibitors are used in cooling water and antifreeze solutions e.g., sodium sulfonates, phosphonates (or) mercaptobenzotriazole.

(c) Organic cationic inhibitors

These compounds are largely aliphatic (or) aromatic compounds containing positively charged amine groups. In concentrated forms, they may be in the form of liquid (or) wax like solids. Corrosion inhibitors based on functionality scheme is the most popular type of classification and it as follows²⁵,

(a) Passivating / anodic inhibitors

Passivating inhibitors shows a large shift towards anode, forcing the metal surface into passivation. Anodic inhibitors are of two types (a) oxidizing anions e.g., chromate, nitrite and nitrate are capable to passivate steel in the absence of oxygen and (b) non-oxidizing ions e.g., phosphate, tungstate and molybdate needs the presence of oxygen to passivate steel. These inhibitors are widely used because they are more effective. The least expensive type inhibitors are chromate-based inhibitors possessing variety of application including in recirculation-cooling system, internal combustion engines, cooling towers, refrigeration units and rectifiers.

(b) Cathodic inhibitors

Cathodic inhibitors either reduce the cathodic reaction by itself (or) selectively precipitate on cathodic areas to increase the surface impedance and limit the penetration of reducible species to these areas. These inhibitors retard the corrosion process by three different mechanisms (a) as cathodic poisons (b) as cathodic precipitates (c) as oxygen scavengers. The compounds such as arsenic and antimony function by making recombination and discharge of hydrogen more difficult. Ions such as Ca, Zn (or) Mg may be precipitated as oxide to form a protective layer on the metal surface. Oxygen scavengers tend to retard corrosion by preventing the cathodic polarisation caused by oxygen e.g., sodium sulphite (Na_2SO_3).

(c) Organic inhibitors

The effects of both anodic and cathodic inhibitor are observed in certain cases in organic inhibitors. These inhibitors affect the whole surface of a corroding metal when they are present in sufficient concentration. A hydrophobic film is formed on the metal surface by organic inhibitor which protects the metal surface. Their effectiveness is based on their chemical composition, structure of the molecule and their affinities towards the metal surface. The strength of the adsorption bond is an important factor for soluble organic inhibitors e.g., ethanol amine.

(d) Precipitation inhibitors

These inhibitors form a protective film on the metal surface, thus hindering both anodic (or) cathodic sites. Precipitation inhibitors are capable of forming a precipitate on the metal surface thus providing a protective film e.g., silicates and phosphates. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites, however they are applied in situations, where non-toxic additives are essential.

(e) Volatile corrosion inhibitors

These compounds are transported in a closed environment to the corrosion site by volatilisation process e.g., volatile solids containing salts of dicyclohexylamine, hexamethylenamine and cyclohexylamine. These compounds adsorb on the surface of the metal, the vapour of these salts condenses and hydrolysed by moisture content and liberate protective ions. An efficient VCI, should last for longer times.

(f) Mixed inhibitors

Substances which have a tendency to inhibit corrosion by decreasing the rate of anodic and cathodic process simultaneously are called as mixed type inhibitors. They tend to form a protective film due to the formation of precipitates on the metal surface thus hindering both anodic as well as cathodic sites e.g., silicates and phosphates.

(g) Synergistic inhibitors

In cooling water systems synergistic inhibitor are preferred because the combination of anodic and cathodic inhibitors provides better protection efficiency. These blends are formed by mixing of multi inhibitors and are known as synergistic blends e.g., chromate-phosphate, zinc-tannins, polyphosphate-silicate, zinc-phosphate.

(h) Green corrosion inhibitors

Natural products extracted from plants are extremely used as corrosion inhibitors due to easy availability, eco-friendly, biodegradability as well as economic. It is reported from literature that these extracts contain a large number of natural products including essential oils, pigments, flavanones, steroids, terpenes, etc., In general, these compounds possess aromatic structures, long aliphatic chains containing nitrogen, sulphur and oxygen atoms which is capable of forming bonds with metal surface. In recent years, researchers are focusing towards green corrosion inhibitors.

1.8 Corrosion protection methods

Corrosion can be controlled by (a) material selection (b) cathodic protection (c) designing (d) inhibitors (e) coatings. In a simple way, corrosion can be controlled by selecting structural materials capable to change composition, eliminate tensile stress and change microstructure stress²⁶. Alternatively, a rational design principle is applied which have a tendency to eliminate many corrosion problems to reduce maintenance cost and repair²⁷. Cathodic protection method is an electrical method to avert the rate of corrosion of metal samples in electrolytes such as soil (or) water. In order to achieve protection, sacrificial anodic protection and impressed current cathodic protection are used²⁸. Coatings is a method to isolate the metal surface from the aggressive environment and it is one of the important method to protect the metal against corrosion. Examples for organic coatings

are polyacrylates, polyesters, polyurethanes. To get the best corrosion protection and considering the optimal economy, corrosion inhibitors are widely used. It has been reported that, the consumption of corrosion inhibitors in USA has reached around \$ 2.5 billion in 2017²⁹.

1.9 Factors responsible for the effective working of the inhibitor

The effectiveness of the inhibitor varies from one system to other system. Therefore, it is essential to consider the following factors while choosing the inhibitor for a particular system.

- Chemical structure of the inhibitor.
- Chemical composition of the aggressive medium.
- Operating conditions such as temperature, pressure, pH, etc.,
- Nature of the metal surface.
- Stability of the inhibitor.
- Solubility of the inhibitor .

Requirements of an inhibitor

- Capable to protect the surface of the metal.
- High activity must be achieved with a minimum quantity of compound.
- Easy to handle and store.
- Less toxicity.
- Inert characteristics .
- Non-contaminant.
- It should act as an emulsifier.
- It should act as a foaming agent.

1.10 Mechanism of inhibitive effect of inhibitor

Corrosion inhibitors are widely applied in industrial sectors due to their effectiveness, compatibility and low toxicity³⁰. These inhibitors can act as anodic and cathodic inhibitors. In general, the corrosion potential shift towards lower values in cathodic type inhibitors retards (or) delay the reactions taking place at the cathode (hydrogen evolution and oxygen reduction).

In contrary, anodic inhibitors are capable to react with the metal cations to produce insoluble hydroxides thus hindering the active sites on the surface of the metal and shift the corrosion potential in the positive direction, which retards further oxidation of the metal thus minimising the corrosion rate. Mixed inhibitors provide the high shielding effect because they affect anodic as well as cathodic reactions. The basic mechanism is to form a protective film on the metal surface by the corrosion inhibitors based on adsorption process in which water molecules are displaced from the metal surface thus protecting it from degradation. This process may be physical adsorption (or) chemical adsorption (or) combination of both. Adsorption depends on nature of the metal, surface charge, type of corrosive medium and distribution of charges in the molecule. Physisorption is connected with electrostatic interaction between the charged metal surface and charged inhibitor molecule. Chemisorption is based on donor-acceptor interactions between free electron pairs and vacant, low energy d-orbital of metal. An efficient organic inhibitor should contain nitrogen, oxygen, sulphur with lone pair of electrons and moiety containing π -electrons (multiple bonds, aromatic rings) capable of interacting with free orbital of d metal, favouring adsorption process³¹. The corrosion inhibition follows the order which is the reverse order of electronegativity,



Heteroatoms are protonated in acidic environment that additionally promotes the interaction between the metal surface and inhibitor. The polar group of the inhibitor molecule is directly attached to metal where as non-polar end is arranged in vertical direction to the surface of the metal which repels aggressive species thus forming a barrier against chemical and electrochemical attack by aggressive medium on the metal surface. The molecular weight and size also plays a major role in inhibition efficiency. Larger the molecule, higher the protection efficiency.

1.11 Monitoring of corrosion

Corrosion monitoring is an important method to determine the corrosivity process. To assess the corrosion impairment, direct and indirect physicochemical analytical techniques are utilised³². Different monitoring methods can be grouped into the following three categories:

- i. Non-Electrochemical methods
- ii. Electrochemical and special methods
- iii. Non-destructive (NDT) methods

i. Non-Electrochemical methods

(a) Gravimetric or weight loss measurements

The widest spread, simplest and longest method to assess corrosion loss is weight loss technique. The metal sample to be tested is degreased, polished, weighed and immersed in an electrolyte solution for a stipulated time. After the reasonable time, metal sample is removed, sluced, degreased and reweighed³³. The corrosion rate is calculated as,

$$\text{Corrosion rate} = \frac{\text{Weight loss (mg)} \times 534}{\text{Area (cm}^2\text{)} \times \text{Time (hrs)} \times \text{Density (g/cm}^3\text{)}}$$

(b) Electrical resistance method

This technique measures the change in resistance of a metal sample as it corrodes. The electrical resistance of the metal is given by the formula,

$$R = \rho L / A$$

where, ρ represents specific resistance, L represents length of the specimen and A represents area. As metal is exposed to the aggressive environment the decrease in cross-sectional area of the metal leads to increase in the electrical resistance. The change in electrical resistance is measured based on Kelvin or Wheatstone bridge and it is proportional to increase in corrosion. The prime advantage of this method is to measure corrosion rate in liquid and vapour state. The interpretation is difficult in the case of non-uniformity. Hence it is not suitable method for pitting (or) stress corrosion.

(ii) Electrochemical methods

(a) Linear polarisation technique

This technique is based on the measurement of apparent resistance of a test cell when it is polarized by a small voltage of the order of 5 mV to 20 mV. The material's

resistance (R_p) is obtained by taking the slope of the potential vs current and the corrosion current density is calculated by using Stern-Geary Equation³⁴,

$$I_{\text{corr}} = (\beta_a \beta_c / 2.303 (\beta_a + \beta_c)) / R_p$$

where β_a , β_c represents the slopes of anodic and cathodic Tafel slopes respectively.

From i_{corr} value, the corrosion rate can be calculated by using the eqn,

$$CR = i_{\text{corr}} * E_q * 10 * 3.15 * 10^7 / F * d$$

where E_q is equivalent mass of metal exposed to corrosion, F is Faraday constant (96500 C), d is density of metal (g/cm^3) and $10 * 3.15 * 10^7$ is the conversion factor used to obtain the result in mm/year ³⁵. This method provides instantaneous rate of corrosion whereas the electrical resistance gives average corrosion rate. This technique is applied to uniform corrosion and it is rarely suitable for pitting and localised corrosions.

(b) Corrosion potential measurement method

This method is helpful to understand the corrosion processes taking place on the materials. It is a simple method and it is applied to the material prone to localized corrosion and hydrogen embrittlement. It provides information about the corrosion potential and implies whether the material is above the critical potential for pitting/crevice corrosion or the order of passivation range in cathodic protection or hydrogen embrittlement regions.

(c) Hydrogen detection method

In the electrochemical measurement types of probe, hydrogen that diffuses through the material wall is sensed electrochemically by mounting a probe on the surface of the wall. In this probe, palladium foil is a working electrode mounted on the wall material and maintained at a constant anodic potential using reference and auxiliary electrode in acidic electrolyte. At a fixed anodic potential of the palladium foil the hydrogen that comes out from the foil is oxidised and the oxidizing current is measured indicating hydrogen penetration rate. This rate is indirectly related to the corrosion reaction.

(d) Impedance method

EIS is a well-established quantitative method for the evaluation of anti-corrosion performance of protective coatings. The result of EIS is the impedance of the electrochemical system as a function of frequency. The corrosion rate is measured based on charge transfer

resistance (R_{ct}). In impedance method an alternating voltage of 10 - 20 mV is applied to the cell and current and phase angle is measured at various frequencies. The cell impedance is resolved into two parts, i.e., real part $Z' = |Z| \cos$ and imaginary part $Z'' = |Z| \sin$. Plot of Z' vs. Z'' is a semicircle, which cuts the Z' axis at high frequency corresponding to $R_s + R_{ct}$. Subtraction of impedance at high frequency from low frequency gives R_{ct} . This technique is useful even for low conducting media since R_s is completely eliminated.

(iii) Non-destructive methods

Non-destructive method is an extensive technique utilised in science and technology industry to assess the properties of a material, component or system without causing destruction. Types of non-destructive method is discussed below,

(a) Visual NDT

The visual and optical testing is the most common NDT method. In many instances, a trained inspector armed with simple tools, such as flash light and magnifying glass, can perform a very effective inspection³⁶. Visual testing is the first line of defence. To inspect the difficult areas, technician or an engineer is provided with a device known as borescope. Borescopes are essentially miniaturized cameras that can be placed on the end of a fiber optic cable. The camera can then be inserted into regions that are obstructed from direct visual inspection, and the resulting images are viewed in real time on a video screen by the inspector.

(b) Ultrasonic and acoustic method

In ultrasonic testing method two probes are connected with the testing material and it is based on transmitting and receiving pulse and it measures the thickness of the material from which corrosion rate is calculated. The atmospheric corrosion of thin plate is measured by acoustic wave devices. To detect the internal flaws or to characterize the metal, very short ultrasonic pulse-waves are transmitted through the material. Acoustic emission sensors are generally piezo ceramic transducers. The basic principle involved is to convert physical displacement into voltage. It is possible to calculate stress-corrosion cracks and ductile fracture of the materials based on change in voltage. Even we can detect the deep internal flaws, capable to estimate size and orientation of defects due to high penetrating power³⁷.

(c) Electromagnetic method

The electromagnetic response of the object is observed by inducing electric currents or magnetic fields or both into the test sample. There are many types of electromagnetic method like,

- **Magnetometer and di-electrometers**

Meandering winding magnetometers (MWM) and Interdigital electrometers (IDED) are used to measure the depth of moisture and hidden corrosion under paint, it is because of reducing the conductivity near a metal surface there is a possibility for oxygen diffuse into the layer on the metal surface indicating the early stage of corrosion³⁸. To measure the property profiles of the material MWM uses magnetic fields and inductive coupling. The IDED uses electric fields and capacitive coupling to measure the properties of multi-layered insulating medium like paint on metal oxides formed during corrosion.

- **Magnetic flux leakage (MFL)**

MFL is a magnetic method utilized to spot the corrosion and pits in steel structures, particularly in storage tanks and pipelines. In this method, to magnetize the steel a powerful magnet is used. At corroded areas, the magnetic field leaks from the metal. MFL tool consists of a magnetic detector kept between the poles of the magnet which helps to identify the leakage field. An array of sensors is placed between the magnetic poles to identify the flux leakage. In general, two type of sensors are used such as coils and hall effect devices. The signal received from the leakage fields are small and requires amplification. By this method the depth of metal loss can be estimated.

(d) Eddy current testing (ECT)

Electromagnetic testing (ET) especially eddy current testing, is generally used to inspect objects throughout their life cycle. In this technique alternating current is applied to a conducting coil held near to the test object. In response, the test object generates eddy currents to oppose the alternating current in the coil³⁹. The eddy currents are then sensed by the same coil, separate coils, or magnetic field sensors. Changes in the induced eddy currents may be caused by changes to a material's electromagnetic properties, changes in

geometry, including the abrupt changes in current flow caused by cracks. Thus ET techniques are highly efficient to identify the cracks present on or below the surface of metallic objects. This equipment is portable and inexpensive.

(e) Radiographic NDT

The most common NDT is radiography. Early literature notes the ability of radiographs to detect discontinuities in castings, forgings and welds in metals. Discontinuities such as pores or inclusions in metals are readily detected in many cases. Cracks may also be detected using radiographic techniques, but attention must be paid to orientation and residual stress issues⁴⁰. Radiography continues to be widely used despite the expense and safety implications of the equipment. Recent advances in digital radiography have helped to reduce the cost of employing this method by eliminating the use of film. Application of radiographic method are internal deposits: radiography which has proven to be very useful in detecting different kinds of internal deposit. Radiography can detect pits very easily. The depth of pit can be determined by measuring the densities of the pitted and sound areas.

In the present situation corrosion mitigation is the major concern throughout the world. The development of eco-friendly, non-toxic corrosion inhibition strategies are needed to achieve a greener environment. In this aspect, the present research focusses on exploring natural and synthetic materials as corrosion mitigators on mild steel in sulphuric acid medium. Increase in environmental damage demands the researchers to focus on green materials. In this regard natural inhibitors namely *Senna auriculata*, *Rosa damascena*, *Cyperus rotundus* and *Cissus quadrangularis* were chosen as corrosion mitigators for metal surface. These materials are readily available, environmentally friendly materials possessing wide range of pharmacological applications. Microwave assisted synthesis is a more effective, efficient green method of synthesis. Hence an attempt was made to synthesise sulphamethazine derivatives namely substituted pyrans, substituted pyridines, substituted pyrazoles, substituted isooxazoles and substituted pyrimidines. To assess the corrosion mitigation effect of natural and synthetic inhibitors mass loss technique was employed. The impact of temperature on corrosion behaviour was analysed. The mechanism of corrosion inhibition based on adsorption was determined by thermodynamic and kinetic parameters. Electrochemical studies such as electrochemical impedance spectroscopy and

potentiodynamic polarisation studies were carried out to deduce the type of inhibitor. The morphological changes on mild steel surface with and without inhibitors was demonstrated by surface analysis. Electrochemical and surface techniques were adopted to analyse rebar corrosion. Studied inhibitors followed Langmuir adsorption isotherm. Further more, the enhancement of anti-corrosion properties of epoxy – modified nanoclay were analysed by corrosion monitoring techniques and predominant compounds existing in the water extract of natural inhibitor was identified by GC-MS analysis. The degradation behaviour of Ti-6Al-4V alloy under simulated biological fluid in the absence and presence of natural inhibitors were also assessed by electrochemical methods and phyto components present in the inhibitors was predicted by GC-MS analysis.

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