CHAPTER I

INTRODUCTION

Aluminium is the second most available metallic element on earth. It has been estimated that the earth’s crust is composed of aluminium, usually found in the oxide form known as bauxite. Pure aluminium is used mostly as cladding material and aluminium alloys are used as protective coating for other metals. Aluminium is light and its density is only one third that of steel. Aluminium retains its strength at low temperature and is often used for cryogenic applications. It is an excellent conductor of heat and electricity. It is highly reflective. It is non-ferromagnetic, property of importance in the electrical and electronic industries [1].

Lightweight performance of aluminium delivers great benefit in transport applications such as aerospace, cars, ships, trains and buses. All aero planes have been made of aluminium alloys. Aluminium plays an important role in urban railways (underground, tramcars), and more recently in high-speed trains. Lightness of aluminium coupled with its strength, conductivity, barrier properties and its excellent corrosion resistance have all been and continue to be its most important advantages and the main reasons for the continued growth in the usage of aluminium.

It is commercially important metal, and one of its many applications is its frequent use as a reliable and cost effective sacrificial anode. Aluminium sacrificial anode is used in major marine projects, e.g., in offshore applications, structures, platforms, pipelines, jetties and power plants.

Aluminium is an active metal whose resistance to corrosion depends on the formation of the protective oxide film on its surface. Aluminum relies on the formation of a compact, strongly adherent and continuous passive oxide film developed on aluminium upon exposure to the atmosphere or aqueous solutions. It is generally believed that a passive film composed of aluminium oxide at about 20 to 100Å in thickness is found on the surface of aluminium, which is exposed to atmospheric air. This film is responsible for the corrosion resistance of aluminium in most environments like atmosphere, fresh water, seawater, most soils, most
foods and many chemicals. However, the oxide film is generally stable in the pH range of 4 - 9 and becomes soluble in strong acid and alkaline media. As a result the metal suffers from a high rate of corrosion under such conditions [2].

1.1. Needs to study corrosion

There are four main reasons to study corrosion. Three of these reasons are based on societal issues regarding (i) human life and safety, (ii) the cost of corrosion, and (iii) conservation of materials. The fourth reason is that corrosion is inherently a difficult phenomenon to understand, and its study is in itself a challenging and interesting pursuit [3].

1.1.1. Human life and safety

The most important factor of impact of corrosion is safety. The corrosion-related accidents or failures in industries emphasize the importance of safety to personnel involved in the industries.

Adverse effects on health may be caused by corroding structures, such as a plumbing system affecting the quality of water and escaping of products into the environment from the corroded structures. Corrosion products may contaminate chemicals, pharmaceuticals, dyes, packaged goods, etc. with dire consequences to the consumers.

The magnitude of corrosion would depend upon the sensitivity of a particular metal or alloy to a specific environment. Corrosion adversely affects the structural integrity of components and makes them susceptible to failure and accident. Leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards. It is well known that at least 25% of water is lost by leakage.

Corrosion can compromise the safety of operating equipment by causing failure (with catastrophic consequences) of, for example, pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms.
1.1.2. The cost of corrosion

Corrosion costs could be divided into direct costs and indirect costs.

The following are some examples of direct costs listed by Uhlig [4]:

i. Capital costs – cost of replacement parts, e.g., automobile mufflers, water lines, hot water heaters, sheet metal roofs.

ii. Control costs – maintenance, repair, and painting.

iii. Design costs – extra cost of using corrosion-resistant alloys, protective coatings, corrosion inhibitors.

Examples of indirect losses are as follows:

i. Shutdown – of power plants and manufacturing plants.

ii. Loss of product due to leakage.

iii. Contamination of product.

1.1.3. Conservation of materials

Materials are precious resources of a country. Corrosion destroys metals by changing them into oxides or other corrosion products. Material resources of iron, aluminium, copper, chromium, manganese, titanium, etc. are dwindling fast. Someday there will be an acute shortage of these materials. To preserve these valuable resources, it is necessary to understand how these resources are destroyed by corrosion and how these resources must be preserved by applying corrosion protection technology.

1.1.4. Corrosion study

Corrosion science is an interdisciplinary subject that includes chemistry, materials science and mechanics. The study of aqueous corrosion processes involves the combination of chemistry and material science. The science of mechanics is essential to understand mechanically assisted corrosion processes such as adhesion, wear etc.,

1.2. Corrosion

When metals are exposed to atmospheric conditions they react with air or water in the environment to form undesirable compounds, usually oxides. This
process is called corrosion. Almost all metals except the less reactive metals such as gold, platinum, and palladium, undergo corrosion. Corrosion of metals is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical or biochemical interaction with the environment. Corrosion is an undesirable and undeliberate process. It may, therefore, be observed that corrosion is a potent force which destroys economy, depletes resources and causes costly and untimely failures of industrial plants, equipments and components. Corrosion is a decay process in which metals exhibit their natural tendency to revert to their native combined state of existence as minerals (eg., oxides, sulphides, carbonates, etc.). A complete knowledge of thermodynamics and electrochemistry are very important to understand and to control corrosion [5].

1.3. Electrochemical principles of corrosion

Corrosion is an electrochemical process. Corrosion of metals is known to occur by the action of local cells, which comprise a partial anodic reaction and a partial cathodic reaction that proceed simultaneously on the metal surface. Corrosion is due to coupled electrochemical half-cell reactions which include anodic oxidation and cathodic reduction reactions. The basic principle of corrosion is that, during metallic corrosion the rate of oxidation equals the rate of reduction. In all corrosion reactions the anodic reaction is the oxidation of a metal to its ion. Examples are:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \] ................................. (1.1)
\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \] ................................. (1.2)\n
The number of electrons produced is equal to the number of valency of the ion. Metallic corrosion involves different cathodic reactions.

Hydrogen evolution \[ 2\text{H}^+ + 2e^- \rightarrow \text{H} \] ................................. (1.3)

Oxygen reduction (acidic solutions) \[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \] ................................. (1.4)

Oxygen reduction (neutral or basic solutions) \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \] .............. (1.5)

Metal ion reduction \[ \text{M}^{3+} + e^- \rightarrow \text{M}^{2+} \] ................................. (1.6)

Metal deposition \[ \text{M}^+ + e^- \rightarrow \text{M} \] .................................(1.7)
On a corroding metal surface, anodic and cathodic reactions occur in a coupled manner at different places on the metal surface. At certain sites on the metal surface, metal atoms pass into solution as metal cations. The electrons produced by this anodic half-cell reaction are consumed elsewhere on the surface to reduce hydrogen ions to hydrogen molecule. The reason that two different electrochemical reactions proceed on the same metal lies in the heterogenous nature of the metal surface [6].

1.4. Forms of corrosion

Corrosion can take many forms and each corrosion type will differ between systems, environments and other operational conditions. The multifaceted nature of corrosion damage has lead to classify corrosion on the basis of appearance of the corroded surface. The importance of such a classification is that a corrosion damage can be recognized as a definite corrosion form by visual inspection, either by the naked eye or by an optical or electronic microscope. So it is convenient to classify various types of corrosion into following forms of corrosion [7]:

i. Uniform corrosion
ii. Galvanic corrosion (two-metal) corrosion
iii. Thermogalvanic corrosion
iv. Crevice corrosion
v. Pitting corrosion
vi. Selective leaching (de-alloying)
vii. Intergranular corrosion
viii. Erosion corrosion
ix. Cavitation corrosion
x. Fretting corrosion
xi. Stress corrosion cracking
xii. Corrosion fatigue
A simple illustration of the various forms of corrosion is shown in figure 1.1[8]:

![Illustration of corrosion types](image)

**Figure 1.1. Different forms of corrosion.**

1.5. Corrosion prevention measures

Corrosion prevention aims to remove or decrease the effect of one or more of the conditions leading to corrosion using the following measures:

i. Selecting a material that does not corrode in the actual environment.

ii. Changing the environment, e.g., removing the oxygen or adding anti-corrosion chemicals (inhibitors).

iii. Using a design that will avoid corrosion, e.g., preventing the collection of water so that the metal surface can be kept dry.

iv. Changing the potential, most often by making the metal more negative and thus counteracting the natural tendency of the positive metal ions to be transferred from the metal to the environment.

v. Applying coating on the metal surface usually in order to make a barrier between the metal and the corrosive environment.
1.6. Corrosion rate

Measurement of corrosion rate is essential for the purpose of material selection in a suitable environment for a definite application. Corrosion involves dissolution of a metal, as a result of which the metallic part loses its mass (or weight) and becomes thinner. Electrochemical reaction kinetics is essential in determining the rate of corrosion of a metal exposed to a corrosive medium which acts like an electrolyte. Thermodynamics predicts the possibility of corrosion, but it does not provide information on how slow or fast corrosion of a metal occurs. The kinetics of a reaction on the metal electrode surface depends on the electrode potential. Thus, corrosion rate strongly depends on the rate of electron flow to or from metal/solution interface. Hence, in comparison, reaction rates are governed by chemical kinetics, while corrosion rates are primarily governed by electrochemical kinetics. Various conventional scales have been suggested to determine the corrosion resistance of metals and the aggressiveness of environment. The rate of corrosion is expressed in several ways. The weight and current indices are used most frequently. The first type involves the weight loss (in grams or kilograms) per unit time (second, hour, day, year) referred to a unit area (square centimeter, square meter) of a specimen. In the second type the corrosion rate is given in terms of current intensity (in amperes or milliamperes) per unit surface area of the specimen [9, 10].

1.6.1. Factors affecting corrosion rate

While variety of natural and environmental factors can have significant effects on the corrosion rate of metals, all these factors are grouped under two important criteria namely nature of metal and nature of environment. The individual factors that cause corrosion of metals are discussed below:

1.6.1.1. Nature of metal

Position of metal in galvanic series: The corrosion rate of a metal is decided by its position in the galvanic series. Among different metals a metal having higher position in galvanic series undergoes corrosion when connected to another metal below it. Also, more difference in the position of galvanic series will cause faster corrosion at anodic metal.
Hydrogen overvoltage: If a base metal (like Zinc, lead, iron etc.,) contains a metal with high hydrogen overvoltage as an impurity the base metal will dissolve in acid solution readily in the presence of air or oxygen.

Purity of metal: Pure metal resists corrosion, but impurities in a metal form a local galvanic cell and result in the corrosion of metal. In such cases metal acts as anode and impurity acts as cathode. Rate of corrosion increases due to more exposure to impurities. In the case of alloys there is no local cell action and corrosion is not possible because the system is a homogeneous solid solution.

Relative areas of anode and cathode: Smaller the area of anode compared to cathode will lead to faster corrosion of anode. The current density will be large at anode because of its small area and larger cathodic area will demand more electron which will be fulfilled by fast reaction at anode (oxidation) that will lead to rapid corrosion.

1.6.1.2. Effect of environment

Environment plays an important role in the corrosion of a metal. Environmental parameters like temperature, humidity, pH, etc. have a great influence on the corrosion rate of a metal. The corrosive environment can be water, air, carbon dioxide, organic liquids, molten salts, or gaseous sulfur.

Temperature: It is well known that increase in temperature leads to an increase in the rate of chemical reactions. The rate of diffusion increases by rise in temperature, hence the rate of corrosion is also increased. At higher temperature, passive metals also become active and undergo corrosion.

Concentration: In general, corrosion rate increases with the concentration of the corrosive agents. But there is no definite relationship between their concentration in air, water, etc. and the corrosion rate.

pH value: In aqueous solutions, pH is a very important factor for the corrosion resistance of metals. In acidic medium (pH less than 7), the rate of corrosion is fast. Also, in basic medium pH > 7, some metals such as Pb, Zn, Al, etc., form complexes and hence corrosion occurs.
The solubility of Al(OH)$_3$, a complex formed on aluminium surface in aqueous alkali solution as a function of pH, is a good example of the influence of pH on corrosion rate. It is well known that steel has a poor resistance to acidic media, and that aluminium has a poor resistance to highly basic media containing sodium or potassium hydroxide.

Nature of acid and base: The nature of the acid (and thus of the anion associated with the proton H$^+$) and of the base (and thus of the cation associated with OH) also need to be taken into account. For example, mineral acids such as hydrochloric acid strongly attack aluminium. The rate of attack increases with increase in concentration of the acid or base.

1.7. Corrosion inhibitors

Inhibition is a preventive measure against corrosive attack on metallic materials. A corrosion inhibitor is any chemical substance which when added in small concentrations to an aggressive environment, is able to decrease corrosion rate of the exposed metal. Inhibitors will reduce the rates of either anodic oxidation and/or cathodic reduction or both of these partial reactions.

In general, corrosion inhibition means the reduction in the oxidation state of the metal by the addition of a chemical compound to the system in contact with the solution. Two processes are involved in the action of the inhibitor on the metal surface. The first step involves the transport of the inhibitor to the metal surface and the second step concerning interaction between the inhibitor and the metal surface. Addition of corrosion inhibitor to a system results in adsorption of the inhibitor molecule at the metal solution interface. This is followed by a change in potential difference between the metal electrode and the solution, due to the non-uniform distribution of electric charges at the interface. The metal/solution is characterized by an electrical double layer. The entry of inhibitor molecules into the electrical double layer modifies its composition and structure. Hence, change in the capacitance of the double layer before and after the addition of the inhibitor can be used to monitor the adsorption of the inhibitor. When an organic compound approaches and adsorbs at the metal solution interface it can be written as

\[ M(nH_2O)_{ads} + I \rightarrow MI_{ads} + nH_2O_{(sol)} \]  

\[ \text{(1.8)} \]
In the above process, the inhibitor I adsorbs on the metal and displaces n water molecules initially adsorbed on the metal. Adsorption of the inhibitor on the metal is due to greater interaction energy between the metal and inhibitor than the interaction energy between the metal and the water molecules [11, 12].

1.7.1. Behaviour of metal in inhibition

The degree of adsorption of inhibitor and hence the corrosion inhibition efficiency of the inhibitors are really influenced by the residual charge on the surface of the metal. The corrosion inhibition phenomena are subjective to some characteristics of the metal, surface state and surface modifications of the metal. In the case of a metal covered with oxide on the surface, the semiconducting nature of the oxide plays an important role in the corrosion inhibition process.

1.8. Classification of inhibitors

Inhibitors adsorb on the metal surface and inhibit the corrosion processes by forming a protective film. Inhibitors reduce corrosion rate by

i. Increasing the anodic or cathodic polarization behavior (Tafel slopes)

ii. Decreasing the movement or diffusion of ions to the metallic surface

iii. Increasing the electrical resistance of the metal surface

Inhibitors can be classified in several different ways. The most common way of classifying inhibitors on the basis of their function is as follows [8]:

1.8.1. Passivating (anodic) inhibitors

Passivating inhibitors cause the anodic curve of polarization to shift such that less current flows. These inhibitors have the ability to passivate the metal surface. There are two types of passivating inhibitors, namely oxidizing anions and non-oxidising anions. Oxidizing anions tend to passivate metal in the absence of oxygen. Typical oxidising anions are chromate, nitrite and nitrate. Non-oxidising ones like phosphate, tungstate and molybdate require oxygen to perform passivation. Anodic inhibitor is by far the most widely used and possesses higher efficiency than others. However, one major drawback of it is that in order to maintain sufficient passivation of the metal the concentration of the inhibitor must be kept well above a critical or minimum concentration. If the concentration is below the minimum value, localised corrosion such as pitting will occur on the metal.
1.8.2. Cathodic inhibitors

Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface and thus increase the surface impedance and lower the diffusion rate. The inhibiting action of cathodic inhibitors occurs by three mechanisms:

i) cathodic poisons: Typical examples of cathodic poisons are arsenic and antimony.

ii) oxygen scavengers: corrosion rates are reduced by the use of oxygen scavengers that react with dissolved oxygen. Sulfite and bisulfite ions are examples of oxygen scavengers that can combine with oxygen to form sulfate.

iii) Cathodic precipitates: compounds such as calcium, magnesium that will precipitate as oxides to form a protective layer which acts as a barrier on the metal surface.

1.8.3. Organic inhibitors

Organic inhibitors affect the whole surface of a metal when added in sufficient concentration. They are typically film forming compounds that cause the formation of hydrophobic film on the metal surface. Effectiveness of these inhibitors depends on the chemical composition, molecular structure and affinity for the metal surface. The protective film of adsorbed molecules on the metal surface acts like a barrier to the dissolution of the metal in the electrolyte.

1.8.4. Precipitation inhibitors

Precipitation causing inhibitors act by blocking both anodic and cathodic sites indirectly. This type of compounds form precipitates on the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this type are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water.
1.8.5. Volatile corrosion inhibitors

Inhibitors that are transported in a closed environment to the site of corrosion by volatilization from a source are called volatile corrosion inhibitors or volatile phase inhibitors. When volatile solids such as dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used, the vapours of these salts condense and are hydrolyzed by any moisture to liberate protective ions. An efficient volatile corrosion inhibitor provides inhibition rapidly and its action lasts for long periods.

1.9. Adsorption of corrosion inhibitors

The adsorption of inhibitors is governed by the residual charge on the surface of the metal and by the nature and chemical structure of the inhibitor. Two main types of adsorption of organic inhibitor that occur on a metal surface are physical or electrostatic adsorption and chemisorption. Physical adsorption is due to the electrostatic interaction between the inhibiting ions or dipoles and the electrically charged surface of the metal. The forces in electrostatic adsorption are generally weak. The inhibiting species adsorbed on the metal due to electrostatic forces can be desorbed easily. A main feature of electrostatic interaction is that the ions are not in direct physical contact with the metal. A layer of water molecules separates the metal from the ions. The physisorption process has low activation energy and it undergoes desorption at higher temperatures.

Chemisorption is probably the most important type of interaction between the metal surfaces and an inhibitor molecule. The adsorbed species is in contact with the metal surface. A coordinate type of bond involving electron transfer from inhibitor to the metal is assumed to take place in the process. The chemisorption process is slower than electrostatic sorption and has higher activation energy. The temperature dependency shows higher inhibition efficiency at higher temperatures. The nature of the metal and that of the organic inhibitor have a decisive effect on the coordinate bond. Electron transfer from inhibitor to the metal is facilitated when the inhibitor molecule has an unsaturated lone pair of electrons on the donor atom of the functional group. Availability of π electrons due to the presence of multiple bonds on aromatic rings in the inhibitor molecule would facilitate electron transfer from the inhibitor to the metal [13].

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1.9.1. Mechanism of inhibition

The efficiency of a corrosion inhibitor depends strongly on its adsorption process. Two main aspects namely geometric and electronic properties of an inhibitor must be taken into consideration of all the necessary factors of the adsorption process. The geometry of the inhibitor molecule strongly influences its adsorbing tendency because it is the most favorable way by which the inhibitor molecule would cover the metal surface. Compounds that possess planar geometry mostly have higher inhibition efficiencies than corresponding compounds with less planar geometry. Information regarding the surface coverage of the metal surface by an inhibitor is provided by its geometry. Electronic properties of an inhibitor indicate which molecule has the greatest tendency to adsorb on the metal surface. Molecular sites with high electron densities would preferably donate electrons to partially filled or vacant d orbitals of the metal resulting in a donor-acceptor bond. Thus mode of interaction between the inhibitor molecule and the metal surface depend strongly on the electron density distribution in the inhibitors [14-18].

1.10. Corrosion characteristics of aluminium

The electrochemical behavior of aluminium is due to the natural oxide film which governs the corrosion resistance of aluminium. The protective oxide film formed in water at ambient temperatures is amorphous and a few nanometres in thickness. The corrosion of the metal in aqueous solutions is severe at 70-80°C [19].

In general, aluminium (1100) is resistant to [2]:

i. Hot or cold NH₄OH.
ii. Hot or cold acetic acid, citric, tartaric and malic acids.
iii. Fatty acids. Aluminium equipment is used for distillation of fatty acids.
iv. Distilled water.
v. Atmospheric exposure. Excellent resistant to rural, urban and industrial atmospheres but lesser resistance to marine atmospheres.
vi. Sulphur, sulphur atmospheres and H₂S. Aluminium is used for mining of sulphur.
vii. Fluorinated refrigerant gases.
Aluminium is not resistant to:

i. Strong acids, such as HCl, HBr, H₂SO₄, HF, HClO₄, H₃PO₄, formic, oxalic and trichloroacetic acids.

ii. Alkalis. Lime and fresh concrete are corrosive, as well as strong alkalis, e.g., NaOH and the very alkaline organic amines.

iii. Mercury and mercury salts.

iv. Sea water. Pitting occurs at crevices and surface deposits, especially when trace amounts of heavy metal ions are present.

v. Waters containing heavy metal ions. e.g., mine waters or waters previously running through copper, brass or ferrous piping.

vi. Chlorinated solvents.

vii. Anhydrous ethyl, propyl, or butyl alcohols at elevated temperatures. A trace of water acts as an inhibitor.

viii. Contact with wet woods, in particular beech wood.

1.11. Potential - pH diagrams

The potential-pH or Pourbaix diagrams are graphical representations about the stability of a metal and its corrosion products as a function of the potential and pH (acidity or alkalinity) of the aqueous solution. These diagrams are helpful to deduce for a given metal at a certain pH with a precise potential corrosion can occur or not. Aluminium corrodes more rapidly both in acids and alkalis. At room temperature, the minimum rate occurs between pH 4-8.5. Corrosion rates of aluminium in the alkaline region greatly increase with pH. The reason is Al³⁺ is readily complexed by OH⁻ forming AlO₂⁻ in accordance with

\[ \text{Al} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaAlO}_2 + \frac{3}{2}\text{H}_2 \text{O} \]  

Figure 1.2 is the potential-pH diagram for aluminium - H₂O system showing all the major species and their ranges of stability [20, 21]. From this, it is clear that with decreasing Al³⁺ activity, the region of stability of aluminium oxide ((Al₂O₃) undergoes compression. It should be noted that Pourbaix diagrams cannot give information on the corrosion rates. In the pH range of 4-8, aluminium oxide forms a protective film and the corrosion rate of aluminium is low.
At pH below 4 and above 8, the corrosion rate may be high because the oxide is soluble under these conditions. The areas of stability of oxide film, soluble ions and the metal are labeled as passivation, corrosion and immunity respectively.

Figure 1.2. Potential –pH diagram of Al-H₂O system at 25°C.

1.12. Electrochemical reactions in the corrosion of aluminium

The fundamental reaction of the corrosion of aluminium in aqueous medium involves the oxidation of aluminum in water according to the equation:

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \quad \text{..........................} \quad (1.10) \]

Metallic aluminium, in oxidation state 0, goes in solution as trivalent cation Al³⁺ when losing three electrons. This reaction is balanced by a simultaneous reduction in ions present in the solution, which capture the released electrons. From thermodynamic consideration only two reduction reactions can occur:

i) reduction of H⁺ protons:

\[ 3\text{H}^+ + 3\text{e}^- \rightarrow \frac{3}{2}\text{H}_2 \quad \text{..........................} \quad (1.11) \]

H⁺ protons results from the dissociation of water molecules:

\[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad \text{..........................} \quad (1.12) \]

ii) reduction of oxygen dissolved in water:
In alkaline or neutral media: \[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \qquad (1.13) \]
In acidic media: \[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \ldots \quad (1.14) \]

The corrosion of aluminium in aqueous media is the sum of two electrochemical reactions, oxidation and reduction:

\[ Al - Al^{3+} + 3e^- \quad \ldots \quad (1.15) \]
\[ 3H^+ + 3e^- \rightarrow \frac{3}{2}H_2 \quad \ldots \quad (1.16) \]
\[ Al + 3H^+ - Al^{3+} + \frac{3}{2}H_2 \]

or
\[ Al + 3H_2O - Al(OH)_3 + \frac{3}{2}H_2 \quad \ldots \quad (1.17) \]

This reaction is accompanied by a change in the oxidation state of aluminium which, from the oxidation state 0 in the metal, into the oxidation state of alumina (+3). Aluminium corrosion results in the formation of alumina Al(OH)$_3$, which is insoluble in water and precipitates as a white gel, which is found in corrosion pits as white gelatinous flakes [22].

1.13. Types of corrosion on aluminium

Different types of corrosion, more or less visible to the naked eye, can occur on aluminium, such as uniform (generalized) corrosion, pitting corrosion, stress corrosion, etc. The predominant type of corrosion will depend on a certain number of factors that are intrinsic to the metal, the medium and the conditions of use.

1.13.1. Uniform corrosion

Uniform (or general) corrosion refers to the relatively uniform reduction of thickness over the surface of a corroding material. This type of corrosion is observed especially in highly acidic or alkaline media, in which the solubility of the natural oxide film is high. The dissolution rate of the film is greater than its rate of formation. The rate of uniform corrosion can be easily determined by measuring the mass loss, or the quantity of released hydrogen. Uniform corrosion is usually controlled by selecting suitable materials, protective coatings, cathodic protection and corrosion inhibitors. This is a useful parameter to evaluate the dissolution rate of aluminium in a pickling bath[23,24].
1.13.2. Pitting corrosion

Aluminium is prone to pitting corrosion in media with a pH close to neutral, which basically covers all natural environments such as surface water, seawater, and moist air. Corrosion pits are covered with white, voluminous and gelatinous pustules of alumina gel Al(OH)₃. These pustules are much bigger than the underlying cavity. Aluminium is prone to localised corrosion caused by a local rupture of the passive film. Pitting corrosion can be assessed using the density (the number of pits per unit area), the rate of deepening, and the probability of pitting (Figure 1.3). The service lifetime will depend on the rate of deepening. The pitting depth is unrelated to the thickness of the metal [25].

![Figure 1.3. Mechanism of pitting corrosion of aluminium.](image)

1.13.3. Transgranular and Intergranular (Intercrystalline) corrosion

Within the metal, at the level of the grain, corrosion may propagate in two different ways (Figure 1.4):

i) Corrosion indifferently affects all the metallurgical constituents with no selective corrosion. This is called transgranular or transcrystalline corrosion because it propagates within the grains in all directions.

ii) Corrosion propagates at grain boundaries with preferential paths. Unlike transgranular corrosion, this form of intercrystalline corrosion consumes only a very small amount of metal, and mass loss is not a significant parameter for assessment of this type of corrosion. It is not detectable with the naked eye but requires microscopic observation.
Copper containing aluminium alloys (2000, 6000 and 7000) are susceptible to intercrystalline corrosion. Aluminium of the series 1000 (including refined aluminium 1199) is also prone to intercrystalline corrosion [26]

![Image](image.png)

Figure 1.4. a) Transcrystalline b) Intercrystalline corrosion.

1.13.4. Exfoliation corrosion

Exfoliation corrosion is a type of selective corrosion that propagates along a large number of planes running parallel to the direction of rolling or extrusion (Figure 1.5.). Between these planes are very thin sheets of sound metal that are not attacked, but gradually pushed away by the swelling of corrosion products, peeling off like pages in a book. Hence the term “exfoliation corrosion”. Aluminium alloys of the type 2000 and 5000 series exhibit this type of corrosion that are intercrystalline [27].

![Image](image.png)

Figure 1.5. Exfoliation corrosion.

1.13.5. Stress corrosion

This type of corrosion results from the combined action of a mechanical stress (bending, tension) and a corrosive environment. Stress corrosion of the 2000 and 5000 series develops only in media containing high amounts of chloride, but not in water having only a low chloride level or in a humid air (Figure 1.6). A good
correlation is found between the sensitivity to intercrystalline corrosion and stress corrosion of these alloys in the marine environment. The propagation rate of stress corrosion cracks is very low. However, propagation, even at this low rate, may lead to catastrophic mechanical failure, due to the weakening of the structures.

![Image](image_url)

Figure 1.6. Stress corrosion crack in aluminium.

1.13.6. Filiform corrosion

Filiform corrosion is specific to lacquered metal. This is mainly an alteration of surface appearance. The underlying metal only suffers a very superficial attack, not exceeding a depth of a few tens of microns. It develops as narrow filaments, about 0.1–0.5 mm wide and a few millimetres long, which propagate at the metal–lacquer interface. Swelling of corrosion products deforms the lacquer film and appears as very narrow wires which progress like mole tunnels underneath the lacquer film. Filiform corrosion always starts at coating defects, such as scratches, and weak points: beards, cut edges or holes. It can be seen after several years of service. This type of corrosion is common in aluminium alloys that are used for aerospace applications. Filiform corrosion occurs with all types of paints, acrylic lacquers, epoxy-ployamides, epoxy-amines and polyurethaness irrespective of the mode of application.

1.13.7. Water line corrosion

When metallic structures are partly immersed in water, a localised and more intense corrosion very often occurs on the immersed portion just below the air–water interface (Figure 1.7). This is caused by the difference in aeration between the surface of the liquid and the zone immediately underneath. The upper part of the meniscus is, therefore, the anodic zone, which corrodes preferentially. Aluminium structure that is partially immersed in sea water is susceptible to water
line corrosion that occurs as rather scattered, superficial pitting, with a depth not exceeding a few tenths of a milimetre. This can be observed on the uncoated aluminium hull of barges[28].

![Diagram of waterline corrosion of aluminium](image.png)

Figure 1.7. Waterline corrosion of aluminium.

1.13.8. Crevice corrosion

Crevice corrosion is a localized corrosion in recesses: overlapping zones for riveting, bolting or welding, zones under joints, and under various deposits (sand, slag, precipitates, etc.). These zones, also called crevices, are very tiny and difficult to access for the aqueous liquid that is covering the rest of the readily accessible surfaces. This type of corrosion is also known as deposit attack. The surface in the recess becomes anodic with respect to the rest of the structure [29].

Unlike certain alloys such as stainless steel, aluminium exhibits a rather low susceptibility to crevice corrosion. When a bolted or riveted assembly that has been exposed to a liquid such as seawater for a long period is dismantled, it appears that crevices are usually sealed by corrosion products of aluminium. Hence aluminium has a rather low susceptibility to crevice corrosion. Crevice corrosion associated with galvanic corrosion may develop under steel washers (ordinary or stainless) used for mounting aluminium wall panels exposed to the seashore [30].

1.13.9. Cavitation

Cavitation occurs when the hydrodynamic pressure exceeds the vapour pressure of a moving liquid. Gas bubbles form within the liquid, which thus
becomes a two-phase system. These bubbles will be crushed against the metal surface at high speed, an attack that leads to cavities with rounded contours. This degradation is caused by the combination of a mechanical effect and corrosion of the metal. The natural oxide film is destroyed and the aluminium is attacked; there is a competition between tearing off the film and reforming it.

1.3.10. Erosion

Corrosion by erosion occurs in moving media. This type of corrosion is related to the flow speed of the fluid. It leads to local thinning of the metal, which results in scratches, gullies, and undulations, which are always oriented in the same direction, namely the flow direction. Acceleration of the attack is due to the destruction or removal of the protective film by mechanical forces[10].

![Diagram of turbulent eddy mechanism for growth of erosion corrosion pit](image)

1.13.11. Microbiological corrosion

The term microbiologically influenced corrosion (MIC) is used to designate corrosion due to the presence and activities of microorganisms, that is, those organisms that cannot be seen individually with the unaided human eye, including microalgae, bacteria, and fungi. It has been shown that corrosion in jet aircraft tanks is mainly caused by the growth of the bacterium Cladosporium Resinae in kerosene [31]. The prevention of microbiological corrosion in tanks of jet aircraft is based on bactericides that are either water-soluble such as strontium chromate, or kerosene-soluble such as mono-ethylene glycol.
1.13.12. Corrosion products

According to the basic corrosion reaction of aluminium:

\[ 2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \]  \hspace{1cm} (1.18)

the corrosion product is aluminium hydroxide Al(OH)$_3$, commonly called alumina. Freshly formed alumina contains a great deal of water. After calcination at 1000°C, the mass loss can reach 60% [32]. Alumina is a gelatinous white gel that covers corrosion pits. After several weeks of exposure to air, part of the water will evaporate and the alumina will look like a white powder. Whether dry or not, the alumina adheres well to the metal surface. Alumina that is formed during corrosion at room temperature is amorphous [33], whatever the type of corrosion from which it originates.

For the elimination of corrosion products on a construction (ship, tank, etc.), in order to refresh the surface, for example, as a preparation for lacquering, sand blasting is the best approach. Solutions of corrosive products should never be introduced in a tank, ship, etc.,

1.14. Environment friendly inhibitors

Chief concerns such as safety, environmental pollution and economics need corrosion inhibitors to be non-toxic, renewable, environment friendly and acceptable. Organic compounds containing functional groups with N, S and O are generally used as corrosion inhibitors. These organic compounds are expensive and also hazardous to the environment. Hence non-toxic, cost effective, and renewable corrosion inhibitors should be identified. So efforts must be focused towards the sustainable development which involves maximum utilization of limited resources with no waste disposal [34].

1.14.1. Green chemistry

The basis of proper choice and application of environment friendly corrosion inhibitors is green chemistry. Rare earth compounds are identified as better alternatives to toxic chromate inhibitors that are widely employed for corrosion of aluminium alloys in conversion coatings, deionizers, anodizing and to inhibit pigments in paints [35-37]. Cerium salts such as cerium chloride, cerium salicylate
and cerium dibutyl sulphate are chiefly used instead of chromates in conversion coatings. Macrocyclic compounds like porphyrins and phthalocyanines are forming non toxic metal-chelate complexes of high stability constants. As early as 1950, lubricants containing phthalocyanins are used as corrosion inhibitors. Many oleochemicals such as ethyl stearate, glyeryl monooleate, stearyl maleate and diethylene glycol monostearate are used as inhibitors for aluminium. Oleochemicals are obtained from vegetable, animal and marine sources. Fatty acids, Fatty alcohols, fatty acid esters, amines and amides are present in oleochemicals.

Plant products are the chief sources of environmentally acceptable corrosion inhibitors. In fact leaves extracts which have proven corrosion inhibiting abilities in acidic and alkaline media are known to contain one or more of the following organic substances namely flavonoids, alkaloids, tannins, triterpenoids, saponins, amino acids, phenols, glycosides, essential oils and carotenoids. These phytoconstituents have aromatic ring systems, hetero atoms in different functional groups and double bonds which are responsible for the inhibiting action of plant products in corrosion reactions. So the present effort involves utmost care and non-hazardous chemical principles for the proper choice and application of sustainable, cost effective, eco friendly green inhibitors for aluminium corrosion in alkaline medium.
References