

Introduction

The fast growing industrialization, development activities and progress in civilization increased the use of metallic materials in all different fields. Materials mainly metals used in the fabrication of machines must be stable. If the metals are unstable, machines made from metals undergo an undesirable obsolescence. It is clear that an industrial civilization depends on the stability of metals and alloys in moist or impure atmosphere. The basic requirements of any metal used in industry or at home are durability and ability to give good services continuously. Corrosion is the deterioration of a metal or a metal alloy and an alteration of its physical properties under the influence of its environment. This phenomenon has major impacts in various fields, particularly in industry. The work stoppage and change of corroded material for the industry is very high financial burden. Corrosion not only has economic implications, but also social and engage the safety and health. So tremendous theoretical and practical concern on protection of metal surfaces against corrosion is an important industrial and scientific task.

The demand for Mild steel and aluminium are increasing year by year due to wide ranges of industrial applications such as construction, marine applications, transportation, and food and in electric industries etc. Corrosion studies of mild steel and aluminium alloys have received considerable attention by researchers because of their technological importance and industrial applications.

1.1 CAUSE OF CORROSION

Metals exist as such in the earth crust as ores. Metals are usually extracted from ores through the application of a energy. In the pure metallic state, the metals are unstable as they are considered in excited state (higher energy state). Therefore as soon as the metals are extracted from their ores, the reverse process begins and form metallic compounds, which are thermodynamically stable (lower energy state). Hence, when metals are used in various forms, they are exposed to environment, the exposed metal surface begin to decay (conversion to more stable compound). This is the basic reason for metallic corrosion. Although corroded metal is thermodynamically more stable than pure metal but due to corrosion, useful properties of a metal like malleability, ductility, hardness, luster and electrical conductivity are lost.

1.2 FORMS OF CORROSION

Corrosion is so prevalent and manifests in different forms, such as uniform or general corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, erosion corrosion, stress corrosion, corrosion fatigue, and fretting corrosion. Classification of the different forms of corrosion may be based on intrinsic and extrinsic modes. Intrinsic modes of corrosion independent of design are general corrosion, pitting, intergranular corrosion, and stress-corrosion cracking. Extrinsic modes of corrosion affected by design are crevice or under deposit corrosion, galvanic corrosion, erosion corrosion, fretting corrosion, and corrosion fatigue. Identification of different forms of corrosion is based on the apparent morphology of corrosion and the basic factor influencing the mechanism of corrosion in each form.

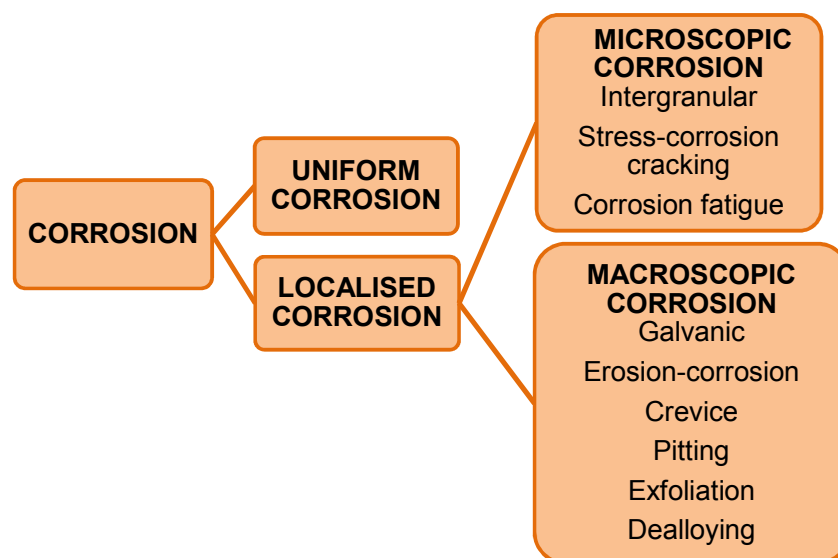


Figure 1.1 Different forms of corrosion

1.3 THEORIES OF CORROSION

Based on the environment, corrosion is classified into

- (i) Dry or Chemical Corrosion (ii) Wet or Electrochemical Corrosion

1.3.1 DRY OR CHEMICAL CORROSION

This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid, etc. The chemical corrosion is defined as the direct chemical attack of metals by the atmospheric gases present in the environment.

1.3.2 WET OR ELECTROCHEMICAL CORROSION

Electrochemical corrosion involves:

- The formation of anodic and cathodic areas or parts in contact with each other
- Presence of a conducting medium
- Corrosion of anodic areas only and
- Formation of corrosion product somewhere between anodic and cathodic areas.

This involves flow of electron-current between the anodic and cathodic areas. This interaction is electrochemical in nature.

ELECTROCHEMICAL THEORY OF CORROSION

The basic process of metallic corrosion in aqueous solution consists of the anodic dissolution of metals and the cathodic reduction of oxidants present in the solution. These reactions are charge-transfer processes that occur across the interface between the metal and the aqueous solution.

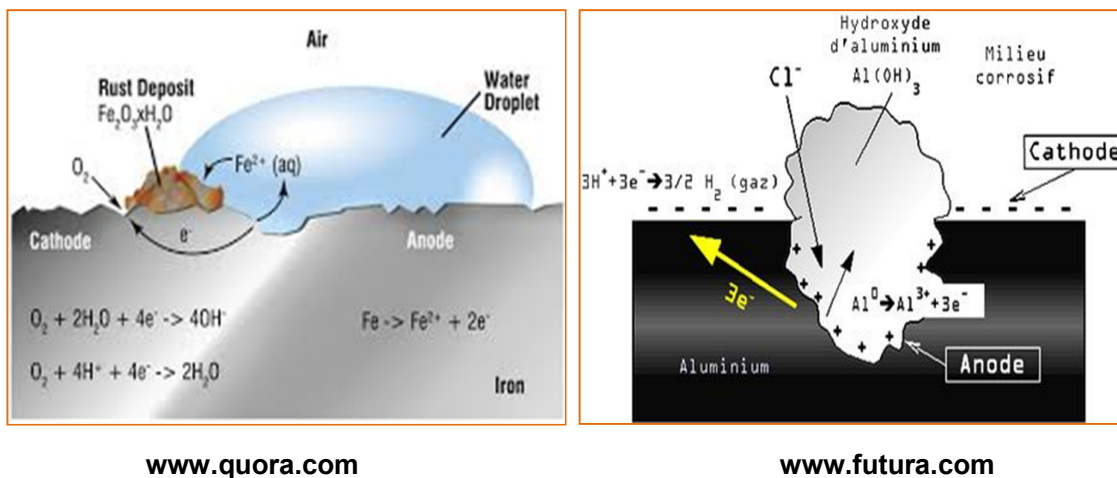
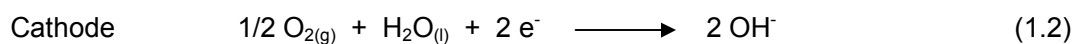


Figure 1.2 Schematic representation of electrochemical corrosion process for Mild steel and Aluminium

The electrochemical corrosion process involves two reactions,

- Oxidation reaction at the anode and
- Reduction at the cathode.

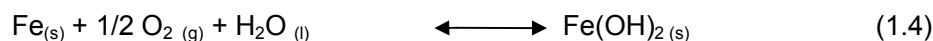


(neutral solution)



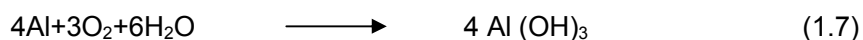
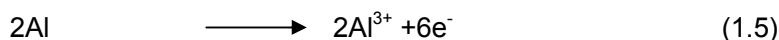
(acidic solution)

The overall cell reaction can be obtained by adding the equations.



Further oxidation of $\text{Fe}(\text{OH})_2$ yields $\text{Fe}(\text{OH})_3$.

For **aluminium corrosion**, the reactions are as follows



1.4 FACTORS INFLUENCING CORROSION

Many factors exert outstanding influence upon the ultimate rate of corrosion. The primary factors which influence corrosion is nature of the metal and the secondary factors more with the specific environment

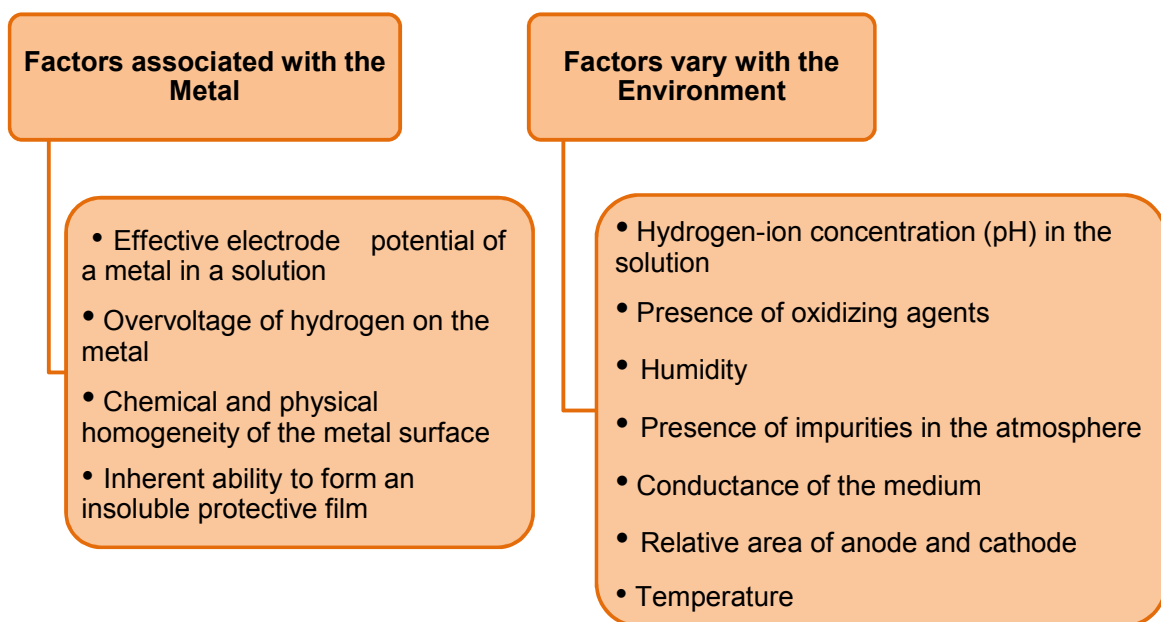


Figure 1.3 Factors affecting corrosion

1.5 STRATEGIC IMPACT OF CORROSION DAMAGE

Corrosion affects our society on a daily basis, causing degradation and damage to household appliances, automobiles, airplanes, highway bridges, energy production and distribution systems, and much more. Corrosion is costly due to any operational downtime necessary for parts replacement. There is also concern about damage to the environment for example the breaking of oil pipelines in the petroleum industry. The effects of corrosion in our daily lives are both direct and indirect.

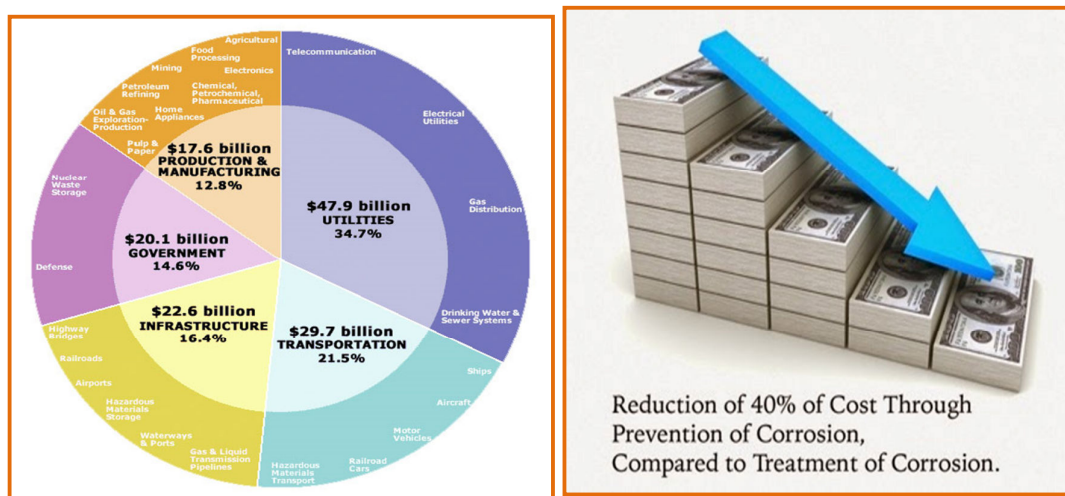


Figure 1.4 Cost of corrosion

Corrosion costs money and lives, resulting in dangerous failures and increased charges for everything from utilities to transportation and more. NACE study estimates global cost of corrosion at US\$2.5 trillion annually equivalent to roughly 3.4 percent of the global Gross Domestic Product (GDP). (**NACE International, March 8, 2016**). The high costs of corrosion have a significant effect on the national economy. The huge annual loss due to corrosion should be minimized. Proper understanding of the basics of corrosion, knowledge of engineering with focus on material design, proper use of materials and the methodology of making corrosion-free component structures can minimise corrosion cost.

1.6 CONSEQUENCES OF CORROSION

The impact of corrosion is felt in three areas of concern-economics, safety, and environmental damage (**Sastri,2011**). It is a major issue in all fields of application of metals and alloys. The loss of metal resources poses a danger to conservation and causes serious economic problems in many sectors.

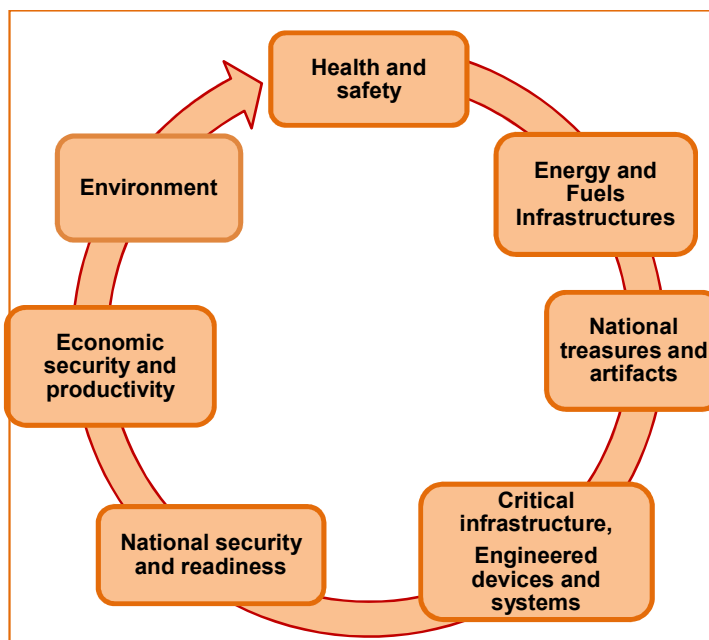


Figure 1.5 Corrosion problems in different sectors (www.nap.edu)

Corrosion not only has economic implications, but also social and engage the safety and health of people. Some of the major harmful effects of corrosion can be summarized as follows:

- ❖ Loss of technically important surface properties of a metallic component.
- ❖ Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.
- ❖ Reduction of metal thickness leading to loss of mechanical strength and plant shutdown.
- ❖ Loss of efficiency and replacement of corroded equipments resulting heavy expenditure.
- ❖ Hazards or injuries to people arising from structural failure or breakdown.
- ❖ Loss of time in availability of profit-making industrial equipment.
- ❖ Reduced value of goods due to deterioration of appearance.
- ❖ High cost of preventive maintenance.
- ❖ Contamination of fluids in vessels and pipes and loss of product from corroded container.
- ❖ Safety requirement measures for fire hazards or explosion.

- ❖ Health problems due to chemicals escaping from corroded equipment.
- ❖ Severe detrimental effects on the environment in the form of water and air pollution, leading to the demise of aquatic life.

1.7 LOSS DUE TO CORROSION

Corrosion is the destructive attack of a material by reaction with its environment. The serious consequences of the corrosion process have become a problem of worldwide significance. The losses due to corrosion are huge. There are many losses due to corrosion some of which are given pictorially in Figure 1.6 below.

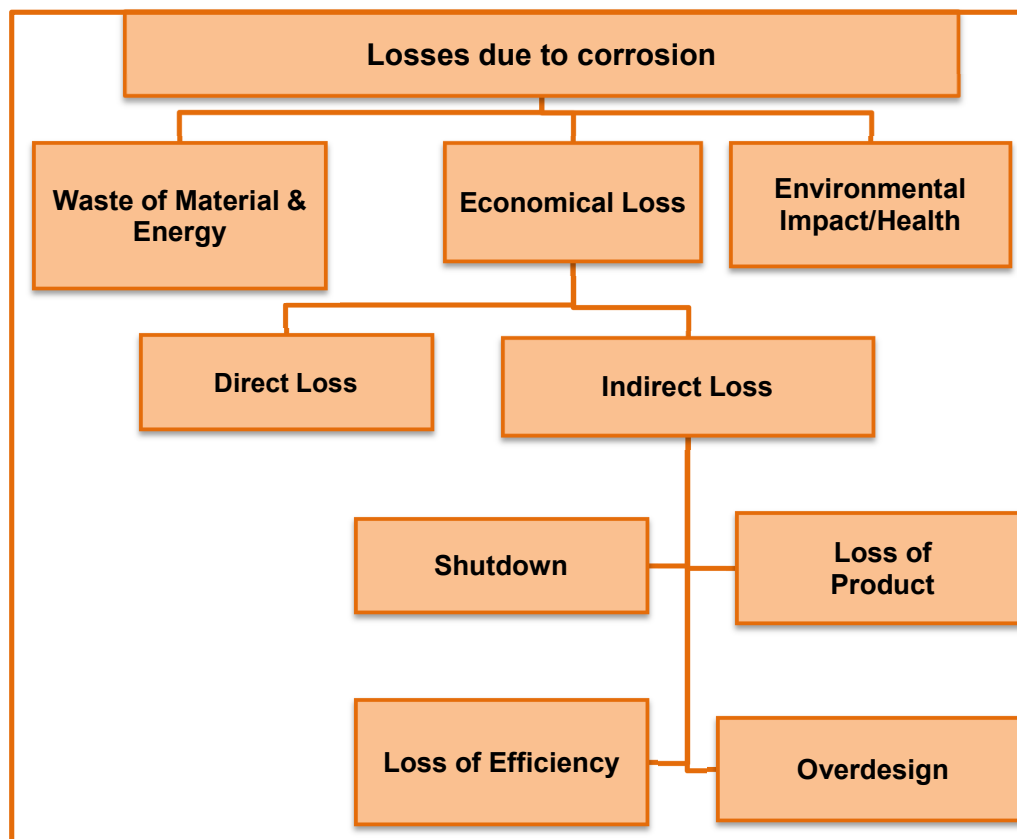


Figure 1.6 Losses due to corrosion

1.8 SOCIAL IMPLICATIONS OF CORROSION

The economic development of any country depends not only on its natural resources and productive activities, but also on the infrastructure that account for the exploitation, processing and marketing of goods. Corrosion is a worldwide crucial problem that strongly affects natural and industrial environments.

1.8.1 CORROSION IN ELECTRONIC INDUSTRY

Corrosion of metal components in the electronics industry may occur at different stages may be during manufacture, storage, shipping and service. Corrosion of one or more of the metallic elements of an electronic component is the primary cause of failure in various electronic equipments. When electronic devices are in more severe environments such as tropical, subtropical, contaminated deserts, etc., they have high failure rates. Thin layers of corrosion products on the surface of the metal component change their electrical characteristics: resistance, capacity and lead to partial or total failure of the electronic system. With the combined increase in miniaturization of electronic systems and the explosive increase in their availability, it is expected that the corrosion and deterioration of electronics will become a societal issue with dire unpredictable consequences. Corrosion in electronic components manifests itself in several ways. Computers, integrated circuits, and microchips are now an integral part of all technology-intensive industry products, ranging from aerospace and automotive to medical equipment and consumer products, and are therefore exposed to a variety of environmental conditions.

1.8.2 CORROSION IN THE AUTOMOTIVE INDUSTRY

The amount and type of materials used in the construction of automotive vehicles are diverse based on the component parts. They are usually constructed of carbon steel, fiberglass, aluminium, magnesium, copper, cast iron, glass, various polymers and metal alloys. The main cause of corrosion of the car body is the accumulation of dust in different closed parts, which stays for a long time by absorbing moisture, The corrosion problem that occurs in the metal car body has been a serious problem that usually arises most often in coastal environments, contaminated with chlorides and rural areas with high humidity and specific contaminants. Many countries use salt (NaCl , CaCl_2 or MgCl_2) to keep the roads free of ice. Under these conditions these salts, in combination with the dust blown by the car, provide conditions for accelerated corrosion.

1.8.3 CORROSION IN PIPE LINES

Corrosion can cause higher costs for a water system due to problems with decreased-pumping capacity, caused by narrowed pipe diameters resulting from corrosion deposits. Decreased water production, caused by corrosion holes in the system, which reduce water pressure and increase the amount of finished water required delivering a gallon of water to the point of consumption. High replacement frequency of water heaters, radiators, valves, pipes, and meters are observed because of corrosion damage.

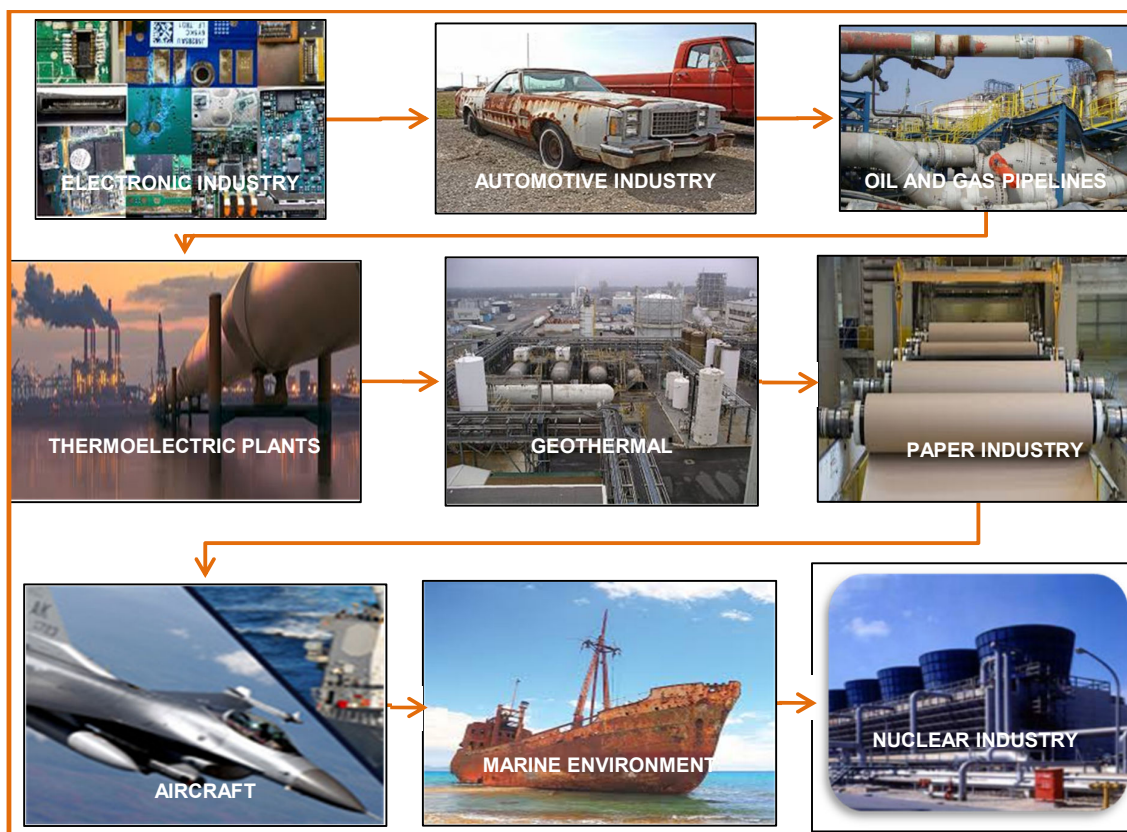


Figure 1.7 Corrosion in various industries

1.8.4 CORROSION IN THERMOELECTRIC PLANTS

Electricity is a key element in ensuring economic growth and social development of a country. generating plants burn fossil fuels such as coal, fuel oil and natural gas. These fuels containing as minor components sulfur compounds (S), nitrogen (N), vanadium (V). and chloride (Cl^-). These are corrosive chemicals attacking the metal infrastructure. Metal components of the turbine rotor disks and blades suffer corrosion by salts, alkalis and solid particles entrained in the vapour.

1.8.5 CORROSION IN GEOTHERMAL ENVIRONMENTS

Geothermal environments can lead to aggressive environments for almost any type of material such as metal, plastic, wood, fiberglass or concrete. Many engineering materials are used as components of the infrastructure. This entire infrastructure is a costly investment and therefore, failure or stoppage of one of them, means economic losses.. In the power plants, the observed corrosion affects components of the steam turbines, condensers and pipelines, and also the cooling towers and concrete structures inside and out- side the building that houses the plant.

1.8.6 CORROSION IN PAPER INDUSTRY

Corrosion occurs in the papermaking machinery, where the white water equipment is subjected to an aggressive environment. The metal surfaces are exposed to immersion in this water. The use of chlorine gas (Cl_2) and oxygen in the bleach plant and pulp bleaching, favours a very aggressive oxidant which promotes the formation of cracks

1.8.7 CORROSION IN SERVICE

Printed circuit boards (PCBs) can suffer from a variety of problems if the surface is contaminated with electrically conducting materials. When combined with moisture, contamination results in a lowering of resistance between tracks and pads that can lead to corrosion of metals. It can also result in the formation of metal filaments, which grow between pads or tracks on rigid or flexible circuits and between oppositely charged metal terminations of components or between the pins of connectors. The essential conditions required for this are a combination of ionic contamination, moisture and an applied voltage.

1.8.8 AIRCRAFT CORROSION

Corrosion damage to aircraft fuselages is an example of atmospheric corrosion. Airports located in marine environments deserve special attention. The risk and cost of corrosion damage are particularly high in aging aircraft. On some military aircraft types, corrosion maintenance hours are known to outstrip flight hours. Corrosion manifests in many different forms. Concentration cell corrosion is the most common type found on airplanes. It can quickly develop into pitting or exfoliation corrosion, depending on the alloy, form, and temper of the material being attacked.

1.8.9 THE MARINE AND OFF- SHORE INDUSTRY

Marine environment is probably the most aggressive common environment in which metals are expected to operate. The corrosion performance record is mixed. For decades unscrupulous owners have consistently cut purchase, operating and maintenance costs, taking advantage of the important international regulation of merchant shipping. Thus in contrast to the success of identical technology in the offshore marine industry, shipping has suffered from every possible aspect of corrosion and management failure.

1.8.10 CORROSION IN THE NUCLEAR INDUSTRY

Like most other power generating systems based on transforming heat into electrical power, the nuclear industry systems are complex and subjected to corrosive environments, high temperatures, and high pressures.

1.9 CORROSION CONTROL

Corrosion is a universal and all time problem. It causes deterioration in structures, machines, metallic equipment, vessels, pipelines etc. Once developed it grows very rapidly to capture all equipment in its vicinity under its influence. If due care and proper protection is not taken it destroys everything very rapidly. Recognizing the symptoms and mechanism of corrosion, it is very essential to find convenient solution to mitigate corrosion. There are five primary methods of corrosion control (**2000 ASM International**) shown in Figure 1.8

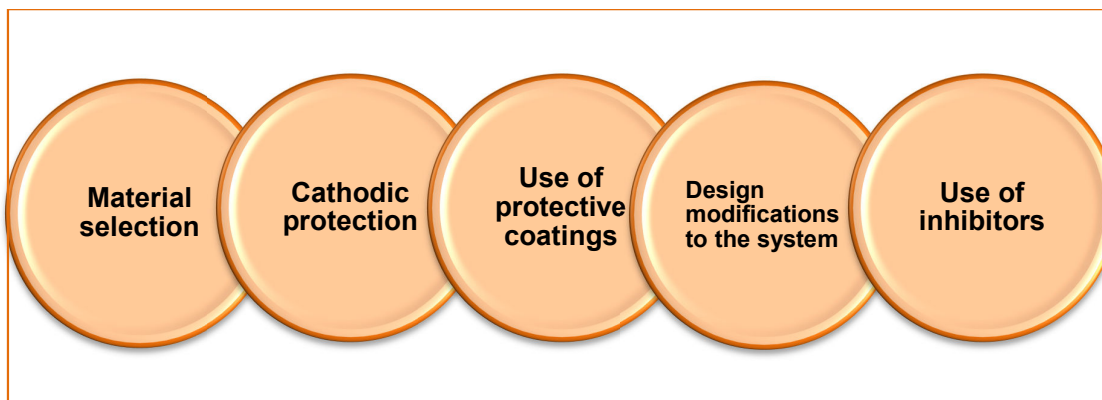


Figure 1.8 Corrosion control methods

1.9.1 Material Selection

Each metal and alloy has unique and inherent corrosion behaviour that can range from the high resistance of noble metals to the low corrosion resistance of active metals, Furthermore, the corrosion resistance of a metal strongly depends on the environment to which it is exposed, that is, the chemical composition, temperature, velocity, and so forth. The general relation between the rate of corrosion, the corrosivity of the environment, and the corrosion resistance of a material is:

$$\frac{\text{Corrosivity of environment}}{\text{corrosion resistance of metal}} \approx \text{Rate of corrosive attack}$$

For a given corrosion resistance of the material, as the corrosivity of the environment increases, the rate of corrosion increases. For a given corrosivity of the environment, as the corrosion resistance of the material increases, the rate of corrosion decreases. Consideration of corrosion resistance is often as important in the selection process as the mechanical properties of the alloy. A common solution to a corrosion problem is to substitute alloy with greater corrosion resistance for the alloy that has corroded.

1.9.2 Cathodic Protection

Cathodic protection suppresses the corrosion current that causes damage in a corrosion cell and forces the current to flow to the metal structure to be protected. Thus, the corrosion or metal dissolution is prevented. In practice, cathodic protection can be achieved by two application methods, which differ based on the source of the protective current. An impressed-current system uses a power source to force current from inert anodes to the structure to be protected. A sacrificial-anode system uses active metal anodes, for example, zinc or magnesium, which are connected to the structure to provide the cathodic-protection current.

1.9.3 Use of protective Coatings

Coatings for corrosion protection can be divided into two broad groups—metallic and non-metallic (organic and inorganic). With either type of coating the intent is the same, that is, to isolate the underlying metal from the corrosive media.

Metallic Coatings: The concept of applying a more noble metal coating on an active metal takes advantage of the greater corrosive resistance of the noble metal. An example of this application is tin-plated steel.

Organic coatings: The primary function of organic coatings in corrosion protection is to isolate the metal from the corrosive environment. Many organic coating formulations exist, as do a variety of application processes to choose from for a given product or service condition.

Inorganic coatings: include porcelain enamels, chemical-setting silicate cement linings, glass coatings and linings, and other corrosion resistant ceramics. Like organic coatings, inorganic coatings for corrosion applications serve as barrier coatings. Some ceramic coatings, such as carbides and silicides, are used for wear-resistant and heat resistant applications, respectively.

1.9.4 Design modifications to the system

The application of rational design principles can eliminate many corrosion problems and greatly reduce the time and cost associated with corrosion maintenance and repair. Corrosion often occurs in dead spaces or crevices where the corrosive medium becomes more corrosive. These areas can be eliminated or minimized in the design process. Where stress-corrosion cracking is possible, the components can be designed to operate at stress levels below the threshold stress for cracking.

1.9.5 Use of Corrosion Inhibitors

The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media (Trabanelli, 1991). Inhibitors may be used in acids, alkalis, cutting fluids, lubricating oils, and many other applications. A corrosion inhibitor is a compound that, when added to a liquid or gas, decreases the corrosion rates of a material, typically a metal or an alloy. Corrosion inhibitors are largely grouped under organic and inorganic products. They function by reducing the rate of either the anodic or cathodic reaction or a combination of both. The suitability of the inhibitor depends on the material of the system it has to act in, the nature of the substances it is added into, and their concentration.

1.9.6 Pickling bath inhibitors

One functional main area of corrosion inhibitor usage is pickling bath applications. Corrosion inhibitors effective in pickling baths are specifically named as “acid inhibitors”. Corrosive effect of acid on metal is kept under control and destruction of metal is inhibited with acid inhibitor action in pickling baths. Pickling baths are used for cleaning metal parts through removing stain, grease, impurity, oxide layer or any other unwanted contamination and corrosion products on material surface.

1.10 GREEN CORROSION INHIBITORS

A large number of synthetic compounds are reported in the literature as good corrosion inhibitors for metals in different corroding systems. Though many synthetic compounds showed good anticorrosive activity, most of them are costly. The use of such synthetic compounds can cause harm to humans and environment. For the safety of the environment as well as economic concerns, it is necessary to develop corrosion protection science, employing green inhibitors. In recent days, many alternative eco-friendly corrosion inhibitors have been studied and developed. Plants are great chemical factories that can supply us with the chemicals required to inhibit the corrosion process. Most of the naturally occurring substances are safe and can be extracted by simple and cheap procedures. Recent literature has many researches that have tested extracts of different plants and plant products as inhibitors for metals and alloys under different environments. The examples are numerous such as *Opuntia* (El-Etre, 2003), *Citrus paradisi* (Olusegun et al,2004), *Hibiscus Sabdariffa* (Oguzie,2008), Black pepper (Quraishi, et al,2009), *Adhatoda Vasica* (Matheswaran and Ramasamy,2010), Ginger (El-Sabbah et al,2015) and many others. Many of these naturally occurring substances have proved their ability to act as corrosion inhibitors for the corrosion of different metals and alloys in

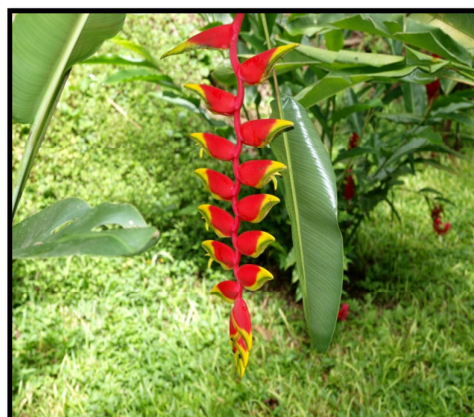
different aggressive media. Interestingly, extracts from natural products (**biomass**) contain several phytochemical constituents, including alkaloids, tannins, Flavonoids, Saponins, amino acids, ascorbic acid, phenolic acids, pigments resins and triterpenoids which possess electronic structures similar to those of conventional organic corrosion inhibitors (**Akalezi et al, 2012**). The study of biomass extracts as metal corrosion inhibitors is beneficial for several reasons as mentioned above. These active compounds may react with the metal surface forming film over the metal surface and inhibit metallic corrosion. In recent years, the research in corrosion is oriented towards the development of green corrosion inhibitors for sustainable environment.

As a contribution to the current interest to discover nontoxic, safe, environmentally friendly green corrosion inhibitor, the present work is carried out to study the inhibitive effect of *Heliconia rostrata* (**HR**) and *Canna indica* (**CI**) as corrosion inhibitor for **Mild steel and Aluminium** in acidic medium. The selected plant species were identified by Botanical Survey of India and the number (**BSI/SRC/5/23/2015/Tech/972&527**) is incorporated in the selected plant specimens.

1.10.1 PLANT DESCRIPTION: I

Heliconia rostrata is one of the most recognized and widely grown species. It is an herbaceous perennial with leathery, dark green leaves which are borne on long petioles arising directly from the ground (**Gilman and Meerow, 1999**). This plant has downward-facing flowers, the flowers thus providing a source of nectar to birds. *Heliconia rostrata* has a pendent inflorescence and the bracts are red with greenish yellow edges. It is a very popular species and one of the more common in cultivation. *Heliconia rostrata* is also known as banana garden tree (**Chavasco et al, 2014**). This unique plant is used as a specimen for tropical gardens.

Kingdom : Plantae – Plants
Subkingdom : Tracheobionta – Vascular plants
Superdivision : Spermatophyta – Seed plants
Division : Magnoliophyta – Flowering plants
Class : Liliopsida – Monocotyledons
Subclass : Zingiberidae
Order : Zingiberales
Family : Heliconiaceae – Heliconia family
Genus : Heliconia L. – heliconia
Species : *Heliconia rostrata* Ruiz & Pav.



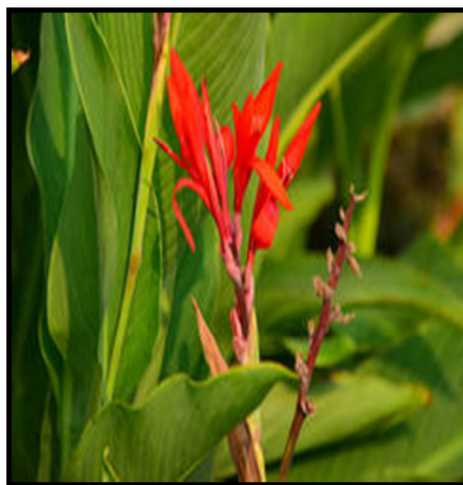
(BSI/SRC/5/23/2015/Tech/972)

Common name: False Bird-of-Paradise, Hanging Lobster Claw

1.10.2 PLANT DESCRIPTION:II

Canna indica is an erect perennial herb widely cultivated throughout India for its beautiful foliage and flowers. ***Canna indica L.*** is commonly known as Indian shot or Canna lily (**Bachheti et al, 2013**). Several varieties are common all over India and are grown in gardens. It is extensively used in constructed wetland for removal of organic pollutants, nitrogen, phosphorous and heavy metals (**DeBust, 1995**). The flowers are red or yellow and showy.

Kingdom : Plantae – Plants
Subkingdom : Tracheobionta – Vascular plants
Superdivision : Spermatophyta – Seed plants
Division : Magnoliophyta – Flowering plants
Class : Liliopsida – Monocotyledons
Subclass : Zingiberidae
Order : Zingiberales
Family : Cannaceae – Canna family
Genus : *Canna L.* – canna
Species : ***Canna indica L.***
Common name : Indian shot



(BSI/SRC/5/23/2015/Tech/527)

1.11 OBJECTIVES

- To find out the phytochemical constituents present in leaves and flowers of ***Heliconia rostrata* (HRL,HRF)** and ***Canna indica* (CIL,CIF)** using preliminary phytochemical screening tests, and characterised by HPTLC, GC-MS , UV and FT-IR.
- To evaluate the role acid extract of leaves and flowers of ***Heliconia rostrata* (HRL,HRF)** and ***Canna indica* (CIL,CIF)** as corrosion inhibitors for mild steel and aluminium AA1100 by electrochemical measurements and conventional mass loss method.
- To ascertain the adsorption of the phytochemical constituents on MS / AA1100 surface by surface analysis method.
- To analyze the surface morphology of mild steel and aluminium in the absence and presence of investigated inhibitors in HCl medium.
- To arrive at Quantum chemical parameters for the selected phytochemicals.