



INTRODUCTION

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Corrosion is the damage of material resulting from exposure and interaction with the environment. It is a major problem that must be confronted for safety, environment and economic reasons. Safety concerns are of utmost importance in every society and in all situations. Environmental concerns include corrosion caused pollution, depletion of resources such as those needed for replacement of the corroded structures and disposal of the corroded structures. To combine the technological progress with environmental safety is one of the key challenges of the millennium.

Corrosion problems have received a considerable amount of attention because of their attack on materials. Most people are familiar with corrosion in some form or another, particularly the rusting of an iron fence, the degradation of steel pilings or boats and boat fixtures. There is nothing mysterious about corrosion. The process metal goes through in changing is slightly complicated, but not especially complex.

Piping is major type of equipment subject to corrosion. This includes water pipes in the home where corrosion attacks mostly from the inside, as well as the underground water, gas, and oil pipelines that crisscross our land. Thus, it would appear safe to say that almost everyone is at least somewhat familiar with corrosion, which is defined in general terms as ***the degradation of a material, usually a metal, or its properties because of a reaction with its environment.***

This definition indicates that properties, as well as the materials themselves, may and do deteriorate. In some forms of corrosion, there is almost no visible weight change or degradation, yet properties change and the material may fail unexpectedly because of certain changes within the material. Such changes may defy ordinary visual examination or weight change determinations.

Corrosion can be best explained in the following way, Iron ore has a chemical composition of two iron atoms bonded with three oxygen atoms. As it is mined out of the ground, it's a brownish-red powder which is useless. But by refining, purifying, and smelting, iron is created, which is useful. It can be used as plain iron, or it can be processed further and combined with other elements to get different types of steel. When iron is left out in the rain, it rusts. If it rusts long and badly enough, the metal

disappears and a pile of brownish-red powder-rust or iron oxide is left behind, which has the same composition as iron ore. This is because iron atoms want to return to their normal state as iron ore, iron oxide, or rust which are all the same. That's the state in which iron is most comfortable and most stable. Left alone, it won't turn into anything else. And most metals used in manufactured products want to do the same—return to their natural state.

Electrochemical Reactions

Iron left out in the rain results in a specific kind of corrosion. It's called an electrochemical reaction, meaning there is an electrical change. Here's how that works:

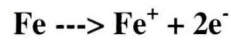
For two iron atoms to really interlock with three oxygen atoms and make iron oxide, they have to share some electrons, which releases a few electrons. Since electricity is just a flow of electrons, those free electrons become a little bit of electricity when the chemical change takes place.

Iron wants to corrode into iron oxide because that is its natural, most stable state. And all it needs for this is oxygen. Water is a supplier of oxygen, so iron rusts fastest when it gets wet. And that same scenario applies to aluminum and aluminum oxide. Those are the deep, dark secrets of corrosion as they apply to metals. Those are also the basics of an electrochemical reaction, which is known as galvanic corrosion. All galvanic corrosion is an electrical reaction. Not all electrochemical reactions, however, are galvanic corrosion.

Chemistry of Corrosion

As in all chemical reactions, *corrosion* reactions occur through an exchange of electrons. In electrochemical reactions, the electrons are produced by a chemical reaction in one area, the anode, travel through a metallic path and are consumed through a different chemical reaction in another area, the cathode. In some cases, such as the common dry cell battery, electrochemical reactions can be used to supply useful amounts of electrical current.

Metal loss at anodic sites in an electrochemical cell occurs when the metal atoms give up one or more electrons and move into the electrolyte as positively charged ions. More than one electron can be lost in the reaction as in the case for iron where the most common anodic reaction is:



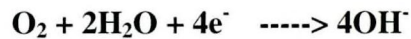
Where:

Fe = metallic iron

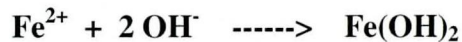
Fe^{2+} = ferrous ion that carries a double negative charge.

The electrons that are produced at anodic sites are consumed at cathodic sites.

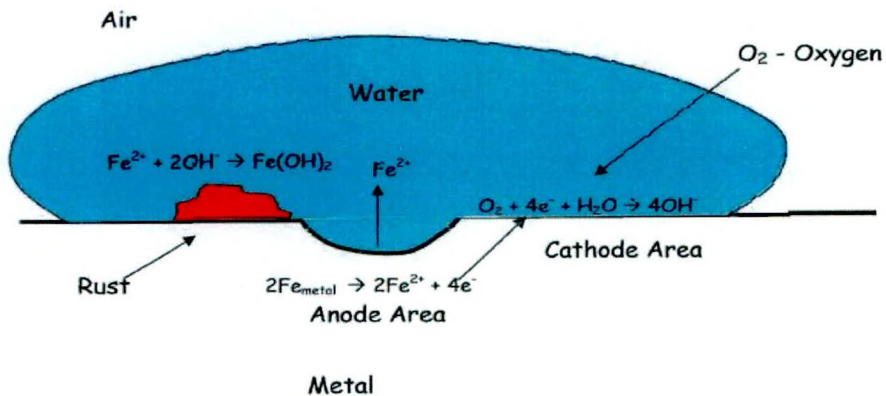
During Corrosion of Steel in contact with water the Cathodic Reactions usually is:



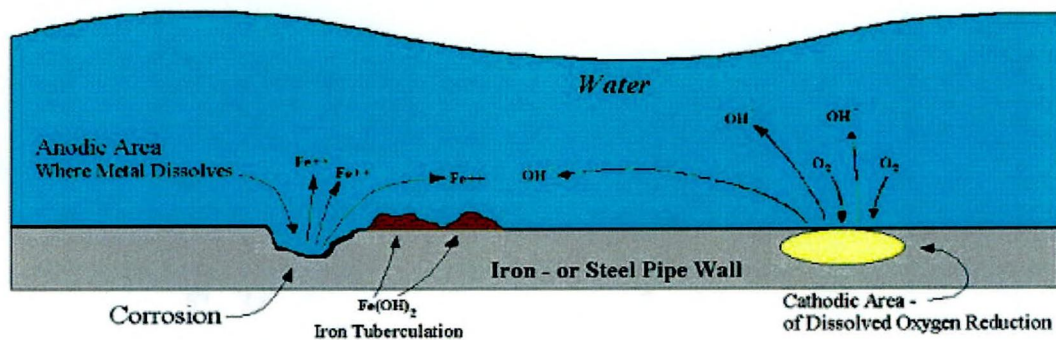
The final reaction in the chemistry of corrosion is the formation of Iron oxides:



$\text{Fe}(\text{OH})_2$ will then react to give Fe_2O_3 and Fe_3O_4 (rust)



The Corrosion Cell:



Every metal surface is covered with innumerable small anodes and cathodes as shown above. These sites usually develop from:

- (A) Surface irregularities from manufacturing;
- (B) Stresses from welding and forming; or
- (C) Metallic compositional differences of at the pipe surface.

Although corrosion is a complicated process, it can be most easily explained as an electrochemical reaction involving three steps as listed below:

- ❖ Metallic loss occurs from that part of the metal pipe called the anodic area (anode). In this case, iron (Fe^0) is lost to the water solution and becomes oxidized to Fe^{++} ion.
- ❖ As a result of the formation of Fe^{++} , two electrons are released to flow through the steel to the cathodic area (cathode).
- ❖ Oxygen (O_2) in the water solution moves to the cathode to form hydroxyl ions (OH^-) at the surface of the metal. In the absence of oxygen, hydrogen ion (H^+) participates in the reaction at the cathode instead of oxygen.
- ❖ If any step is prevented from occurring, then corrosion stops.

Factors affecting corrosion

Corrosion of bare conductors will happen at a rate that varies substantially, depending on the conditions.

Factors that affect corrosion

- Conductors
 - ◆ Nature of the material or alloy.
 - ◆ Surface condition/roughness.
 - ◆ Conductor configuration.
 - ◆ Conductor-conductor spacing

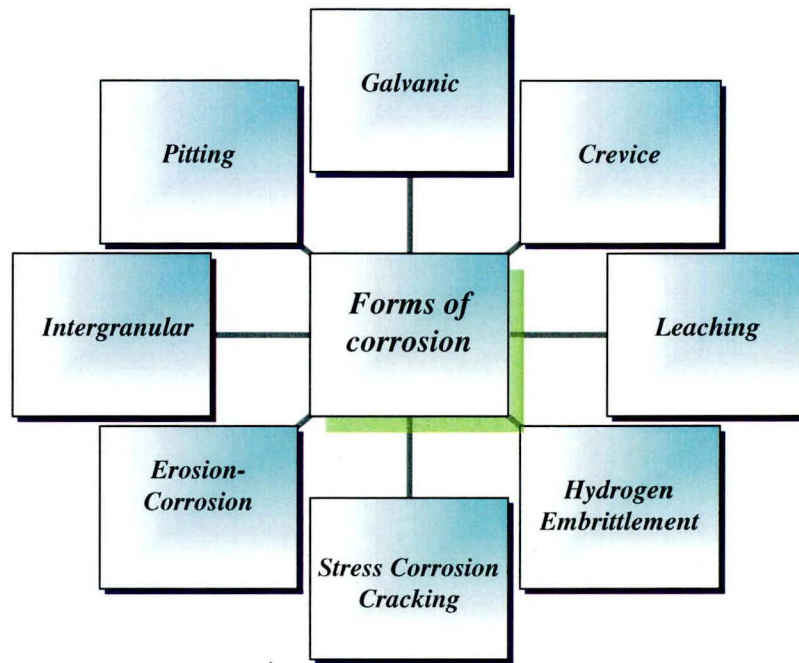
- Substrate
 - ◆ Composition
 - ◆ Moisture absorptivity
 - ◆ Structure
 - ◆ Nature of any reinforcement
- Environment
 - ◆ Temperature
 - ◆ Humidity
 - ◆ Corrosive elements (type; concentration)

Another factor that affects the rate of progress of corrosion is the nature of the 'corrosion product'. If the material produced by corrosion is insoluble and forms an impervious and tenacious layer, the corrosion reaction becomes self-limiting, as the corrosive medium can no longer diffuse through the corrosion product. A useful example of this is the oxidation of aluminium, which forms a thin protective layer of aluminium oxide; as 'anodised' aluminium, this is a good example of self-passivation.

If, on the other hand, the corrosion product is soluble or porous, corrosion will continue until the material is depleted, and no further reaction can occur. This is seen with the rusting of iron, where the oxide/hydroxide 'rust' has a different crystal structure from the iron, and creates only a porous, poorly adherent layer which does not protect against continued attack.

Corrosion Forms

The general types of Corrosion include uniform, electrochemical, galvanic, concentration cell, erosion, embrittlement, stress corrosion, filiform, corrosion fatigue, intergranular, fretting, impingement, dezincification, and chemical reaction. For convenience it can be categorized into eight different forms. Those eight forms are



GALVANIC:

Galvanic corrosion can result when a metal is in contact with another *dissimilar* metal. In order for galvanic attack to take place, there must be four things present. First, there must be an *anode*. This is the material which corrodes (e.g., the formation of rust takes place if the metal is iron). Second, there also must be another electrode called the *cathode*. Third, an *electrical connection* must exist between the *anode* and *cathode* through which electrons can flow. Finally there must be an *electrolyte* through which chemical ions can flow. This is generally an aqueous (water) solution yet even damp soil can make an excellent electrical conductor. The arrangement of these four specific components is always necessary for an electrochemical chemical cell to function. However in the case of galvanic corrosion, the anode and cathode are clearly dissimilar metals, copper and zinc, iron and brass, or mild steel and cast iron, for examples.

CREVICE:

Consider a sheet of stainless steel that has been immersed in the ocean for some time, years perhaps. It has had a bolt with a washer on it to hold it in place. It is noticed that corrosion has taken place underneath the washer. The reason for the corrosion is that a crevice had been created under the washer. Stagnate water, an electrolyte, accumulated in the crevice. An electrochemical, corrosion cell had been

produced and corrosion resulted. This cell is called a differential aeration, or oxygen concentration cell. It results because there is a difference in the composition of the electrolyte under the washer and that outside of the washer. There is a higher oxygen concentration in the solution that surrounds the washer than which is under the washer. Corrosion takes place at the lower oxygen concentration whenever there is an oxygen concentration cell. In the case of a crevice, or a pit, there are two oxygen concentrations in the electrochemical cell that has is such that corrosion takes place at the lower oxygen concentration.

PITTING:

Some materials are more subject to *pitting* than others. Imagine a stainless steel spoon lying on the beach near the ocean where it has been for several days. It has corroded. Little pits have formed. *Pitting corrosion* is a form of corrosion that is seen on almost a daily basis. This corrosion cell, i.e., the electrochemical mechanism of the corrosion, is very similar to that of crevice corrosion. There is a stagnant solution at the bottom of the pit, i.e., a lower oxygen concentration is outside of the pit than inside, resulting in another *oxygen concentration* cell. Corrosion takes place at the bottom of the pit. Generally, as the pit gets deeper, the solution at the bottom of the pit becomes more stagnant creating more driving force to promote corrosion. A pit is said to be *self-catalyzing*.

INTERGRANULAR:

Consider a stainless sheet that has been welded to another. Along each side of the weld there is corrosion attack called *weld decay*. This attack takes place by *intergranular corrosion*. That is, the attack is into the boundaries of the metallic grains that make up the metal. As the metal is heated during the weld, chromium is precipitated out of the heated grains and deposits in the grain boundary, an area that separates the grains and is burdened with impurities. Again, the components of a chemical corrosion cell are the result.

LEACHING:

Selective leaching corrosion is corrosion accelerated by the selective leaching of an alloying element out of the alloy matrix. The most common form of this type of corrosion is Dezincification, the selective leaching of zinc out of the brass matrix. Brass is made of zinc and copper. Zinc is considerably more corrosive than is copper. In certain cases, e.g., when brass is exposed to an aggressive environment, the zinc will corrode preferentially and *leaching* zinc from the brass alloy leaving behind a weak network of copper. It may look strong but it has been severely weakened.

HYDROGEN EMBRITTLEMENT:

In general, "embrittlement corrosion" is corrosion that causes a ductile material to fail without localized yielding or shearing. More specifically, hydrogen embrittlement assumes several different forms with a general similarity. This damage takes place at the cathode, an area that is normally thought to be safe from corrosion. Hydrogen ions are reduced to hydrogen molecules at the cathode. Those atoms usually pair-up to become hydrogen molecules. These molecules harmlessly bubble off as hydrogen gas. However, some metals are very susceptible to letting hydrogen atoms permeate into the grains. This is done while the hydrogen exists as an atom, before it becomes a molecule. Once inside the metal the hydrogen atoms can do all sorts of mischief that result in *hydrogen damage*.

STRESS CORROSION CRACKING:

Stress corrosion cracking (SCC) is a form of localized damage that refers to cracking under the combined influence of tensile stress and a corrosive environment. The macroscopic fracture appearance tends to be of the "brittle" type, even if the metal/alloy is of a mechanically ductile variety. Multiple variables affect stress corrosion cracking phenomena, such as stress level, alloy composition, microstructure, concentration of corrosive species, surface finish, micro-environmental surface effects, temperature, electrochemical potential, etc. Further complications are initiation and propagation phases, and the observation that in some cases cracks initiate at the base of corrosion pits.

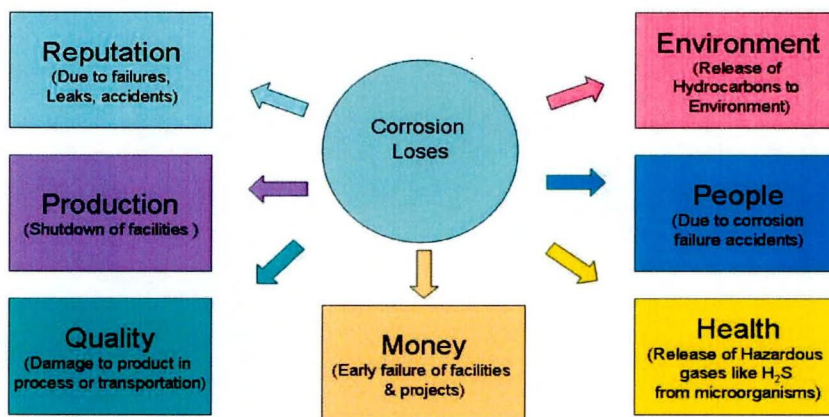
EROSION CORROSION:

Erosion-corrosion arises from a combination of chemical attack and the physical abrasion as a consequence of the fluid motion. Virtually all alloy or metals are susceptible to some type of erosion-corrosion as this type of corrosion is very dependent on the fluid. Materials that rely on a passive layer are especially sensitive to erosion-corrosion. Once the passive layer has been removed, the bare metal surface is exposed to the corrosive material. If the passive layer cannot be regenerated quickly enough, significant damage can be seen. Fluids that contain suspended solids are often times responsible for erosion-corrosion.

Corrosion, why Bother?

In many countries still corrosion loses are more and more. Especially this is having more impact on the developing countries. A considerable percentage of Gross domestic products is going as corrosion loses. Many projects are facing corrosion failure before their life period, which will put the need for some more money and hamper to do other projects.

Corrosion Loses



In a modern business environment, successful enterprises cannot tolerate major corrosion failures, especially those involving personal injuries, fatalities, unscheduled shutdowns and environmental contamination. For this reason considerable efforts are generally expended in corrosion control at the design stage and in the operational phase.

Corrosion can lead to failures in plant infrastructure and machines which are usually costly to repair, costly in terms of lost or contaminated product, in terms of environmental damage, and possibly costly in terms of human safety. Decisions regarding the future integrity of a structure or its components depend upon an accurate assessment of the conditions affecting its corrosion and rate of deterioration. With this information an informed decision can be made as to the type, cost and urgency of possible remedial measures.

Strategic Impact and Cost of Corrosion Damage

It is the belief of many that corrosion is an inevitable foe that should be accepted as an inevitable process. Actually, something can and should be done to prolong the life of metallic structures and components exposed to the environments. As products and manufacturing processes have become more complex and the penalties of failures from corrosion, including safety hazards and interruptions in plant operations, have become more costly and more specifically recognized, the attention that is being given to the control and prevention of corrosion has increased.

By estimating the percentage of U.S. gross national product (GNP) for the sectors for which corrosion costs were determined and by extrapolating the figures to the entire U.S. economy, a total cost of corrosion of **276 billion dollars** was estimated. This value shows that the impact of corrosion is approximately **3.1 percent** of United States' GNP. The indirect cost of corrosion was conservatively estimated to be equal to the direct cost, giving a total direct plus indirect cost of **552 billion dollars or 6% of the GNP**.

Corrosion costs studies of various forms and importance have since then been undertaken by several countries including, the **United States, United Kingdom, Japan, Australia, Kuwait, Germany, Finland, Sweden, India, and China**. A common finding of these studies has been that the annual corrosion costs range from approximately **1 to 5 percent of the** Gross national products of each nation. India's corrosion loss has been estimated as Rs. 1.52 lakh crore annually which could be reduced to Rs.80, 000 crore with proper management (NACE, International India sector, Mumbai, 2007).

Protection of Metal from Corrosion

There are four basic methods to Protect Metal from Corrosion:

1. Materials resistant to Corrosion
2. Protective coatings
3. Cathodic protection
4. Corrosion Inhibitors- Modify the operating environment.

In most cases, effective corrosion control is obtained by combining two or more of these methods.

Corrosion control should be considered at the design stage of a given facility or system.

Materials resistant to Corrosion

The methods selected must be appropriate for the materials used, for the configurations, and for the types and forms of corrosion which must be controlled.

There are no materials that are immune to corrosion in all environments. Materials must be matched to the environment that they will encounter in service.

Protective coatings

Protective coatings are the most widely used corrosion control technique. Essentially, protective coatings protect metal from corrosion by separating the surfaces that are susceptible to corrosion from the factors in the environment which cause corrosion to occur.

Cathodic protection

They protect metal from corrosion by interfering with the natural action of the electrochemical cells that are responsible for corrosion. Cathodic protection can be effectively applied to control corrosion of surfaces that are immersed in water or exposed to soil.

Corrosion Inhibitor

It *protect* metal from corrosion by one or more of these mechanisms:

1. By adsorption as a thin film on the surface of a corroding material.
2. By inducing formation of a thick corrosion product.
3. By forming a passive film on the metal surface
4. By changing characteristics of the environment either by producing protective precipitates or by removing or inactivating an aggressive constituent.

Corrosion prevention by inhibitors

A corrosion inhibitor is a substance that when added in small amounts to a corrosive medium, reduces its corrosivity. Corrosion inhibitors function by interfering with either the anodic or cathodic reactions or both. The use of inhibitors is one of the most practical methods for protection against corrosion. Corrosion inhibitors are chemical compounds added to the corrosive medium to reduce the rate of its attack on the metal or alloy. The chemicals which can act as corrosion inhibitors may be inorganic or organic. The inorganic compounds such as chromates inhibit the corrosion process via formation of passive oxide film on the metal surface and thus prevent the corrosive medium to attack the base metal. On the other hand, the organic compounds adsorb on the metal surface forming a barrier between the metal and the corrosive environment. Some structural features of the organic compounds help them to do so. These include the presence of oxygen, nitrogen or sulfur atoms as well as presence of double bonds. The lone pair electrons of the mentioned atoms facilitate the adsorption process.

Choice of chemical compounds for inhibition of corrosion

The study of corrosion is of high practical and technological interest. Acids find applications in industrial acid cleaning, acid pickling, acid descaling and oil well acidizing. Inhibitors are commonly employed in these environments to minimize the base metal corrosion by the acids. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, temperature, velocity, presence of dissolved solids and the type of metallic materials involved. The important prerequisites for a compound to be an efficient inhibitor are:

- i) It should form a defect free, compact barrier film.
- ii) It should chemisorb on to the metal surface.
- iii) It should be polymeric /polymerise in sites on the metal and
- iv) The barrier thus formed should increase the inner layer thickness.

Most of the well-known inhibitors used for inhibition of iron in acidic medium are organic compounds containing nitrogen, sulphur and /or oxygen atoms. It has been observed that most of the organic inhibitors act by adsorption on the metal surface. This phenomenon is influenced by the nature and surface charge of metal, by the type of aggressive electrolyte and by the chemical structure of inhibitors.

The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is an accepted practice. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency. But, unfortunately most of these compounds are not only expensive but also toxic to living beings. Upon looking around one finds very rich resources for substances with wide varieties of chemical structures. The plant is the great chemical factory which 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 full of researches which test different extracts for corrosion inhibition applications. The examples are numerous such as henna, olive, shirsh zallouh, vanillin, natural honey, khella, onion, ficus, opuntia, many oils extracted from different parts of different plants and many others (Prof Ali El-Etre 2008). Many of these naturally occurring substances proved their ability to act as corrosion inhibitors for the corrosion of different metals and alloys in different aggressive media.

Due to the biodegradability, the trend of using these less toxic natural compounds are going on and the present work is a commencement made to study the inhibition potential of agricultural waste of coconut (*leaf sheath and staminate flower*) for mild steel in hydrochloric acid medium.



Staminate flower



leaf sheath

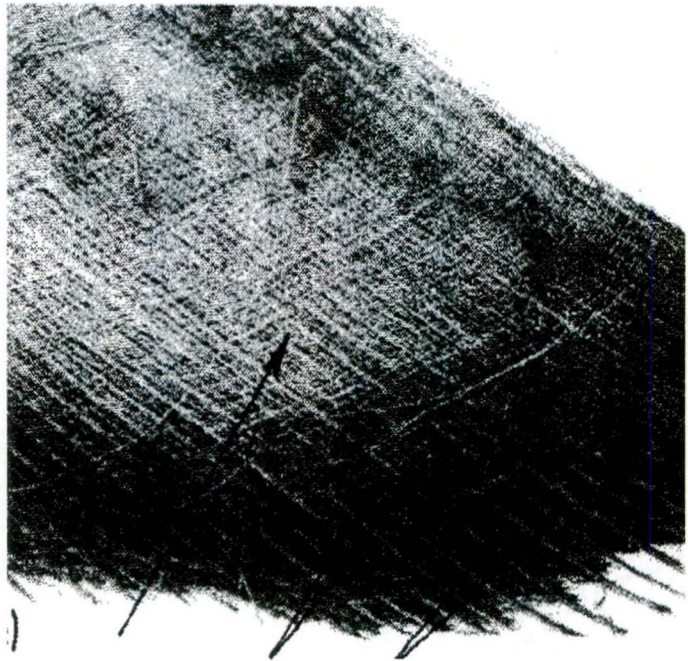
COCOS NUCIFERA

The coconut palm (*Cocos nucifera*) is found throughout the tropics, where it is interwoven into the lives of the local people. It is particularly important in the low islands of the Pacific where, in the absence of land-based natural resources, it provides almost all the necessities of life—food, drink, oil, medicine, fiber, timber, thatch, mats, fuel, and domestic utensils. For good reason, it has been called the “tree of heaven” and “tree of life.” Today it remains an important economic and subsistence crop in many small Pacific island states. It is non-invasive, and people have been largely responsible for its spread, particularly inland from its natural habitat. It thrives under warm and humid conditions but will tolerate short periods of temperatures below 21°C (70°F). Its crown of feather-like fronds and bunches of large fruits carried atop long slender stems makes it easily recognizable.

Leaf sheath

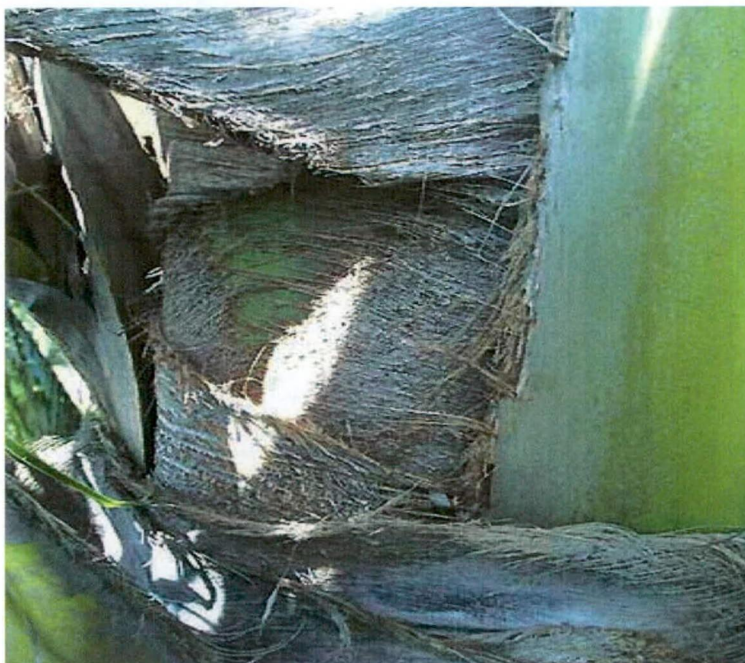
The coconut tree is the most common palm of the tropics. It has a tall, unbranched, light grey coloured trunk, ringed at intervals by leaf scars. From the swollen base, adventitious roots arise, which are strong enough to anchor the palm even during hurricanes and storms. This tree can grow 20-30m high and live 80-100years. The stem has only one terminal growing point. During the initial years of growth the stem gradually increases in thickness and then this diameter is maintained until about 10m when there is a gradual decrease in the diameter. Early rapid stem growth occurs until fruiting then the rate of stem growth declines. Stem strength and flexibility is due to the *fibrous sheath* surrounding the numerous vascular bundles in the stem periphery and a large number of smaller bundle fibers in the stem vascular bundles.

The major chemical constituents of these fibers are found to be (K.G. Sathyanarayana et al., 1982)



Cellulose (39 to 46%) and

Lignin (13 to 25%)



Staminate Flowers

The coconut palm is monoecious i.e. the *staminate* and pistillate (male and female) flowers are produced on the same inflorescence (spadix). The flowers are pale and yellow coloured. The first inflorescence may be all male, later inflorescence will also produce female flowers. Each branch (rachilla) bears one or more female flowers near the base and numerous male flowers above. There are generally up to about 50 female flowers per bunch and possibly thousands of small male flowers.

The staminate flowers are small (3mm), non-symmetrical with small sepals and three longer petals and six stamens. Pollinating insects are attracted by a small drop of nectar in each newly opened male flower.

Each inflorescence bears only a few female flowers because most fall off in the first two months. So each inflorescence bears 3 to 6 fruits to maturity with a pair of male flowers at the base of the branches. Most of the male flowers are borne singly or in pairs towards the branch tips. The male flowers mature and wither before the female flowers become receptive, a sequence called protandry. So the male flowers in the same inflorescence cannot pollinate the female flowers. This arrangement ensures the cross pollination between the different palm trees.



The coconut flower extract was found to be containing the following: (Vijayam et al., 2004)



1. **Steroids:** a) Progesterone b) Hydroxy progesterone caproate
2. **Cations:** a) Sodium b) Ammonium c) Magnesium d) Calcium e) Iron f) Zinc
3. **Anions:** a) Chloride b) Phosphate c) Sulphate
4. **Acetate:** a) Lauric Acid b) Capric Acid c) Vitamin B6

Due to the biodegradability and eco-friendliness, the trend of using such less/non- toxic natural compounds is increasing everyday and in this direction an evaluation of 1M HCl extracts of leaf sheath and staminate flower of *Cocos nucifera* have been made in the present work.

OBJECTIVE

- ❖ To select eco friendly, cost effective, naturally occurring plant materials as corrosion inhibitors for mild steel in HCl.
- ❖ Utilization of the naturally occurring plant extracts such as leaf sheath (LS) and staminate flower (SF) of *Cocos nucifera* as inhibitors for the present study.
- ❖ To evaluate the corrosion studies of mild steel in 1M HCl at room temperature and higher temperature using the classical weight loss method.
- ❖ To determine the corrosion rates for these extracts on various concentrations at different time intervals.
- ❖ To calculate the activation energy and thermodynamic parameter using results of temperature study.
- ❖ To find out the shelf life of the plant extracts.
- ❖ To assess mode of action of the inhibitor under study- cathodic, anodic or mixed type, by conducting electrochemical studies, linear polarization resistance, impedance technique and Tafel polarization.
- ❖ To evolve a suitable mechanism for the adsorption process.
- ❖ To correlate the results obtained by weight loss and electrochemical techniques.
- ❖ To enlighten the kinetic and mechanistic aspects of the plant materials under study in the inhibitive action.
- ❖ To analyse the surface of MS in the presence of investigated inhibitors using optical electron microscope.
- ❖ To confirm the adsorbed products on the MS by FTIR technique.