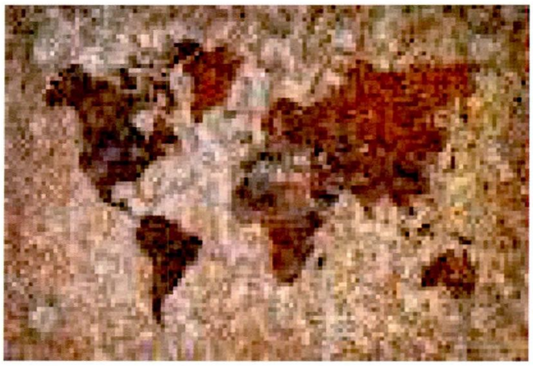


INTRODUCTION

CHAPTER - I

INTRODUCTION

Metallic materials are still the most widely used group of materials particularly in both mechanical engineering and the transportation industry. In addition, metals are commonly used in electronics and increasingly also in the construction industry. However the usefulness of metals and alloys is constrained by one common problem known as corrosion. Corrosion is a naturally occurring phenomenon commonly defined as deterioration of metal surfaces caused by the reaction with the surrounding environmental conditions. Corrosion can cause disastrous damage to metal and alloy structures causing economic consequences in terms of repair, replacement, product losses, safety and environmental pollution. Due to these harmful effects, corrosion is an undesirable phenomenon that ought to be prevented.

Corrosion is the natural process and is a result of the inherent tendency of metals to revert to their more stable compounds, usually oxides. Most metals are found in nature in the form of various chemical compounds called ores. In the refining process, energy is added to the ore, to produce the metal. It is this same energy that provides the driving force to cause the metal to revert back to the more stable compounds. (Figure - 1)

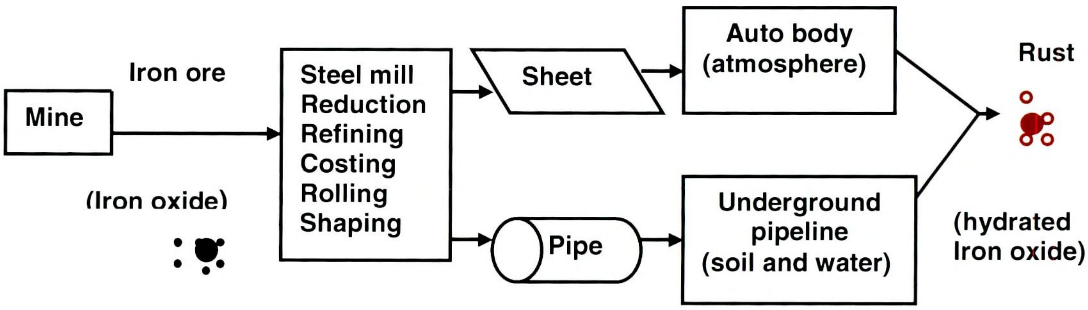


Figure - 1 Schematic representation of corrosion process

1.1 IMPORTANCE OF CORROSION STUDIES

It is necessary to devote more attention to metallic corrosion nowadays than earlier due to:

- A more corrosive environment due to the increasing pollution of air and water.
- An increased use of metals within all fields of technology.
- The use for special applications as in the atomic energy field of rare and expensive metals.

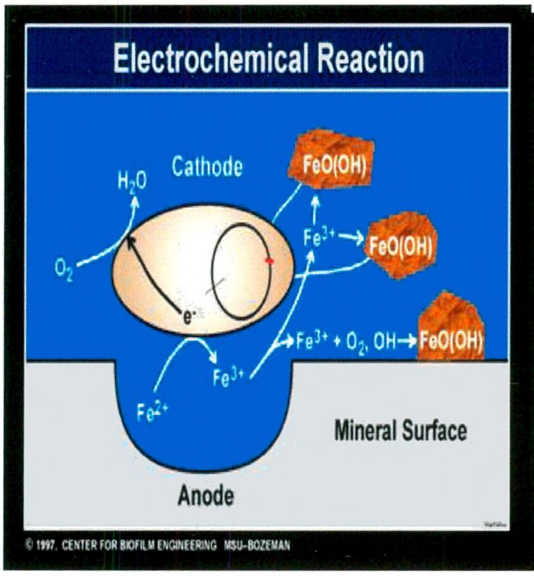
1.2 CLASSIFICATION OF CORROSION

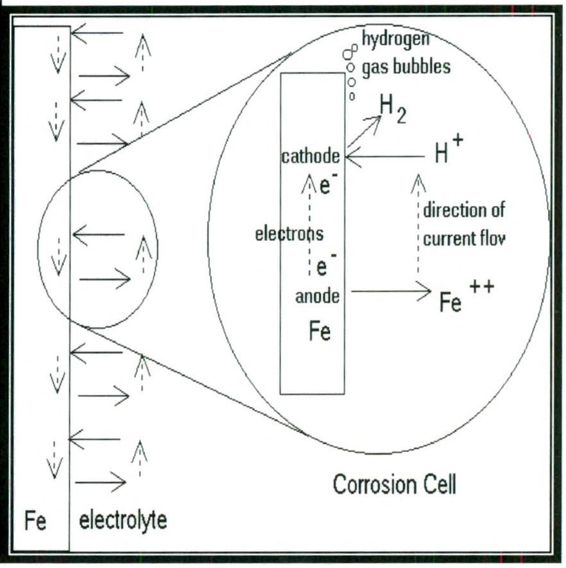
Corrosion occurs in two ways via dry corrosion and wet corrosion.

- The chemical attack or dry corrosion occurs under dry conditions, such as high temperatures in gaseous environments, molten salts and liquid metals. Dry corrosion process is a direct reaction between a metal and the corrosive environment.
- Wet corrosion is an electrochemical process. The electrochemical corrosion results from reaction between a metal surface and an ion-conducting environment. This process can occur if the metal contact with an electrolyte for transport of electric current. Most cases of electrochemical corrosion proceed in aqueous media such as natural water, atmospheric moisture, rain and wet soil.

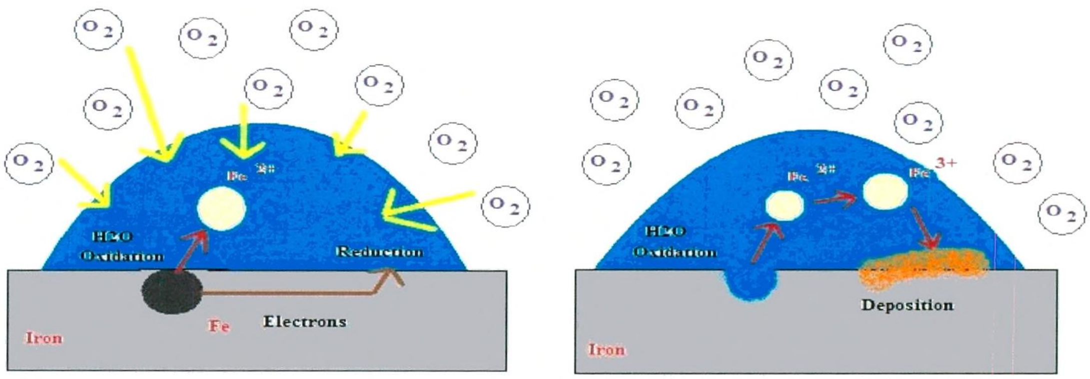
1.3 ELECTROCHEMICAL THEORY OF CORROSION

In iron or steel corrosion, electrochemical reactions may take place as follows:





(a) www.biofilm.montana.edu **(b)** www.txins1.com



(c) http://chemwiki.ucdavis.edu

Figure - 2 Schematic representation of electrochemical corrosion process

At the anodic areas

$Fe \rightarrow Fe^{2+} + 2e^-$ (1.1)

When iron corrodes, the rate is usually controlled by the cathodic reaction. There are several different cathodic reactions that are frequently encountered in metallic corrosion (Figure - 2a and b). The most common are:

Hydrogen evolution	$2H^+ + 2e^- \rightarrow H_2$	(1.2)
Oxygen reduction (acid solution)	$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$	(1.3)
Oxygen reduction (neutral or basic solution)	$O_2 + 4\ H_2O + 4e^- \rightarrow 4OH^-$	(1.4)
Metal ion reduction	$M^{3+} + e^- \rightarrow M^{2+}$	(1.5)
Metal deposition	$M^+ + e^- \rightarrow M$	(1.6)

Hydrogen evolution is a common cathodic reaction since acidic media are frequently encountered (Figure - 2c). Oxygen reduction is very common, since any aqueous solution in contact with air is capable of reducing this reaction. Metal ion reduction and metal deposition are less common. All the above reactions are consuming electrons.

Since the anodic and cathodic reactions occurring during corrosion are mutually dependent, it is possible to reduce corrosion by reducing the rates of either reaction. So, if the surface of the metal is coated with paint or other conducting film, the rates of both anodic and cathodic reactions will be greatly reduced and corrosion will be retarded. The corrosion behaviour of metals, and thus the corrosion-inhibiting processes as well, depend greatly on the anion composition of the electrolyte.

1.4 FORMS OF CORROSION

The forms of corrosion can be grouped into localized corrosion, mechanical corrosion and general corrosion.

Localized corrosion is the accelerated attack of a passive metal in a corrosive environment at discrete sites where the otherwise protective passive film has broken down. Common forms of localized corrosion include pitting on a boldly exposed surface, corrosion in a creviced region shielded from the bulk environment, inter-granular corrosion of an alloy with a susceptible grain boundary region, exfoliation corrosion, filiform corrosion, stray current corrosion that occurs when sources of direct current are connected to gate structures.

Mechanical corrosion includes erosion, fretting and cavitation corrosion. In the general corrosion, the thickness of the plate varies uniformly and in localized corrosion, the thickness varies non-uniformly. 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 shown in Figure - 3.

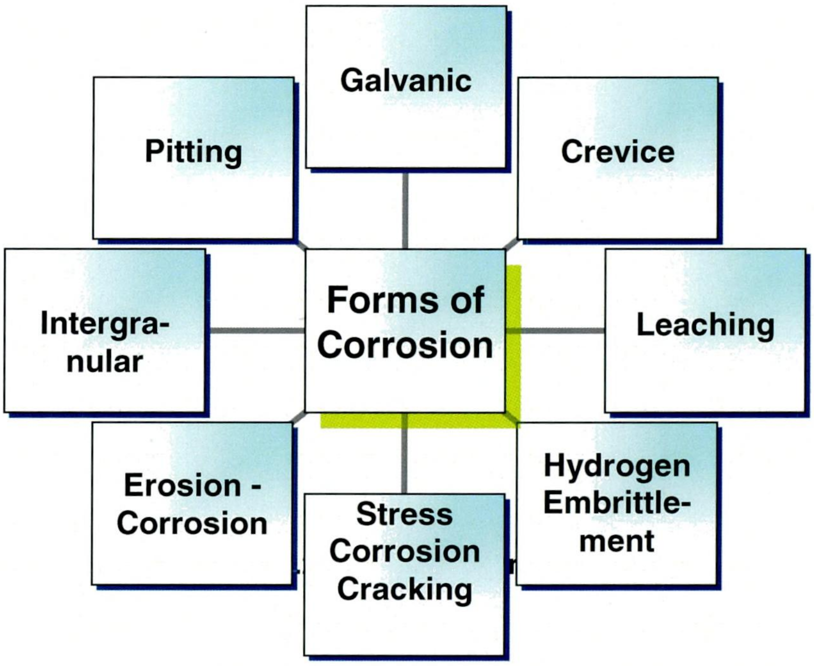


Figure - 3 Forms of corrosion

1.4.1 Factors affecting corrosion

Factors affecting corrosion can be broadly classified into two groups according to the nature of metal and the nature of the environment (Figure - 4).

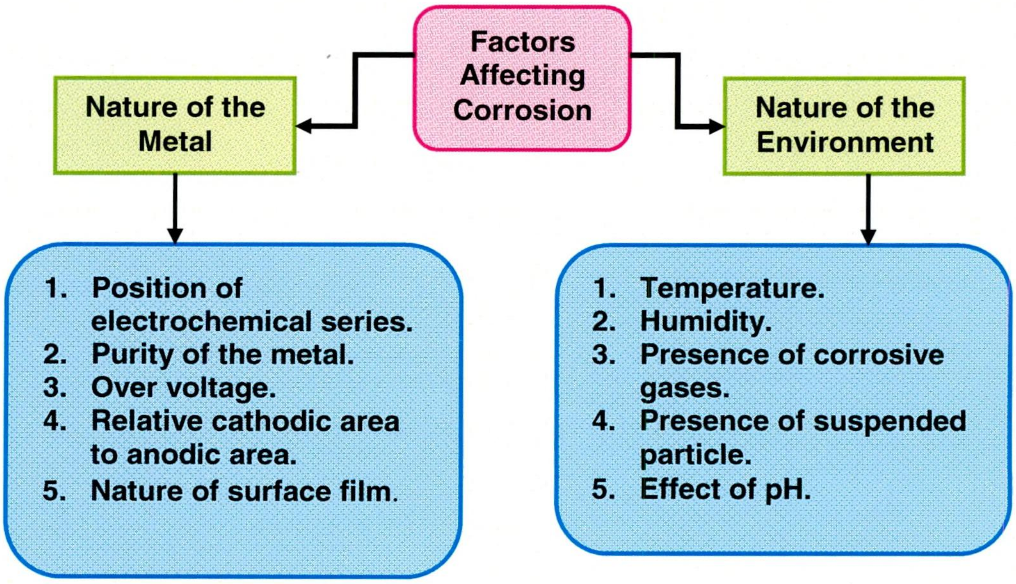


Figure - 4 Factors affecting corrosion

1.4.2 Consequences of corrosion

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than simple loss of mass of a metal. Failures of various kinds and the need for expensive replacement may occur even though the amount of metal destroyed is quite small. Some of the disastrous effects of corrosion can be summarized below:

- Hazards or injuries to people arising from structural failure or breakdown.
- Reduced value of goods due to deterioration of appearance.
- Contamination of fluids in vessels and pipes.
- Loss of technically important surface properties of a metallic component.
- Perforation of vessel and pipes allowing escape of their contents and possible harm to the surroundings.
- Loss of time availability profile – making industrial equipment.
- Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown.
- Added complexity and expensive of equipment.
- Mechanical damage to valves, pumps, etc.

Virtually all corrosion reactions are electrochemical in nature consisting of anodic and cathodic sites. At the anodic site, dissolution of the metal takes effect leading to the release of electrons whereas at the cathodic site, the electrons react with some reducible component of the electrolyte and they are removed from the metal.

1.5 CORROSION IN INDUSTRIES

International Corrosion Awareness Day builds upon Earth Day, April 22, as it highlights the damage to the environment, and impact on people, and waste of resources, such as water, resulting from corrosion of pipelines, oil and gas, chemical processing, water and wastewater systems, particularly industrial structures, treatment facilities, and process industry equipment. Corrosion is a primary cause of recent bridge collapses, deterioration of roads, piers and transportation equipment such as automobiles and aircraft (Figure - 5). In addition to causing severe damage and threat to public safety, corrosion disrupts operations and requires extensive repair and replacement of failed assets. Corrosion is one of the key limiting factors of the world's critical infrastructure.

1.5.1 Strategic Impact and Cost of Corrosion Damage

"The cost of corrosion works out to much higher than any of the calamities the nation has faced over the years." – NACE International India.

The economic consequences of corrosion affect technology. A great deal of the development of new technology is held back by corrosion problems because materials are required to withstand, in many cases simultaneously, higher temperatures, higher pressures, and more highly corrosive environments. Corrosion problems that are less

Figure - 5 Corrosion in various industries

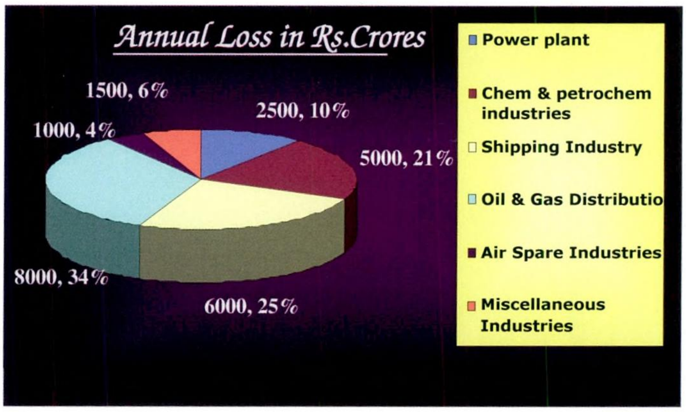


Figure - 6 Illustration of economic impact of corrosion in various industries

difficult to solve affect solar energy systems, which require alloys to withstand hot circulating heat transfer fluids for long periods of time, and geothermal systems, which require materials to withstand highly concentrated solutions of corrosive salts at high temperatures and pressures. Another example, the drilling for oil in the sea and on land, involves overcoming such corrosion problems namely sulfide stress corrosion, microbiological corrosion, and the vast array of difficulties involved in working in the highly corrosive marine environment. **In many of these instances, corrosion is a limiting factor preventing the development of economically or even technologically workable systems. Annual loss in rupees crore occurred in various industries in India is depicted in Figure - 6.** The overall loss due to corrosion alone amount to at least 2 to 4 % GNP, 25% of this could be avoided by using appropriate corrosion control technique.

The common finding of corrosion studies undertaken by several countries is that the annual corrosion costs ranged from approximately 1 to 5 per cent of the GDP of each nation. India's corrosion loss has been estimated as Rs. 2 lakh crore annually corrosion management committee chairman Confederation of Indian Industry (CII) and Director Indira Gandhi Centre for Atomic Research, Baldev Raj, communicated that India loses a staggering figure of over Rs.2 lakh crore per year due to corrosion infrastructure, industrial equipment and other vital installations.

1.6 ECONOMIC CONSEQUENCES OF CORROSION

Like other natural hazards such as earthquakes, corrosion can cause dangerous and expensive damage to everything from cars, home appliances,

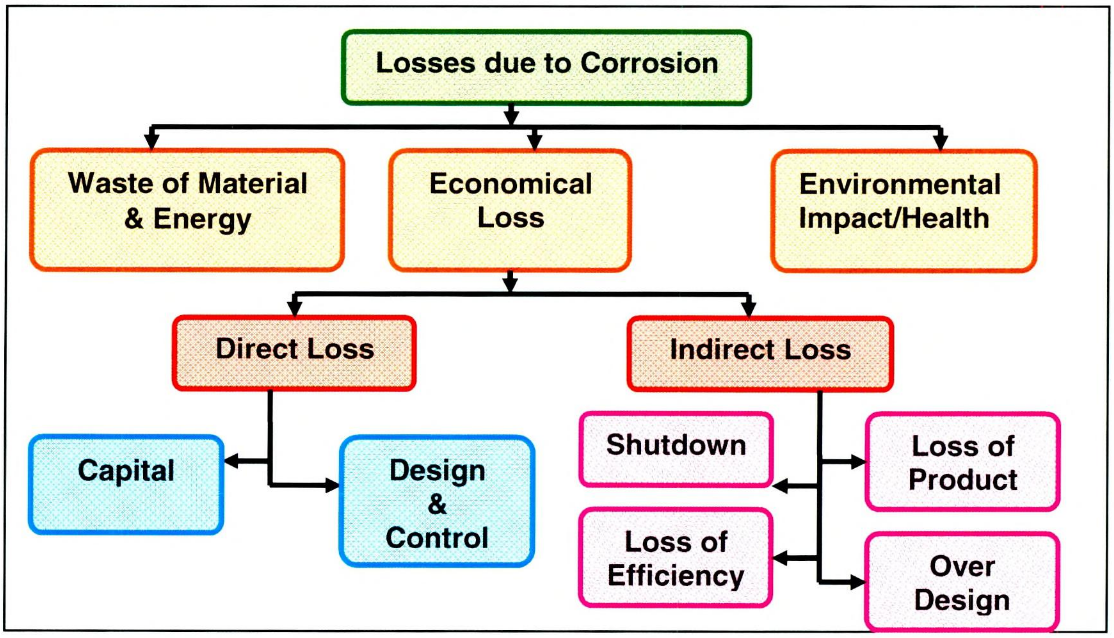


Figure - 7 Losses due to corrosion

bridges…etc. Therefore, corrosion is causing a heavy burden to economy all over the world. The corrosion costs should be drawn between the direct and indirect costs (Figure - 7).

1.7 CORROSION CONTROL METHODS

Effective corrosion control may contribute towards the limitation of economic, social and personnel loss. All these consequences increased the pressure of society to control the corrosion attack and to safe the environment. The corrosion control methods that were considered include (Figure - 8):

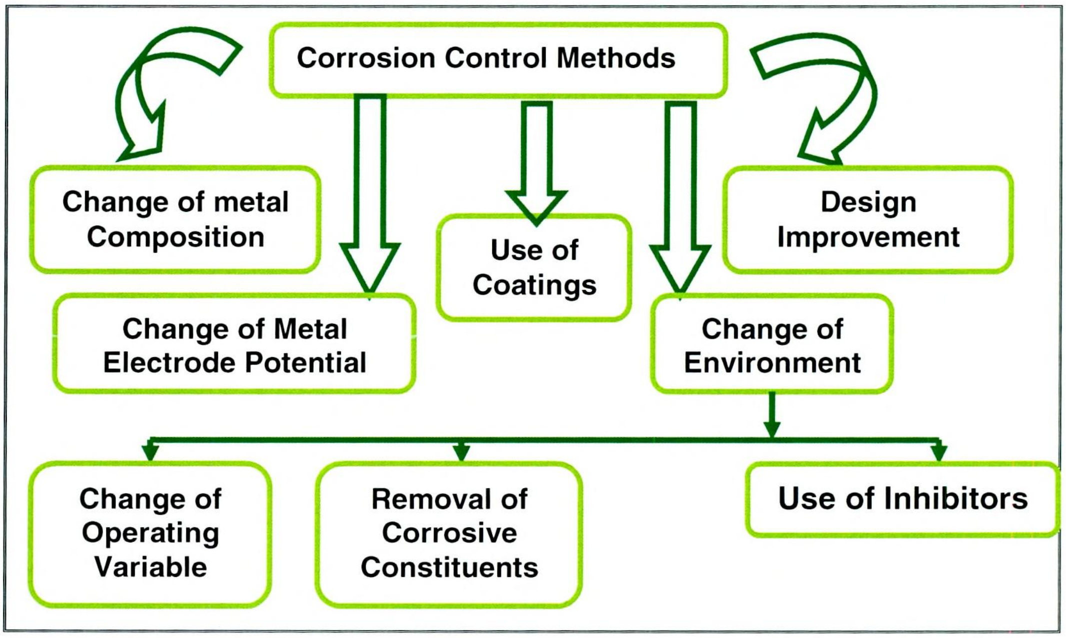


Figure - 8 Corrosion Control Methods

1.7.1 An overview of inhibitors - Historical perspectives

It is stated by **Hackerman, (1989)** that "all corrosion reduction processes are inhibitors". However, by the common use, the term inhibitors is taken to mean retardation of the metal oxidation rate ($M \rightarrow M^{+n} + ne^{-}$) by the addition of chemicals to the system *via* the fluid phase. Corrosion inhibitor must be felt on the metal side of the metal/fluid interface (i.e., the inhibitor should be transported to the interface of the metal or alloys surface to perform inhibition) **(Talbot and Talbot, 1998).** Therefore, metal and alloy surfaces are very important to be well processed and well finished. This is to decrease the surfaces' defects as possible as it can.

Classification of Inhibitor

The range of inhibitors is wide and a way to classify (Figure - 9) them is to consider their mechanism action and their composition **(Fontana, 1988; Shreir *et al.*, 1994):**

* The largest class comprises the adsorption-type inhibitors (or interface inhibitors).They are usually organic compounds and are adsorbed on the surface of the metal. In this way, the metal dissolution and the reduction reaction are suppressed. Inhibitors act on both the anodic and cathodic processes, but usually with an unequal effect.
* Each molecule adsorbed on the metal surface may or may not desorb later on. This explains why the degree of electrode surface coverage (θ) will never be 100%, neither will the inhibitor efficiency. This effect is shown with the Langmuir's isotherm as the concentration of inhibitor increases, the surface coverage increases but will never reach 100%.
* Hydrogen-evolution poisons will act to retard the evolution of the hydrogen. These compounds (eg., arsenic and antimony ions) are very efficient in acid solutions but are not efficient if the cathodic reactions are controlled by other processes such as oxygen reduction.

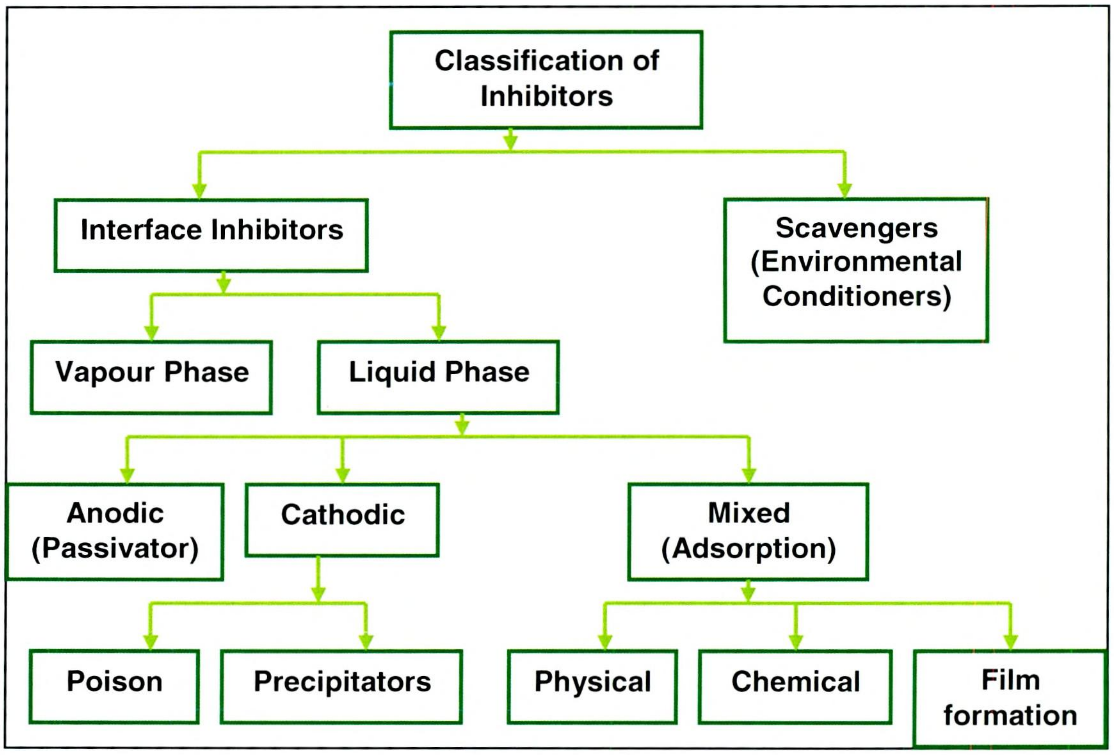


Figure - 9 Classifications of Inhibitors (Uhlig and Revie, 1985)

* Oxidizing and non-oxidizing agents are characterized by their ability to passivate the metal. While the oxidizing agents do not need any oxygen presence, the non-oxidizing ones require the presence of oxygen in the solution to maintain the passive oxide film.

* The scavengers' way of action is the removal of corrosive reagents such as O_2 from solution. These inhibitors are very efficient in the case of an oxygen reduction controlled reaction, but are ineffective in strong acid solution.

  All the inhibitors belonging to the previous sorting as well can be classified as either 'safe' or 'dangerous' inhibitors. To be efficient, an inhibitor has to be present in a concentration greater than a certain limit. If the concentration used is below that limit, the inhibitor may:
* Still allow a uniform corrosion at a rate smaller than that obtained in an inhibited system. This is the case for the 'safe' inhibitors.
* Or lead to enhanced localized attack (eg., pitting) and make the situation worse, this is the case of the 'dangerous' type.

Based on their mode of action inhibitor are classified as:

Anodic Inhibitors

An anodic inhibitor increases anodic polarization and displaces the corrosion potential in the negative direction. They displace the corrosion potential (E_{corr}) in the positive direction and reduce corrosion current (I_{corr}) thereby retard anodic reaction and suppress the corrosion rate.

Cathodic Inhibitors

A cathodic inhibitor increases the cathodic polarization and hence moves the corrosion potential in the anodic direction. Cathodic inhibitors may be divided into 3 categories, namely

1. Those that absorb oxygen.
2. Those that reduce the area of the cathode and
3. Those that increase the hydrogen over potential of the cathodic process.

Mixed Inhibitors

Such type of inhibitors retards both the anodic and cathodic processes. The shift in the potential is smaller and the direction is determined by the relative size of the anodic and cathodic sites. Such inhibitors will have the advantage over other inhibitors in that they control both the cathodic and anodic corrosion reactions and hence are very safe to apply.

Vapour Phase Inhibitors

Vapour phase inhibitors are organic inhibitors which readily sublime and form a protective layer on the metal surface.

Global Corrosion Inhibitors Trends and Forecasts (2010 - 2015)

A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rates of a material, typically a metal or an alloy. Corrosion inhibitors will remain the largest product segment within water treatment chemicals market. Corrosion inhibitor is expected to be worth $5.98 billion in 2015, at a CAGR of 4.5%. Corrosion inhibitors are largely grouped under organic and inorganic products. The suitability of any given chemical for a task in hand depends on the material of the system it has to act in, the nature of the substances it is added into, and their relative PPM levels. Most of the corrosion inhibitors would apply to industrial applications such as power generation, oil & gas, refinery, pulp & paper, chemical processing and metal & mining **(www.fastmr.com/prod/150454).**

1.7.2 Environmentally Friendly Inhibitors

In fact, much attention should be given when selecting inhibitors for investigation or application to ensure the environmental regulations. The inhibitor must be environmentally friendly to replace the older, which is more toxic and harmful to the environment **(Blaser, 1976; Anatas and Williamson, 1996)**. When applying the ideas of green chemistry to the area of corrosion inhibitors, the major improvement is in the area of eliminating environmentally toxic compounds, such as chromates, dichromate and nitrites, and replacing them with more environmentally friendly chemicals.

A corrosion inhibitor is a substances 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. Many of these inhibitors are organic compounds. It is generally assumed that corrosion inhibition performed by adsorption of the additives (ion or neutral polar molecules) to the metal-solution interface. It is known that the potential difference between a metal electrode and the solution is due to a non-uniform distribution of electric charges at the interface. The interaction of ions or neutral molecules at the electrical double layer, changes its properties and structures. The water molecules preadsorbed at the metal surface in contact with the aqueous solution are involved in the successive adsorption processes. Adsorption of organic molecule occurs because the interaction energy between the metal surface and the inhibitor is higher than the interaction energy between the metal surface and the water molecules.

Natural products of plant origin contain various organic compounds such as alkaloids, flavonoids, terpenoids, primary and secondary alcohols, quinones, fatty acids, steroids and other minor components. These compounds are known to have inhibitive action. Reports have shown that the *Areca catechu* (species of palm) acts as a corrosion inhibitor for mild steel in hydrochloric acid medium **(Vinod Kumar *et al.,* 2011)**. Because of the toxic nature and high cost of synthetic inhibitors currently in use, it is necessary available and renewable source for wide range of inhibitors.

They are the rich sources of nature. Natural products can be considered as a good source for this purpose.

Due to their biodegradability the trend of using these less toxic compounds are going on and in this direction the present work is undertaken to study the use of the aqueous extract obtained from destructive distillation method (without a carrier solvent) of agricultural waste of shell, leaf stalk and peduncle of coconut palm (*Cocos nucifera* L.) and palmyra palm (*Borassus flabellifer* L.) as potential inhibitors for mild steel in 0.5 M H_2SO_4 and 1 M HCl solutions.

In the present work the product obtained by destructive distillation from two popular species: *Cocos nucifera* L. (Coconut palm) and *Borassus flabellifer* L. (Palmyra palm) are utilized for corrosion inhibition studies in acid media.

1.8 PLANT DESCRIPTION

The descriptions of palm trees are believed to be among the oldest flowering plants in the world **(Redhead, 1989).** For centuries, many palm species have been tapped throughout the tropical world in order to produce fresh juice, fermented drinks, syrup, brown sugar or refined sugar. Most tapped palm trees do not only produce sap but are multipurpose (edible fruits, building materials, fuel, fibers, wax, etc.,) and their socio-economic importance can be critical for the rural poor. Another outstanding example is the **coconut palm**, for which every part is used. This tree is called in India "Tree of Heaven". There are at least 1,000 uses for the coconut palm. **Palm trees** are also often associated with crops and pastures.

The palmyra palm products are used in dozen of major classes, as follows: beverages; building materials; chemicals and industrial products; cosmetics and hygiene; feeds; fertilizers; food; fuel; handicrafts; medicines and rituals; ornamental plants; and structure and shelter. **The agricultural waste such as shell, leaf stalk and peduncle of *Cocos nucifera* L. (CN) (Figure - 10.a) and *Borassus flabellifer* L. (BF) (Figure - 11.a) are used as raw material for corrosion inhibition studies in acid media.**

The plant profile for the *Cocos nucifera* L. and *Borassus flabellifer* L. are same

Kingdom	*Plantae* – Plants
Subkingdom	*Tracheobionta* – Vascular plants
Superdivision	*Spermatophyta* – Seed plants
Division	*Magnoliophyta* – Flowering plants
Class	*Liliopsida* Monocotyledons
Subclass	*Arecidae*
Order	*Arecales*
Family	*Arecaceae* – Palm family

They differ only in Genus and Species.

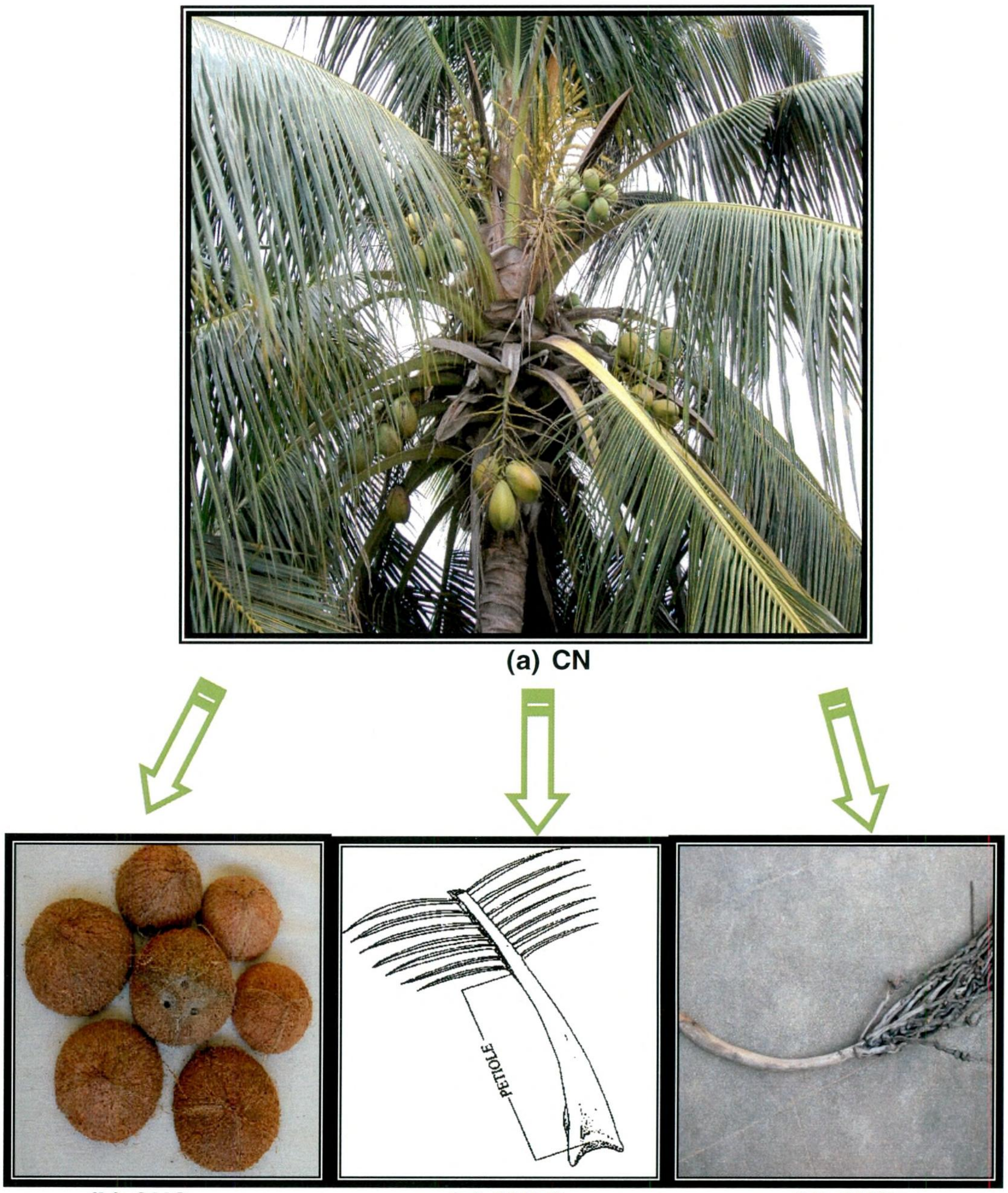
1.8.1 *Cocos nucifera* L. (CN)

1.8.1.1 *Cocos nucifera* L. Shell (CNS)

The mature fruit of the coconut palm is a 3-sided fibrous dry drupe. It contains the largest seed although larger fruits exist. The round “coconut” is a dehusked fruit. It consists of the coconut milk, and “meat” (kernel, endosperm) and hard stony shell (endocarp). (Figure - 10.b)

Genus *Cocos* L. – coconut palm

Species *Cocos nucifers* L.– coconut palm



(a) CN

(b) CNS (c) CNLS (d) CNP

Figure - 10 *Cocos nucifera* L. plant parts

1.8.1.2 *Cocos nucifera* L. Leaf Stalk (CNLS)

The lamina of the entire leaves separate into leaflets caused by splitting between the leaf veins to form a compound leaf (frond or pinnate frond). The palm bears the fronds at the top of the palm in a terminal radiating crown. The parts of the frond are the leaf base, leaf stalk (petiole) midrib (rachis) and leaflets (pinnae). Each side of a frond has about 100 leaflets. The bottom of the frond stalk has a broad leaf base with a cushion on the underside connected to the trunk and a keel or thick body to strengthen it. Bits of fiber stick to each side of the leaf base to form a fibrous sheath. (Figure - 10.c)

1.8.1.3 *Cocos nucifera* L. Peduncle (CNP)

Inflorescences form in each leaf axil at the base of each frond, with many male flowers on the upper section of the branch and few female flowers on the lower section of the branch. All the flower bunches on one palm will always hang out of the same side of the leaf stalk, either right or left. A spear-like green tube or sheath formed from a bract (spathe or spadix) encloses the flower bunch. The spathe emerges in the frond axil and splits, releasing the flower bunch. Each flower bunch has a central stalk (peduncle) with many lateral branches. (Figure - 10.d)

1.8.2 *Borassus flabellifer* L. (BF)

1.8.2.1 *Borassus flabellifer* L. Shell (BFS)

The seed consists almost exclusively of endosperm, Upper portion of palmyra seed, albumen in a cavity in showing the embryo, embedded in endosperm, which is lodged the relatively very minute embryo. (Figure - 11.b)

Genus *Borassus* L. – borassus palm

Species *Borassus flabellifer* L .– palmyra palm

These are the general characteristics by which this very well-defined order may be discriminated, but, in a group containing considerably more than a thousand species.

1.8.2.2 *Borassus flabellifer* L. Leaf Stalk (BFLS)

The adult leaf of palmyra palm generally presents a sheathing base tapering upwards into the leaf stalk, and this again bearing the lamina or blade. The sheath and the petiole very often bear stout spines, as in the rattan palms. (Figure - 11.c)

1.8.2.3 *Borassus flabellifer* L. Peduncle (BFP)

The flowers are borne on simple or branching spikes, very generally protected by a spathe or spathes, and each consists typically of a perianth of six greenish, somewhat inconspicuous segments in two rows, with six stamens, or pistil of 1-3 carpel's, each with a single ovule and a succulent or dry fruit. (Figure - 11.d)

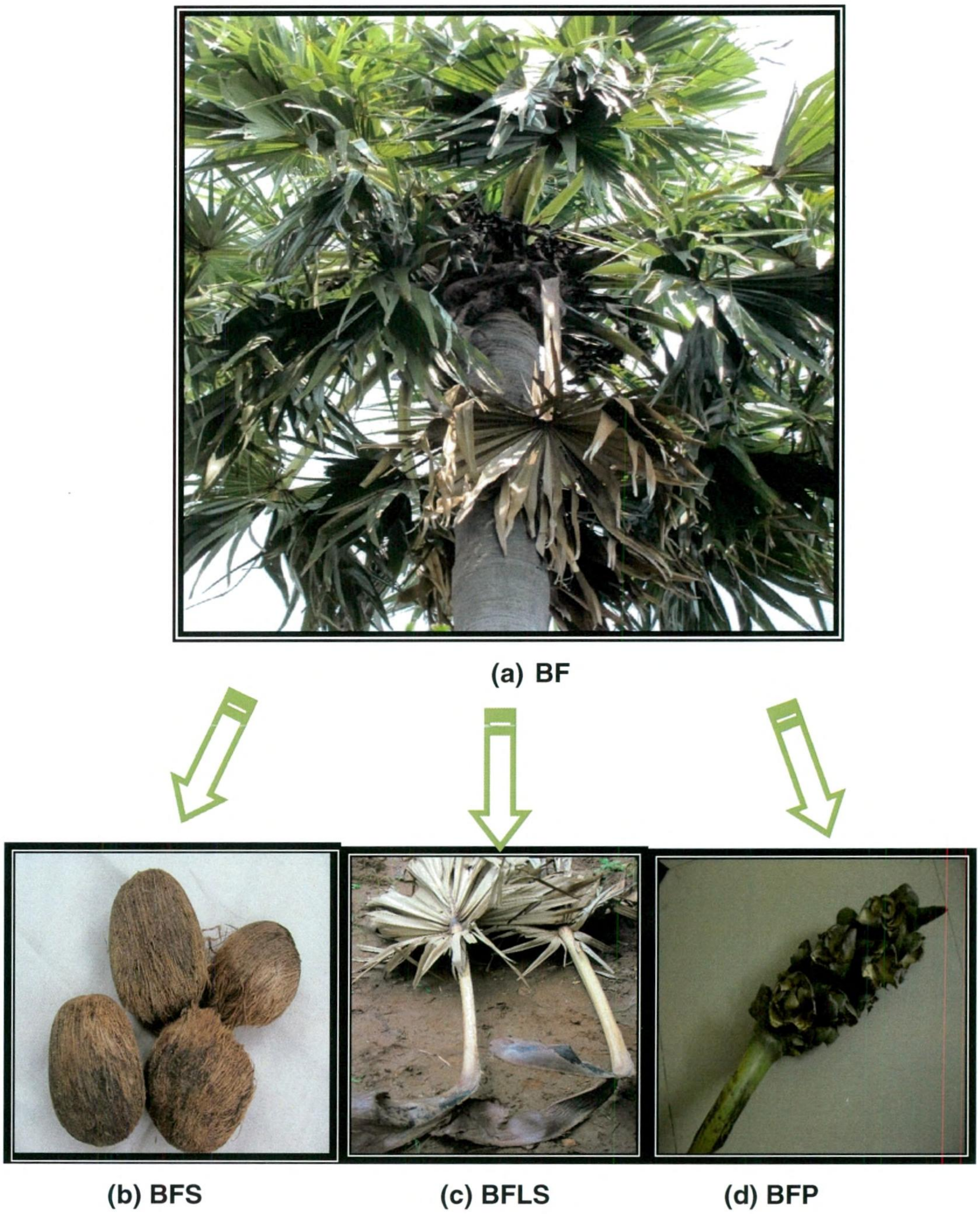


Figure - 11 *Borassus flabellifer* L. plant parts

1.9 OBJECTIVES

The purpose of this project was

* To evaluate the role of shell, leaf stalk and peduncle of CN and BF aqueous extract obtained from distractive distillation corrosion inhibitors.
* To establish the effectiveness of CN and BF extract as corrosion inhibitor.
* To study the effect of temperature on the corrosion process in the absence and presence of extract.

* To understand the phytochemical constituents present in shell, leaf stalk and peduncle of CN and BF using GC-MS and FT-IR.
* To study the inhibitive action of mild steel coupons in 0.5 M H_2SO_4 and 1M HCl acidic media by mass loss method.
* To evaluate the effect of inhibitor on the corrosion of mild steel in 0.5 M H_2SO_4 and 1M HCl at different concentrations for various periods of immersion.
* To assess the stability of the inhibitors at higher temperature.
* To calculate the thermodynamic parameters such as the energy of activation, change in free energy, change in enthalpy and change in entropy.
* To fit a suitable adsorption isotherm for the above experimental data.
* To assess the inhibition efficiency using electrochemical techniques - Tafel intercept method, LPR method and impedance spectroscopy method.
* To compare the performance of the inhibitor by mass loss method and electrochemical techniques.
* To suggest a possible mechanism for the inhibition process.
* To carry out Quantum chemical studies for the main constituents of CN and BF using **Gaussian 03** code of programs using B3LYP/6-31G (d).

Having discussed the need for corrosion control and objectives of the current investigation, a detailed **Review of related literature** is given in **Chapter II.**