INTRODUCTION

1. INTRODUCTION

Corrosion phenomena, their prevention and control have become a perpetual struggle between man and nature, particularly in view of the modern age technological developments and the increasing need and use of the metallic materials in the technology. This issue has necessitated the increasing interest in research into the environment and metal interface reactions and the means of mitigating the damaging effects of corrosion on metals and alloys. Since corrosion of materials is inevitable, effective and successful corrosion control is one of the most urgent needs for the development of our country.

DEFINITION

Corrosion is defined as the deterioration or destruction of the metal.

Corrosion is the degradation of a material's properties or mass over time due to environmental effects. It is the natural tendency of a material's compositional elements to return to their most thermodynamically stable state. For most metallic materials, this means the formation of oxides, sulfides, or other basic metallic compounds generally considered to be ores. Fortunately, the rate at which most of these processes progress is slow enough to provide useful building materials. Only inert atmospheres and vacuum can be considered free of corrosion for most metallic materials.

Corrosion may be considered as the natural and spontaneous deterioration of a material by chemical or electrochemical attack, due to the inherent metastability of metals.

1.1 Chemical process of corrosion

Corrosion commonly occurs at metal surfaces in the presence of oxygen and moisture and involves two electrochemical reactions. Oxidation takes place at the anodic site and reduction at the cathodic site. In acidic medium hydrogen evolution reaction predominates, while in neutral medium reduction of oxygen takes place.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I_{corr}. Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface. The most common and important electrochemical reactions in the corrosion of iron are thus

Anodic reaction (corrosion)

$$\mathbf{Fe \rightarrow Fe^{2+} + 2e^-} \quad (1)$$

Cathodic reactions

$$\mathbf{2H^+ + 2e^- \rightarrow H_2} \quad (2a)$$

or

$$\mathbf{H_2O + 1/2\ O_2 + 2e \rightarrow 2OH^-} \quad (2b)$$

Reaction 2a is most common in acids and in the pH range 6.5 – 8.5 (alkaline or neutral medium) the most important reaction is oxygen reduction 2b. In the latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

$$\mathbf{Fe^{2+} + 2OH^- \rightarrow Fe\,(OH)_2}$$

iron(II) hydroxide

Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish colour due to partial oxidation in air.

$$\mathbf{2Fe\,(OH)_2 + H_2O \rightarrow 2Fe(OH)_3}$$

hydrated iron(III) oxide

Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements which are present. For other metals or different environments different types of anodic and cathodic reactions may occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation these may provide a highly protective surface film which retards further corrosion, the surface is then said to be "passive". An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidizing conditions or elevated temperatures.

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^-$$

1.2 Classification of corrosion

Corrosion is classified broadly as Dry or Chemical corrosion and Wet or Electrochemical corrosion.

Dry corrosion or Chemical corrosion

This type of corrosion occurs mainly through the direct chemical action of environment or atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphurdioxide, nitrogen or anhydrous inorganic liquid with metal surfaces in immediate proximity.

Oxidation corrosion is brought about by the direct action of oxygen at low or high temperatures on metals, in the absence of moisture. Alkali metals (Li, Na, K, Rb etc.,) and alkaline earth metals (Be, Ca, St etc.,) are rapidly oxidized at low temperatures. At high temperatures almost all metals (except Ag, Au, Pt) are oxidized.

$$2M \rightarrow 2M^{n+} + 2ne^- \quad \text{(loss of electrons)}$$

Metal ions

$$n/2\ O_2 + 2ne^- \rightarrow nO^{2-} \quad \text{(gain of electrons)}$$

Oxide ions

$$2M + nO_2 \rightarrow 2M^{n+} + 2nO^{2-}$$

Metal oxide

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action.

Wet or electrochemical corrosion

This type of corrosion occurs a) **When a conducting liquid is in contact with metal** or **b) When two dissimilar metals or alloys are either immersed or dipped partially in a solution.**

Electrochemical corrosion occurs due to the existence of separate anodic and cathodic areas between which current flows through the conducting solution. At anodic area, oxidation reactions take place. At cathodic area, reduction reaction takes place.

Depending on the nature of the corrosive environment, the cathodic reaction consumes electrons with either,

- ✓ **Evolution of hydrogen** or
- ✓ **Absorption of oxygen**

Corrosion under wet conditions is determined by

- ***Dissolved oxygen content***
- ***Temperature***
- ***pH***
- ***Depth of immersion or mode of exposure***
- ***Velocity***
- ***Concentration of electrolyte***

1.3 Forms of Corrosion

The following are the basic forms of corrosion that metallic materials may be subjected to:

Uniform corrosion

The type of corrosion, where uniform thinning of metal occurs is said to be uniform corrosion.

Pitting corrosion

Pitting corrosion is a form of extremely localized attack, the rate of attack being greater at some areas than at others. Pitting is the most destructive form of corrosion and results in sudden failure of the equipment due to formation of holes.

Exfoliation

Loss of material in the form of layers or leaves from a solid metal or alloy is called exfoliation. This type of corrosion is generally observed in wrought products which exhibit elongated structures.

Galvanic corrosion

Galvanic corrosion occurs when two or more dissimilar metals in electrical contact are placed in an electrolyte. This results from the existence of a potential difference between the metals, which causes a flow of current between them.

Erosion corrosion

Erosion corrosion can be defined as the increase in corrosion rate caused by relative motion between the metal surface and the corrosive environment which may be a liquid or gas. It is also known as impingement corrosion. This type of attack usually occurs in systems where high velocities of the corrosive fluid are encountered. Copper and brass condenser tubes are subjected to this type of attack.

Fretting corrosion

Fretting corrosion results from the slight relative motion of two substances in contact, one or both of which are metals.

Cavitation

This type of corrosion, resulting from the formation and collapse of bubbles at a dynamic metal- liquid interface is called cavitation and is generally exhibited on rotors of pumps or on trailing faces of propellers.

Intergranular corrosion

This is a localized type of attack at the grain boundaries of metals, resulting in the loss of strength and ductility.

Stress corrosion

If metal is subjected to a constant tensile stress and is exposed to a corrosive environment, a crack develops. This type of failure is called stress cracking. Two classic examples of stress corrosion are caustic embrittlement of riveted steel boilers and the season cracking of brass cartridge cases.

Corrosion fatigue

The damaging effect of the simultaneous action of corrosion and cyclic stress alternately or repeated tensile stress on metal is known as corrosion fatigue. The components susceptible to corrosion fatigue are marine propeller shaft, super heater tubes, boiler, turbine rotors, blades and casing, drill pipes in oil field and rock drills in mines.

Filliform corrosion

Filliform corrosion is a type of attack advancing outwards along thread like tracks, commonly occurring under coatings of paints, rubber, lacquered surfaces, tin, silver, enamel, paper, etc.,

Dealloying

It is the type of attack where one or more reactive components of alloys corrode preferentially, leaving a porous, less ductile, mechanically weak residue that may retain the original shape of alloy, eg., Zinc alloy.

Crevice corrosion

This corrosion is produced at the point of contact of usually non-metallic materials with passive metals. It occurs at washers sand grains and at pockets formed by threaded joints. This type of corrosion is also called as deposit corrosion or gasket corrosion.

Hydrogen embrittlement

Hydrogen embrittlement of metals generally occurs when they are stressed in tension in a hydrogen environment. Hydrogen diffuses into the metal matrix in atomic form inducing embrittlement. The gas may originate from such operations as Pickling, Welding, Cathodic protection, Electroplating, Corrosion in aqueous environments, exposure to gaseous hydrogen, etc. **(Raj Narayanan, 1988)**

Tarnishing, scaling, rusting, wastage, pitting are the familiar manifestations of corrosion.

1.4 Consequences of corrosion

As a result of corrosion, metallic materials lose or alter the properties which have served as selection criteria for different specific applications.

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 the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarised as follows:

Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localized zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.

1. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).
2. Loss of time in availability of profile-making industrial equipment.
3. Reduced value of goods due to deterioration of appearance.
4. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small
5. quantity of heavy metals are released by corrosion).
6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.
7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.

8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.
9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

1.5 Losses due to corrosion

Corrosion wastes metals, a non renewable resource

Metals, especially the common non ferrous metals are being corroded and dissipated over the globe and are needed by the future society.

Losses due to corrosion may be direct or indirect.

Direct losses may include

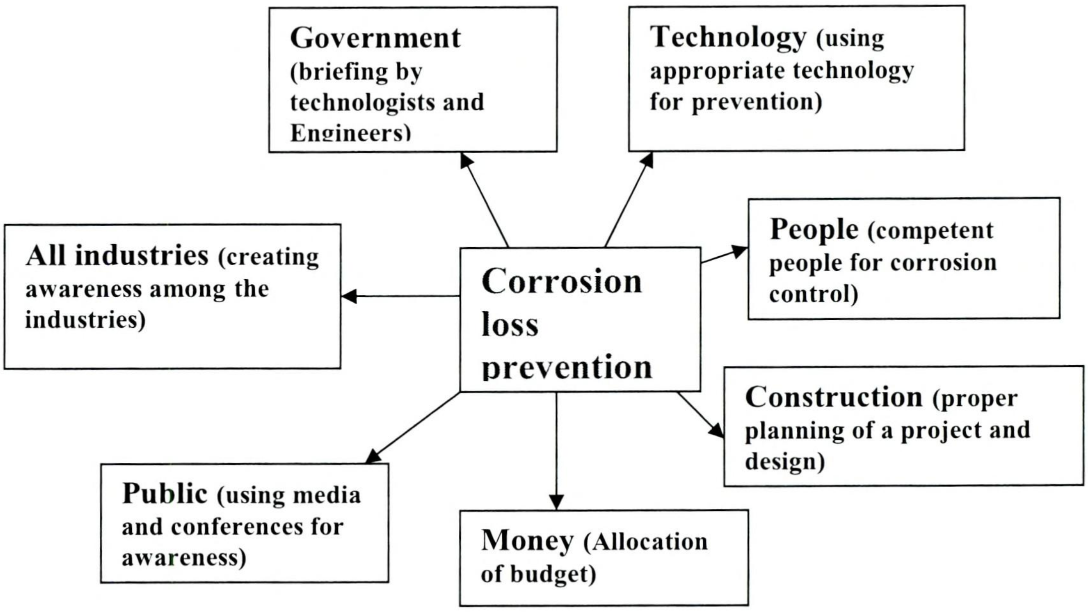
- Inability to use otherwise desirable materials.
- Over-design to allow for corrosion.
- The cost of repair or replacement of the corroded component or equipment.
- Cost of anti-corrosive painting or other protection methods.

Indirect losses may be either economical or social. These may include

- contamination of the product
- loss of valuable product from a container that has corroded through
- damage of equipment adjacent to that in which corrosion failure occurs
- loss of production
- Safety eg., sudden failure of equipment may cause fire, explosion or release of toxic product.
- Appearance, eg., corroded metal is usually unpleasant to the eye.

  Corrosion leads to an accelerated depletion of mineral reserves.

Corrosion loss can be reduced by adopting the preventing methods in different sectors as given in the following chart.



1.6 Corrosion cost

Corrosion is a major degradation process by which the components and structures in industry and infrastructures fail prematurely and cause significant economic losses. Corrosion of assets and protection of the environment are very important which affect the country. The real cost of corrosion damage to the global environment is largely incalculable.

The method of estimating total cost of corrosion was used by Uhlig in one of his studies that examined the cost of corrosion in the United States and Japan. The corrosion control methods that were considered for the estimation of corrosion cost include protective coatings, corrosion-resistant metals and alloys, corrosion inhibitors, polymers, anodic and cathodic protection, corrosion control services, corrosion research and development, and education and training. **(Pierre Roberge, 2000).**

The total annual cost of corrosion estimated for the year of 1998 was $121.41 billion or 1.381 percent of the $8.79 trillion Gross Domestic Product (GDP). The cost of corrosion was estimated to be around $364 billion as of 2004. This estimation does not include the indirect cost and other consequential damages. If this was taken into account, it would go up several times from the present level of 3.1% of GDP, as reported by Houston-based NACE International president George Hays during his presentation at the NACE International India Section conclave in Mumbai. The cost of corrosion in India was estimated to touch Rs 36,000 crore and that in US was over $360 billion. India Inc was footing an annual bill of close to Rs 1.5 lakh crore on account of losses due to corrosion, according to the Indian chapter of NACE International, a global forum of over 16,000 corrosion engineers. The cost works out to much higher than any of the calamities the nation has faced over the years, as reported by Mr Rajan Bahri, Trustee NACE International India.

The study in the United States estimated the direct costs of corrosion to be approximately 4.9% of the gross national product for an industrialized nation. This cost is greater than the financial cost of all the fires, floods, hurricanes and earthquakes in the nation. Of this 4.9%, 1-2% is avoidable by implementing proper technologies that are already available.

The annual corrosion cost of key sectors such as infrastructure has been put at Rs 22,600 crore, utility services — Rs 47,100 crore, production and manufacturing — Rs 17,650 crore and Defence and nuclear waste — Rs 20,000 crore. Correspondingly, cost of mitigation has been estimated at one per cent of the savings.

Corrosion of metals cost the U.S. economy almost $300 billion per year at 1995 prices. Broader application of corrosion-resistant materials and the application of the best corrosion-related technical practices could reduce approximately one-third of these costs. These estimates result from a recent update by Battelle scientists of an earlier study reported in 1978. The initial work, based upon an elaborate model of more than 130 economic sectors, had revealed that metallic corrosion cost the United States $82 billion in 1975, or 4.9 percent of its GNP. It was also found that 60 percent of that cost was unavoidable.

The cost of corrosion to US industries and the American public is currently estimated at $170 billion per year. Although corrosion is only nature`s method of recycling, or of returning a metal to its lowest energy form, it is an insidious enemy that destroys our cars, plumbing, buildings, bridges, engines, and factories.

Corrosion awareness is lacking in India. The huge amount of losses on account of corrosion; viz., over 3% of the GDP, can be controlled to some modest level by simply improving corrosion awareness. Simple engineering techniques and materials selections can be used to prevent and retard corrosion. The cost of corrosion to industry is very large. A sizeable fraction of these costs could be saved by a wider appreciation of known techniques for corrosion prevention, coupled with the development of more effective methods of protection.

The loss of mild steel in India was estimated worth Rs.25,000 crores per annum and about 33% of the amount can be saved by the available corrosion combating methods **(Smita varma and Mehta, 1999).**

1.7 Importance of corrosion studies

It is presently necessary to pay more attention to metallic corrosion than was done earlier due to

- Increasing use of metals in all fields of technology.
- Use of rare and expensive metals whose protection requires special precautions.
- Use of new high strength alloys which are usually more susceptible to certain types of corrosive attack.
- Increasing the pollution of air and water, also resulting in a more corrosive environment.
- Strict safety standards of operating equipment, which may fail in a catastrophic manner due to corrosion. **(Raj Narayanan, 1988)**

1.8 Corrosion principles

1.8.1 Thermodynamic principles

Different metals have different tendencies to corrode in a given corrosive environment. Corrosion occurs in a given environment because of the thermodynamic instability of a material in that environment. Thermodynamic approach has been widely used to explain the corrosion problems. The corrosion of metals is electrochemical in nature. Corrosion reactions of metals are therefore considered as electrochemical cells formed due to electrochemical reactions. The amount of work done by the cell is equal to the quantity of electrical energy generated. The electrical energy available is equal to the product of the potential difference E and the quantity of electricity Q.

Net work done = Q x E

where, Q is equal to one Faraday for each gram equivalent of the reactants.

If n electrons are involved in the reaction, **Q = nF**

Any work performed by the cell can be accomplished only at the expense of a decrease in free energy of the cell reaction.

$$\Delta G = -nFE$$

Where ΔG is the free energy change in joules

E is the emf of cell in volts.

1.8.2 Pourbaix Diagrams

In order to extend the thermodynamic treatment, it is necessary to consider other types of equilibria, particularly formation of metal hydroxides and oxides

$$M + nH_2O \rightarrow \quad M(OH)_n + ne^- + nH^+$$

$$M + 2nOH^- \rightarrow \quad MO^{n-} + nH_2O + ne^-$$

Both the reactions are electron transfer reactions and so potential dependent but they are also pH- dependent. Other reactions which are purely chemical but pH-dependent are

$$M^{n+} + nOH^- \rightarrow \quad M(OH)_n$$

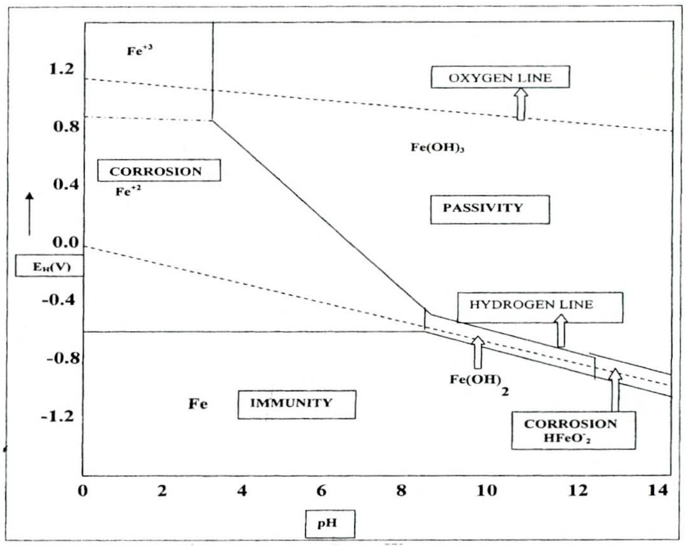
$$MO_n^{n-} + nH^+ \rightarrow \quad M(OH)_n$$

Potential-pH plots are known as Pourbaix diagrams. E-pH diagrams are typically plotted for various equilibria on normal cartesian coordinates with potential (E) as the ordinate (y axis) and pH as the abscissa (x axis) for a given metal under standard thermodynamic conditions. These diagrams relate the electrochemical and corrosion behavior of any metal in water. In practice, Pourbaix diagrams are suitable for studies of corrosion, electrowinning, electroplating, hydrometallurgy, electrolysis, electrical cells, and water treatment since they are electrochemical maps indicating the domain of stability of ions, oxides and hydroxides. This map provides the oxidizing power in an electrochemical field measured as potential and the acidity and alkalinity of species measured as pH. The possible reactions that may occur in an electrochemical system, a simplified Pourbaix diagram gives important areas for designing and analyzing electrochemical systems. These areas are known as corrosion, passivation, and immunity **(Nestor Perez, 2004)**

The potential –pH diagram of Fe in water is given in figure 1.1.

Figure 1.1

Pourbaix diagram for Fe-Water system



There are three general types of solid line on the pourbaix diagram, each line representing equilibrium between the metal and other species.

- Horizontal lines indicate reactions which are only potential-dependent
- Vertical lines indicate reactions which are only pH- dependent
- Sloping lines indicate reactions which are both potential and pH-dependent.

In the application of E-pH diagrams to corrosion, thermodynamic data can be used to map out the occurrence of corrosion, passivity, and nobility of a metal as a function of pH and potential. The operating environment can also be specified with the same coordinates, facilitating a thermodynamic prediction of the nature of corrosion damage. A particular environmental diagram showing the thermodynamic stability of different chemical species associated with water can also be derived thermodynamically.

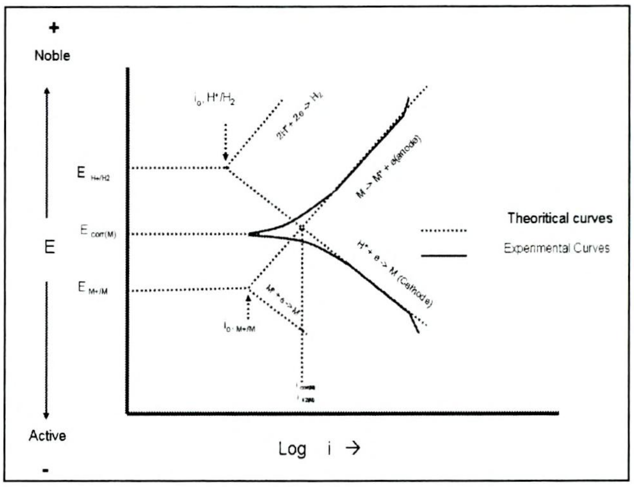
1.8.3 Electrochemical principle

A deeper insight into the fundamental concepts of corrosion phenomenon is provided by the theory of mixed potentials. The mixed potential theory consists of two simple hypothesis,

1. Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions
2. There can be no net accumulation of electrical charge during an electrochemical reaction

The application of mixed potential theory can be demonstrated by polarization diagrams of the corroding metals called the Evan's diagram (figure 1.2). Evan's diagram is the graph of potential versus log current density.

Figure 1.2
Evan's diagram



1.9 Theories of corrosion inhibition

The mechanism of inhibition of the inhibitors may not be generalized. Based on the nature of action of the inhibitor, the theory of inhibitor action can be classified as

- ✓ **Adsorption theory**
- ✓ **Hydrogen overvoltage theory**
- ✓ **Film theory**
- ✓ **Quantum chemical approach**

1.9.1 Adsorption theory

According to this theory, inhibitors get adsorbed on the metal surface forming a protective layer that act as a barrier between the metal and the medium. The mode of adsorption may be physisorption or chemisorption. Physical adsorption is due to the electrostatic interaction between the charged molecules and the charged metal. It involves low activation energy and is independent of the temperature. Chemical adsorption involves sharing or transfer of electrons from the inhibitor molecules to the metal surface forming a bond. Chemisorption involves higher activation energy.

1.9.2 Hydrogen overvoltage theory

This theory explains that the inhibitor adsorbed on the metal retard either the anodic or the cathodic reactions or in some cases both the reactions leading to the polarization of anodic and cathodic sites. Thus the corrosion rate of the metal is reduced.

1.9.3 Film theory

This theory explains that the metal is better protected by the inhibitor due to the formation of an insoluble or slightly soluble layer of the corrosion products. The effectiveness of the inhibitor depends on the stability of the film formed.

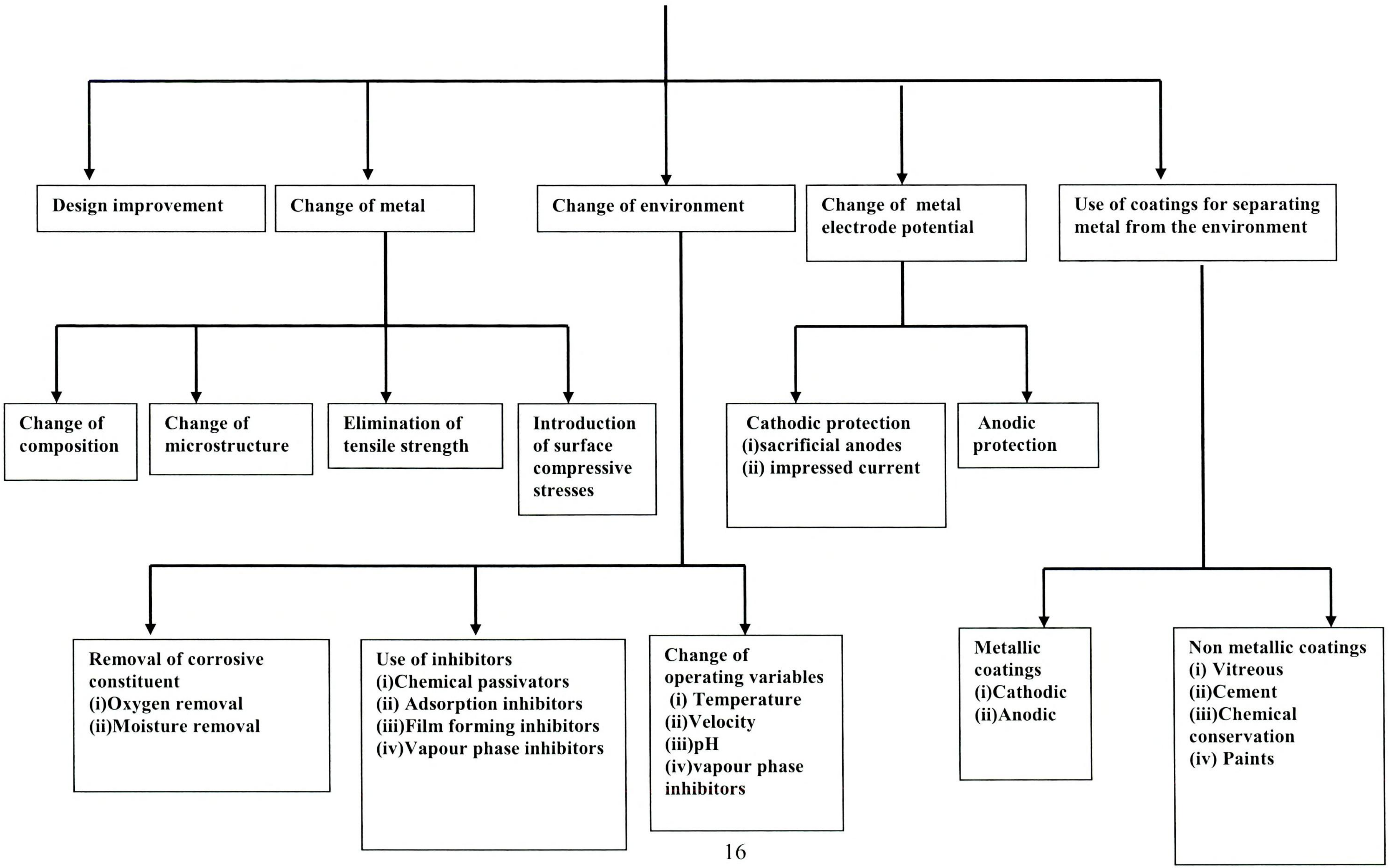
1.9.4 Quantum chemical approach

Direct interaction between the metal atoms and the outermost electrons of the inhibitor molecules sometimes lead to chemisorption. In this case the binding energy may be correlated to the energy difference between the lowest unoccupied molecular orbital (LUMO) of the metal atoms and the highest occupied molecular orbital (HOMO) of the inhibitor.

1.10 Corrosion prevention

Corrosion protection is an important part of industrial development. Effective methods of corrosion control prolong life of the equipment and machinery and this way minimizes use of natural resources including ore, oil, petroleum, water, etc.

Corrosion prevention



1.11 Corrosion control methods

Selection of corrosion resistant materials, isolating the materials from the environment, using organic, inorganic or metallic coatings, altering the environment through process changes, employing electrochemical control and manufacturing design to minimize localized corrosion are some of the common corrosion control methods.

Corrosion control in chemical process plants

Corrosion can be controlled by the following different methods

Cathodic Protection

Cathodic protection is achieved by supplying electrons to the metal structure to be protected. There are two ways to protect a structure cathodically.

i) by an external power supply- Impressed current cathodic protection

ii) by appropriate galvanic coupling-Sacrificial anodic protection

Anodic Protection

Anodic protection is based on the formation of protective film on metals by externally applied anodic currents. It is limited to passive metals.

Coatings

A thin coating of metallic and inorganic materials or organic materials can provide an effective barrier. Metal coatings are applied by electrodeposition, flame spraying, cladding, hot dipping and vapour deposition. Organic coatings include paints, varnishes, lacquers etc.,

Application of Inhibitors

An inhibitor when added to an environment decreases the corrosion rate. It acts in different ways. Based on its mechanism of action it is classified as adsorption type inhibitors, hydrogen evolution poisons, scavengers, oxidizers and vapour phase inhibitors.

Importance of inhibitors

The highly corrosive nature of aqueous mineral acids on most metals requires some degree of restraint to achieve economic maintenance and operation of equipment, minimum loss of chemical product and maximum safety conditions. Thus, the inhibition of corrosion of iron and steel in aqueous acidic solutions become a necessity.

The use of an inhibitor to prevent corrosion is a simple approach to give effective corrosion control. Eventhough there is a widespread use of inhibitors to control corrosion, there is still a need for systematic study to understand their effectiveness and mode of action.

1.12 Inhibitors

One of the very important methods of minimizing corrosion today is the use of corrosion inhibitor. A corrosion inhibitor may be defined, in general terms as a substance which, when added in a small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to that environment. Inhibition is used internally with carbon steel pipes and vessels as an economic corrosion control alternative to stainless steels and alloys, coatings, or non-metallic composites. A particular advantage of corrosion inhibition is that it often can be implemented or changed in-situ without disturbing a process. The major industries using corrosion inhibitors are oil and gas exploration and production, petroleum refining, chemical manufacturing, heavy manufacturing, water treatment, and the product additive industries.

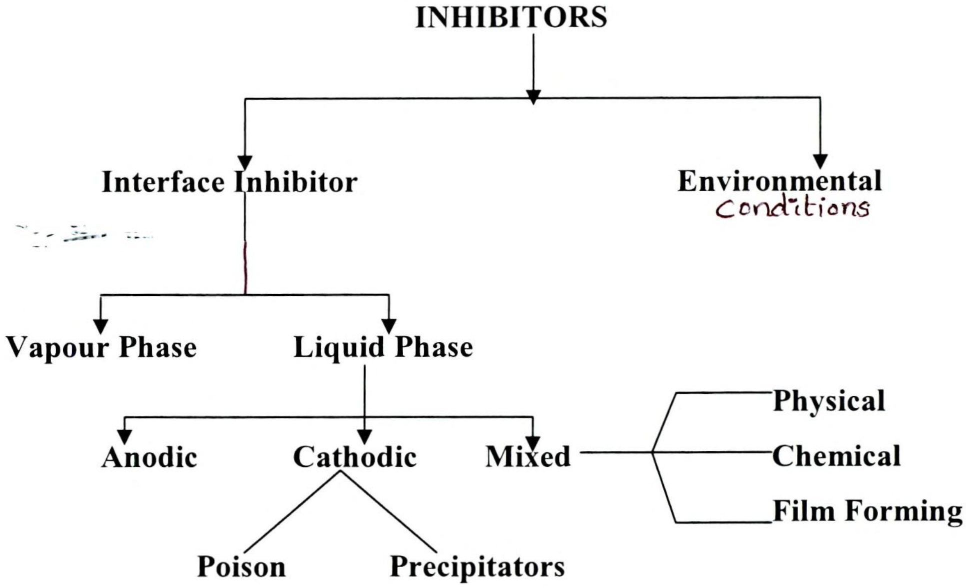
A **corrosion inhibitor** is a compound that, when added to a fluid or gas, decreases the corrosion rate of a metal or an alloy. Corrosion inhibitors reduce or prevent the electrochemical reactions, they are adsorbed onto the metal surface and act by forming a barrier to oxygen and moisture, by complexing with metal ions or by removing corrodants from the environment, some of the inhibitors facilitate the formation of passivating film on the metal surface.

Acid inhibitors find wide applications in the industrial field as a component in pretreatment composition, in cleaning solution for industrial equipments and in acidization of oil wells.

Types of inhibitors

Correct selection of inhibitor and quantity makes it possible to achieve high efficiency of about 90-99%. Inhibitors may act by the formation of a passivation layer (a thin film on the surface of the material that stops access of the corrosive substance to the metal), inhibiting either the oxidation or reduction part of the redox corrosion system (anodic and cathodic inhibitors), or scavenging the dissolved oxygen.

CLASSIFICATION OF INHIBITORS



The corrosion inhibitors reduce corrosion either acting as a barrier by forming an adsorbed layer or retarding the cathodic and/ or anodic process. A **Cathodic inhibitor** increases the cathodic polarization and hence moves the corrosion potential in the anodic direction. **Cathodic inhibitor** retards the corrosion by inhibiting the reduction of water to hydrogen gas. *Cathodic inhibitors are safer to use but less efficient.* An **Anodic inhibitor** increases anodic polarization and displaces the corrosion potential in the negative direction. It forms a passivation layer on the metal which prevents the oxidation of the metal. Unfortunately, many inhibitors are hazardous to human beings. If anodic inhibitors are used at too low concentration, they can actually aggravate pitting corrosion, as they form a non uniform layer with local anodes. Nitrite, Chromate and pertechnetate are some of the anodic inhibitors. *Anodic inhibitors are more efficient but dangerous.*

It is also possible that with correct choice, few compounds can form a protective film on the metal and, at the same time, act as an anodic inhibitor. Substances which increase both the cathodic and the anodic polarizations are called **mixed inhibitors**. Example – amine. *Mixed inhibitors are efficient and safe.*

Adsorption type corrosion inhibitors

Many organic inhibitors work by an adsorption mechanism. The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. The main functional groups capable of forming chemisorbed bonds with metal surfaces are amino, carboxyl and phosphonate although other functional groups or atoms can form co-ordinate bonds with metal surfaces.

Vapour Phase Inhibitors

VPIs (vapor phase corrosion inhibitors) extend their corrosion-inhibiting properties by volatilization and condensation to form a protective film on metal surface. Vapor phase self-assembled films of VPIs have become an attractive means to prevent metal from corrosion.

Some examples of corrosion inhibitors are hexamine, phenylenediamine, dimethylethanolamine, sodium nitrite, cinnamaldehyde, condensation products of aldehydes and amines (imines), chromates, nitrites, phosphates, hydrazine, ascorbic acid, and others. The suitability of an inhibitor for a process depends on many factors like the nature of the material, the nature of the substances they are added into and their operating temperature.

1.13 Pickling and metal finishing

Pickling is a surface treatment used to remove impurities, such as stains, inorganic contaminants, rust or scale, from ferrous metals, copper, and aluminium alloys. A solution called *pickle liquor*, which contains strong acids, is used to remove the surface impurities. It is commonly used to descale or clean steel in various steelmaking processes. (http://en.wikipedia.org/wiki/Pickling /metal).

Many hotworking processes and other processes that occur at high temperatures leave a discoloring oxide layer or scale on the surface. In order to remove the scale the workpiece is dipped into a vat of pickle liquor.

The primary acid used is hydrochloric acid, although sulphuric acid was previously more common. Hydrochloric acid is more expensive than sulfuric acid, but it pickles much faster while minimizing base metal loss. Carbon steels, with an alloy content less than or equal to 6%, are often pickled in hydrochloric or sulfuric acid. Steels with an alloy content greater than 6% must be pickled in two steps and other acids are used, such as phosphoric, nitric and hydrofluoric acid. Rust and acid resistant chromium-nickel steels are pickled in a bath of hydrochloric and nitric acid. Most copper alloys are pickled in dilute sulfuric acid, but brass is picked in concentrated sulfuric and nitric acid mixed with sodium chloride and soot.

In jewelry making, pickling is used to remove the oxidation layer from copper surfaces, which occurs after heating. A diluted sulfuric acid pickling bath is used. Sheet steel that undergoes acid pickling will oxidize (rust) when exposed to atmospheric conditions of moderately high humidity. For this reason, a thin film of oil or similar waterproof coating is applied to create a barrier to moisture in the air. This oil film must later be removed for many fabrication, plating or painting processes.

Pickling plays an important role for removing scales from steel sheets. Particularly it is very essential to pickle them after hot or cold working and after heat treatment for locating the inclusion surface defects.

Disadvantages

Acid cleaning has limitations in that it is difficult to handle because of its corrosiveness, and it is not applicable to all steels. Hydrogen embrittlement becomes a problem for some alloys and high-carbon steels. The hydrogen from the acid reacts with the surface and makes it brittle and causes cracks. Because of its high reactance to treatable steels, acid concentrations and solution temperatures must be kept under control to assure desired pickling rates.

Problems due to pickling

Huge consumption of acid, acid mist formation, which is unhygienic to the working environment and loss of base metal are a few problems that arise due to pickling process in industries.

The problem of pickling can be tackled by different methods by using the following types of baths

i) Baths consisting of aqueous acid solutions

ii) Molten alkali baths

iii) Electrolytic descaling in suitable aqueous or molten baths.

Pickling Baths

A number of baths can be used for the pickling of steels. An acidic bath to descale steel sheets after various stages of rolling and heat treatment is of interest here. Different combination of acids at a wide range of concentrations was used for pickling at different temperatures in wooden baths. Due to cost factors and other complications, the choice fell on the use of HCl or H_2SO_4.

Pickling inhibitors

Inhibitors are extensively used in metal pickling and vary in type according to the acid used in the pickling operation. During pickling, corrosion inhibitors are added to the solution in order to reduce the degree of metal attack and rate of acid consumption.

Metal Finishing

The main purpose of metal finishing is to impart desirable surface characteristics such as resistance to corrosion and abrasion. It is also used to provide desirable mechanical and physical property at the same time providing the better appearance of the surface. **(Shashi Chawla, 2002).**

1.14 Need for Green inhibitors [Plant materials]

Most of the corrosion inhibitors are expensive synthetic chemicals having hazardous properties to living creatures and environment. So, it is important to choose low cost and safely handled compounds to be used as corrosion inhibitors.

The use of naturally occurring substances to inhibit the corrosion of metals in acidic or alkaline environment is the recent trend. The natural extracts are found to be effective inhibitors in the acidic media and can be safely used without hydrogen damage, toxic effects and pollution problems. Due to the bio-degradability, less toxicity and easy availability of these compounds, the trend of using them have become increasingly important in the recent years.

Mild steel

Mild steel is used in fabrication of reaction vessels, storage tanks by industries, which either manufacture or use organic acids as reactant. Mild steel is a prominent material of construction and frequently comes in contact with aqueous solution which may be acidic in nature, may be as a part of industrial process.

Mild steel has been extensively used under different conditions in chemical and allied industries in handling alkalis, acids and salt solution. Mild Steel undergoes corrosion during acid cleaning, pickling, descaling, mining and oxidizing of oil wells. Hence mild steel is selected for the study.

Acid

Acids are used to remove oxides and other contaminants from metal surfaces. Acids are also used for derusting and pickling, industrial acid cleaning, acid descaling, oil well acidizing, the cleaning of refinery equipment and the removal of calcareous deposits from boilers, radiators of vehicles, pipelines carrying water or petroleum products, heat exchangers etc., Corrosion in mineral acid occurs through electrochemical mechanism. It can be generally prevented or reduced by proper material selection.

Sulphuric and Hydrochloric acid are the most commonly used acids in pickling baths at high temperatures upto 60°C. To remove unwanted scale such as rust or mill scale formed during manufacture, carbon steel is immersed in acid solution.

Inorganic acids such as hydrochloric acid derived from the decay of plastics like polyvinyl chloride and nitric and sulphuric acids derived from air pollution will attack metals which are either in the same storage environment as the plastic or in the open air.

Hydrochloric acid

Among various acids, hydrochloric acid is widely used in pickling processes. Because of the extremely aggressive nature of the medium the practice of inhibition is commonly used to reduce acid attack on the substrate metal. Heat exchangers can be cleaned on-stream by injecting hydrochloric acid solution of 1-2 N concentration directly into cooling water immediately before it enters an operating heat exchanger.

For oil well stimulation, large quantities of acid usually 10 – 15 % or sometimes 28% HCl are pumped at high rates of flow through the oil well tubing into the producing formation **(George Gardner).** HCl is probably the most corrosive solution encountered by oil and gas tubulars and downhole tools.

Sulphuric acid

Sulphuric acid is used directly or indirectly in nearly all industries and is a vital commodity in our national economy. The consumption rate of sulphuric acid, like steel production or electric power is more. The principal uses of sulphuric acid are for production of hydrochloric acid, other chemicals, and their derivatives; pickling of steel and other metals; manufacture of fertilizers, dyes, drugs, pigments, explosives, synthetic detergents, rayon and other textiles; petroleum refining; storage batteries; metal refining and production of rubbers. Corrosion problems occur in plants for making the acid and also in consumer's plants when it is utilized for a variety of conditions.

1.15 Bioaccumulation

Bioaccumulation refers to the accumulation of substances, such as pesticides, or other organic chemicals in an organism. Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost. Thus, the longer the biological half-life of the substance the greater the risk of chronic poisoning, even if environmental levels of the toxin are not very high.

Bioaccumulation explains why chronic poisoning is a common aspect of environmental science in the workplace. Repeated exposure to very low levels of toxins in these environments can be lethal over time.

Bioconcentration is a related but more specific term, referring to uptake and accumulation of a substance from water alone. By contrast, bioaccumulation refers to uptake from all sources combined (e.g. water, food, air, etc.).

1.16 Objectives

Research activities in recent times are geared towards finding alternative corrosion inhibitors to replace non-biodegradable and toxic organic or inorganic compounds. Naturally occurring substances satisfy this need. These are readily available, cost effective, renewable sources of materials, ecofriendly and biodegradable.

The leaves of *Bougainvillea spectabilis, Cassia fistula* and the flowers of *Mirabilis jalapa* are selected since they occur naturally and are easily available. They are grown as ornamental plants and so there is ample availability for these plants.

Coping with the recent trend of using environment friendly, green, corrosion inhibitors, the present study is aimed at the investigation of the inhibiting effect of the acid extract of leaves of *Bougainvillea spectabilis, Cassia fistula* and flowers of *Mirabilis jalapa* on mild steel corrosion in 1M HCl and 0.5M H_2SO_4.

The present research is to replace highly toxic substances with less or non-toxic, environmentally safe materials for corrosion resistance.

- To assess the inhibition efficiency of the selected plant material on the mild steel dissolution in acidic media by Weight loss method and Electrochemical method
- To identify the optimal experimental conditions (concentration, temperature and period of immersion) for their maximum inhibition efficiency
- To derive the adsorption kinetics from the weight loss data

- To find the best inhibitor among the used materials
- To study the mechanism of corrosion inhibition by the selected plant extracts
- To evaluate the storage stability and durability of the plant extracts
- To monitor the effectiveness of the pickling bath for repeated usage in presence of the plant extracts
- To evaluate the efficiency of acid extracts prepared after washing with petroleum ether
- To prepare extracts by dipping the materials in the acidic medium for 12 hours and evaluating its inhibiting ability
- To assess the environmental safety of the extracts during its use
- To evaluate the industrial applicability of the selected plant extracts for corrosion resistance

1.17 Plant profile of inhibitors selected

Cassia fistula Leaves (Sarakondrai)

Family	: Caesulpinaceae
Genus	: *Cassia*
Species	: *fistula*
Botanical Name	: *Cassia fistula*
Common Name	: Fistula, Laburnum, Purging Fistula, Golden Shower, Amaltas
Tamil name	: Sarakondrai

A tropical ornamental tree with a trunk consisting of hard reddish wood, growing up to 40 feet tall. The wood is hard and heavy; it is used for cabinet, inlay work etc. It has showy racemes, up to 2" long, with bright, yellow, fragrant flowers. These flowers are attractive to bees and butterflies. The fruits are dark-brown cylindrical pods, also 2' long, which also hold the flattish, brown seeds (up to 100 in one pod). These seeds are in cells, each containing a single seed. Bark of tree is rich in tannins.

Figure 1.3

***Cassia fistula* leaves**

Characteristics and Constituents:

The leaves of Cassia fistula contain free rhein, glucoside and sennosides A and B. A butanol extract of the powdered stem bark contained tannins while the benzene extract yielded lupeol, 1-sitosterol and hexacosanol. From the alcoholic extract of the pods an anthraquinone (fistulic acid) was obtained and identified as 1,4-dihydroxy-6,7-dimethoxy,2-methyl anthraquinone-3-carboxylic acid. Kaempferol and a proanthocyanidin have been isolated from the flowers and leucope-largonidin trimer from the bark.

Bougainvillea spectabilis Leaves (Kakithapu)

Family	:	Nyctaginacaea
Genus	:	*Bougainvillea*
Species	:	*spectabilis*
Botanical name	:	*Bougainvillea spectabilis*
Tamil name	:	Kakithapu

Bougainvillea is a genus of flowering plants native to South America from Brazil west to Peru and south to southern Argentina (Chubut Province). Different authors accept between four and 18 species in the genus. The name comes from Louis

Antoine de Bougainville an admiral in the French Navy who encountered the plant in Brazil in 1768 and first described it to Europeans.

They are thorny, woody, vines growing anywhere from 1-12 meters tall, scrambling over other plants with their hooked thorns. The thorns are tipped with a black, waxy substance that is easily left in the flesh of an unsuspecting victim. They are evergreen where rainfall occurs all year, or deciduous if there is a dry season. The leaves are alternate, simple ovate-acuminate, 4-13 cm long and 2-6 cm broad. The actual flower of the plant is small and generally white, but each cluster of three flowers is surrounded by three or six bracts with the bright colors associated with the plant, including pink, magenta, purple, red, orange, white, or yellow. *Bougainvillea glabra* is sometimes referred to as "paper flower" because the bracts are thin and papery. The fruit is a narrow five-lobed achene. (http://en.wikipedia.org/wiki/Bougainvillea)

Figure 1.4

Bougainvillea spectabilis leaves

Mirabilis jalapa flowers(Anthimalli or 4'O' Clock)

Family	:	Nyctaginaceae
Genus	:	*Mirabilis*
Species	:	*jalapa*
Botanical name	:	*Mirabilis jalapa*
Tamil name	:	*Nalu Mani Poo or Anthimalli*

Figure 1.5

***Mirabilis jalapa* flower**

Mirabilis jalapa (The **four o'clock flower** or **marvel of Peru**) is the most commonly grown ornamental species of *Mirabilis*, and is available in a range of colours. Mirabilis in Latin means wonderful and Jalapa is a town in Mexico.

The common garden variety four-o'clock (Mirabilis jalapa) is also known as Marvels of Peru. Four o'clock received its name because of its habit of opening in the late afternoon. It is not actually the time of day that causes the flowers to open, but the drop in temperature. The flowers close the next morning, except on dull, cloudy days. A curious aspect of this plant is that flowers of different colours can be found simultaneously on the same plant. Additionally, an individual flower can be splashed with different colours. Another interesting point is a colour-changing phenomenon. For example, in the yellow variety, as the plant matures, it can display flowers that gradually change to a dark pink color. Similarly white flowers can change to light violet.