INTRODUCTION

CHAPTER I

INTRODUCTION

1.1 Importance of Corrosion Studies:

It is nowadays 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 pollution of air and water resulting in a more corrosive environment.
- strict safety standards of operating equipment which may fail in a catastrophic manner due to corrosion.

Corrosion studies have become important due to increasing awareness of the need to conserve the world's metal resources. Rapidly diminishing metal resources will have more profound effect on civilization than the much publicized energy crisis. Many energy resources are still available for commercial exploitation. However, as yet, there exist no practical substitutes to many commonly used metals and alloys whose specific engineering properties make them indispensable. Evidently more concern must be shown for conservation of metals by minimizing losses due to corrosion.

1.2 Corrosion in Industries:

Occurrence of corrosion and its practical control is an area of study covering a wide range of scientific knowledge. Corrosion Science provides a medium for the communication of ideas, developments and research in all aspects of this field and includes both metallic and non-metallic corrosion. Corrosion is a huge issue for materials, mechanical, civil and petrochemical engineers.

In recent years, numerous failures of industries due to corrosion are reported. Most of the failures can be avoided by the addition of suitable corrosion inhibitors (Figure – 1).

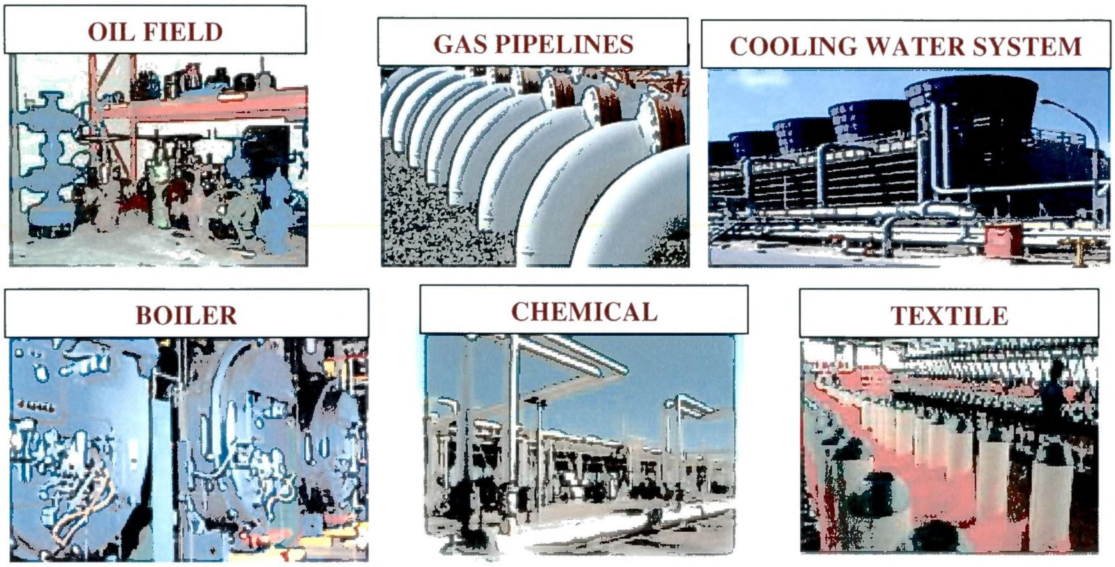

Figure - 1 Corrosion in Various Industries

Within the petroleum producing industry corrosion is responsible for millions of U.S. dollars of cost associated with the loss of equipment through breakdowns caused by the loss of metals both from inside as well as outside. Corrosion affects all stages in the exploitation of crude oil ranging from drilling of wells through the separation process export pipelines, storage tanks, refineries and even the internal combustion engine.

Several kinds of inhibitors can be used to inhibit the corrosion of natural gas pipelines. Eg: organic, inorganic or natural product inhibitors.

Organic inhibitors for cooling water treatment are specially designed to handle various maintenance parameters such as controlling corrosion in cooling and heating systems and controlling calcium scale formation.

Global competition forces manufacturing companies to reduce production costs, where energy and metal prices are increasing rapidly. Therefore a good way to decrease production cost is to make maximum use of the energy available and to install systems with much longer usable lifetime. We need to use more technology in both installation and corrosion protection.

In the chemical industry corrosion is often responsible for significant shutdown and maintenance costs. Shutdowns are costly expensive terms of productivity losses, restart energy and material costs. Benefits from improving corrosion management will be extensive in the chemical industry, many other industries and the economy.

There are several problems within a boiler system some of which require chemical treatment and other mechanical means to overcome them. The major problems are:

- Scale
- Boiler water carryover
- Sludge Deposition

Corrosion monitoring techniques can help in several ways. A large number of corrosion monitoring techniques exist. Most of the industries utilize corrosion inhibitors to reduce corrosion.

World consumption of corrosion inhibitors is expected to grow to over 930 thousand metric tons during 2005 – 2010 (Figure – 2). The relatively low growth rates projected for corrosion inhibitors, all below GDP growth in each region, reflect the high level of maturity of most of the basic industries in the developed markets. They also reflect the replacement of steel by plastics, ceramics and corrosion resistant alloys in the industries. Industries have also used corrosion inhibitors more efficiently by employing better monitoring and control techniques to minimize discharges in the effluent streams and their impact on the environment.

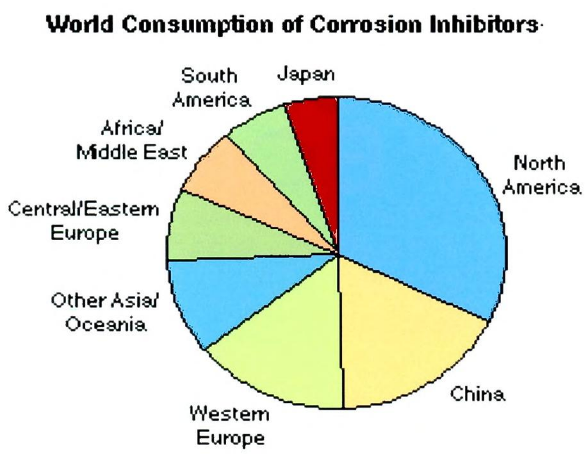

Figure – 2 World Consumption of Corrosion Inhibitors

Corrosion is so prevalent and takes so many forms that its occurrence and associated expenses cannot be eliminated completely. Corrosion affects our society on a daily basis, causing degradation and damage to household appliances, automobiles, air planes, highway bridges, energy production and distribution systems and much more. The cost of controlling this naturally occurring phenomenon- and costs associated with the damage it causes is substantial.

1.3 Economic considerations

In general, corrosion costs in most countries are in the range of 2-4% of the gross national product. Current losses due to corrosion in India are estimated at approximately over Rs 1.5 lakh Crore. (Dr.Thanki, Director, Corrosion Control & Monitoring Consultancy).

The losses due to corrosion may be direct loss or indirect loss which are listed below:

1.3.1 Losses due to corrosion:

Losses due to corrosion could be **direct** or **indirect (Figure – 3)**

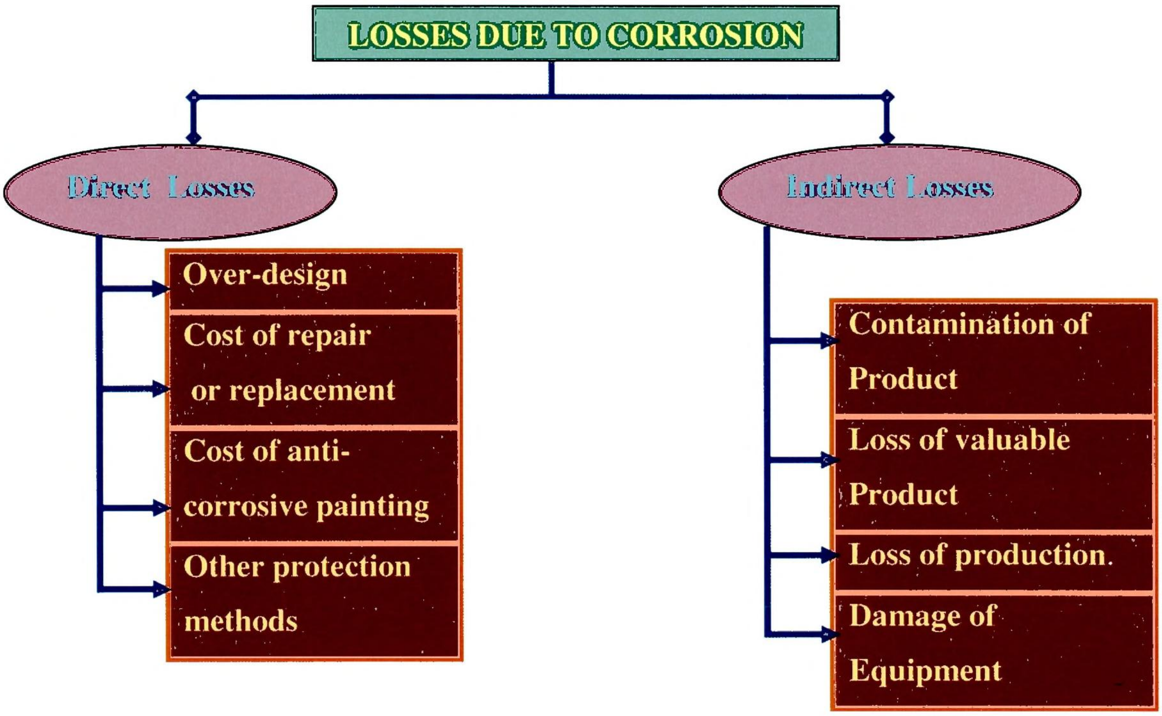

Figure – 3 Losses due to Corrosion

1.3.2 Cost of Corrosion:

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 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 -4

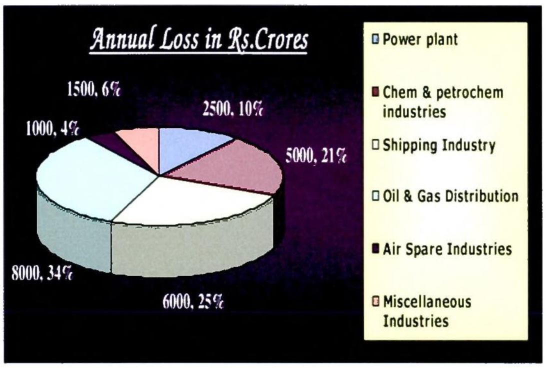

Figure – 4 Illustration of Economic impact of corrosion in various Industries

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.

1.3.2.1Corrosion losses & measurement in India:

Annual loss due to corrosion in India is Rs 1.5 lakh crore (Dr.Thanki, Director, Corrosion Control & Monitoring Consultancy.)

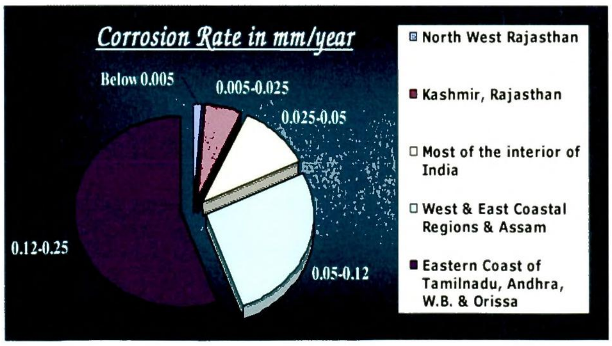

Figure – 5 Corrosion Rate in mm/year

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 expensive and more specifically recognized, the attention that is being given to the control and prevention of corrosion has increased. 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 Product 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).

1.4 Definition of Corrosion

Corrosion may be defined in several ways. "Corrosion is largely an electrochemical phenomenon, which may be defined as destruction by electrochemical or chemical agencies" – **Ulick R. Evans**, the British Scientist who is considered the 'Father of Corrosion'.

"Corrosion is the destructive result of chemical reaction between a metal or metal alloy and its environment" – **Denny A Jones, 1992.**

The international standard definition of corrosion is as follows:-

"Physicochemical interaction between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment or the technical system of which these form a part" (ISO 8044-1986).

A broader, but widely accepted alternate definition, from the International Union of Pure and Applied Chemistry (IUPAC) encompasses the degradation of non-metals as well as metallic materials, as follows:

"Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in consumption of the material or dissolution into the material of a component of the environment".

1.5 Principles of Corrosion

Corrosion resistance of a material depends on many factors. To understand corrosion principles one should have knowledge of several disciplines.

- Thermodynamic principles
- Electrochemical principles
- Metallurgical principles
- Physical and Chemical principles

1.5.1 Thermodynamic principles

Thermodynamic and electrochemical principles have maximum importance in determining the corrosion behavior of materials. Thermodynamic principles can indicate the spontaneity of a chemical reaction. They are used to determine whether corrosion is theoretically possible.

1.5.2 Electrochemical principles

Electrochemical corrosion involves two half-cell reactions; an oxidation reaction at the **anode** and a reduction reaction at the **cathode**. For iron corroding in water with a near neutral pH, these half-cell reactions can be represented as:

Anode reaction : $2Fe => 2Fe^{2+} + 4e^-$

Cathode reaction : $O_2 + 2H_2O + 4e^- => 4OH^-$

There are obviously different anodic and cathodic reactions for different alloys exposed to various environments. These half-cell reactions are thought to occur (at least initially) at microscopic anodes and cathodes covering a corroding surface.

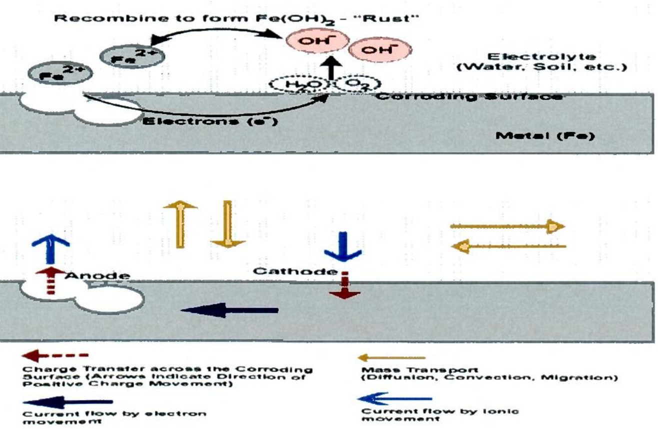

Figure -6 Schematic representation of electrochemical corrosion process (aqueous corrosion of iron under near neutral pH conditions)

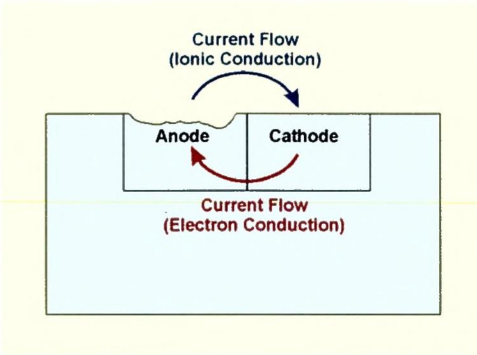

Figure - 7 Schematic representation of current flow (conventional current direction) in a simple corrosion cell

From the above theory it should be apparent that there are four fundamental components in an electrochemical corrosion cell:

- An anode.
- A cathode.
- A conducting environment for ionic movement (electrolyte).
- An electrical connection between the anode and cathode for the flow of electron current.

If any of the above components is missing or disabled, the electrochemical corrosion process will be stopped. Clearly, these elements are thus fundamentally important for corrosion control.

1.5.3 Metallurgical principles

Metallurgical principles help to understand corrosion behaviour of a metal. In many cases the metallurgical structure of an alloy can be so changed as to improve its corrosion resistance.

1.5.4 Physical and Chemical principles

Physical chemistry and its various disciplines are most useful for studying the mechanism of corrosion reactions, the surface conditions of metals and other surface conditions of metals and other basic properties.

1.6 Classification of Corrosion

Corrosion of metals occurs by the attack of surrounding environment or medium on the surfaces of metals. Corrosion is classified into two types

1.6.1 Dry corrosion

These are generally metal/gas or metal/vapour reaction involving oxygen or halogen *etc*.

1.6.2 Wet corrosion

These are reactions of metals with aqueous environments. For this reason, this is known as immersion corrosion. Underground corrosion is classified as a wet corrosion.

1.6.3 Electrochemical corrosion

Metals corrode due to their thermodynamic instability. Most of the metals are stable in their oxidized form. There is a decrease in free energy during the corrosion process of metals.

All wet type corrosion reactions are electrochemical. The corrosion process consists of two reactions namely anodic and cathodic reactions.

The anodic reaction involves metal dissolution.

$$M \rightarrow M^{Z+} + Ze^- \quad \text{(or)}$$

$$M + H_2O \rightarrow MO + 2H^+ + 2e^-$$

The cathodic reaction depends on the environment.

(i) During atmospheric and underground exposure of metals, the most common cathodic reaction is

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

(ii) The cathodic reaction under immersed condition is

a) $2H^+ + 2e^- \rightarrow H_2$ (acid solution)

b) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (neutral solution)

c) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (basic solution)

The above cathodic and anodic reactions occur simultaneously on numerous local anode and cathode areas of the metals at equal rates. The electrons produced during anode reaction are consumed at cathode due to the corresponding reduction reaction. Thus, there exists a current flow between anode and cathode areas of the metal.

1.6.4 Chemical corrosion

This involves direct chemical reaction of a metal with its environment. There is no transport of electric charge and the metal remains film free. It is of three types namely,

(i) Oxidation corrosion

(ii) Hydrogen corrosion and

(iii) Liquid-Metal corrosion.

1.7 Forms of corrosion

Various forms of corrosion are pictorially depicted in Figure - 8

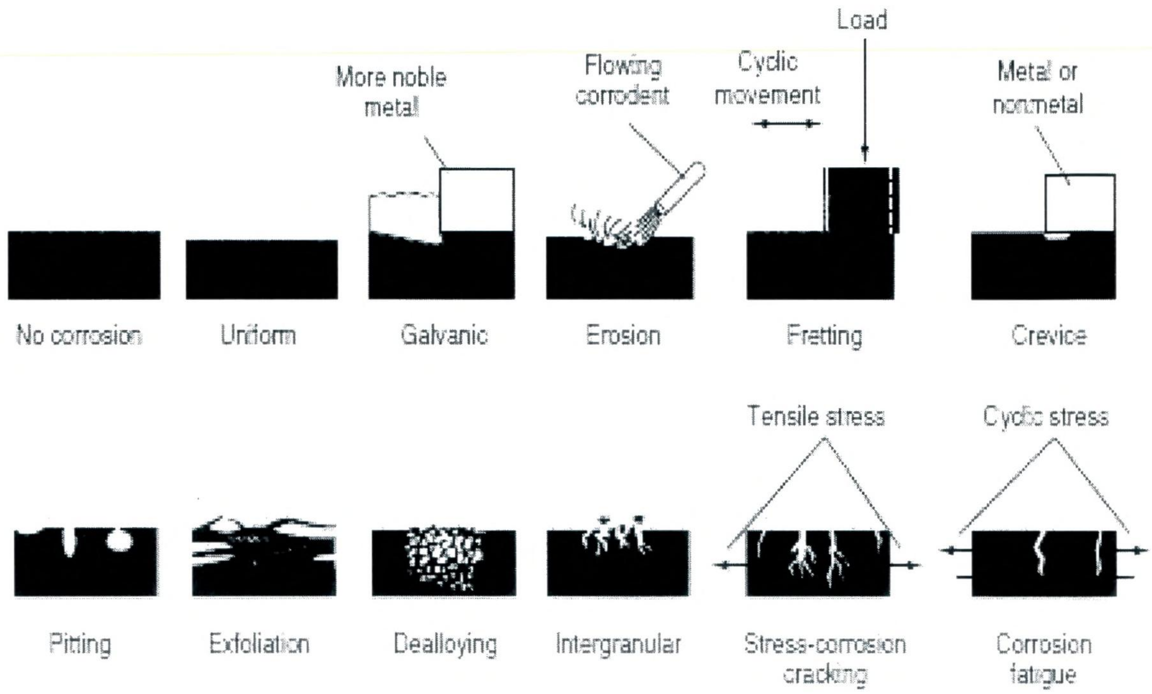

Figure – 8 Schematic representation of the common forms of corrosion

1.8 Corrosion Monitoring Techniques

The field of corrosion measurement, control and prevention covers a very broad spectrum of technical acitivities. Corrosion measurement involves measuring the corrosion rate of the metal in the environment to which it is subjected. The methods involved in measuring are qualitiative and gives feedback to enable corrosion control and prevention methods to be optimized.

A wide variety of corrosion monitoring techniques are available. They include:

- Non Destructive Testing Analytical Chemistry
- Analytical Chemistry
- Operational Data
- Fluid Electrochemistry
- Corrosion Monitoring

1.8.1 The Need for Corrosion Monitoring

The rate of corrosion indictates how long any process plant can be usefully and safely operated. The measurement of corrosion and the action to remedy high corrosion rates permits the most cost effective plant operation to be achieved while reducing the life-cycle costs associated with the operation.

Corrosion monitoring techniques can help in several ways:

- ❖ by providing an early warning that damaging process conditions exist which may result in a corrosion-induced failure.
- ❖ by studying the correlation of changes in process parameters and their effect on system corrosivity.
- ❖ by diagnosing a particular corrosion problem, identifying its cause and the rate controlling parameters, such as pressure, temperature, pH, flow rate, etc.
- ❖ by evaluating the effectiveness of a corrosion control/prevention technique such as chemical inhibition and the determination of optimal applications.
- ❖ by providing management information relating to the maintenance requirements and ongoing condition of plant.
- ❖ A large number of corrosion monitoring techniques exist. The following list details the most common techniques which are used in industrial applications:

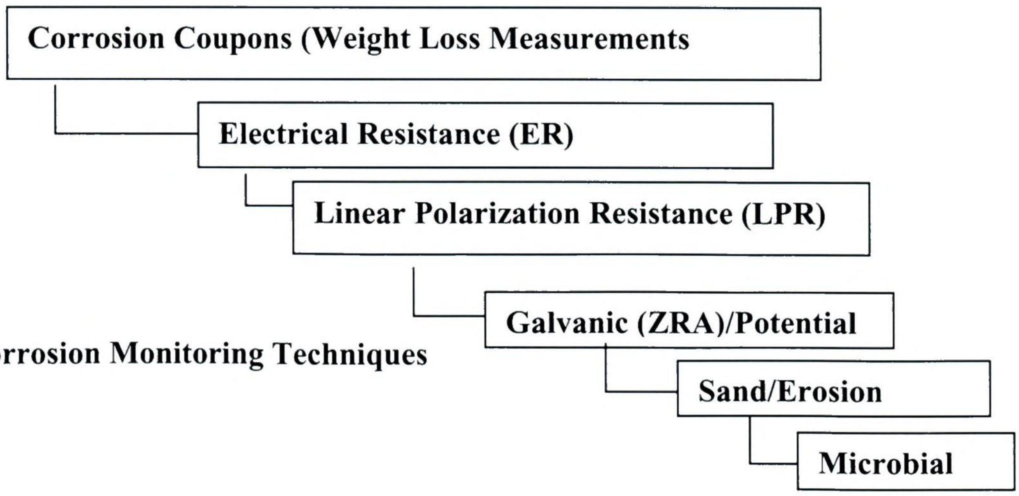

Figure – 9 Corrosion Monitoring Techniques

Of the techniques listed above, corrosion coupons, ER, and LPR form the core of industrial corrosion monitoring systems. The other four techniques are normally found in specialized applications.

These corrosion monitoring techniques have been successfully applied and are used in an increasing range of applications because:

- The techniques are easy to understand and implement.
- Equipment reliability has been demonstrated in the field environment over many years of operational application.
- Results are easy to interpret.
- Measuring equipment can be made intrinsically safe for hazardous area operation.
- Users have experienced significant economic benefit through reduced plant down time and plant life extension.

1.8.2 Corrosion Control Methods:

Metallic corrosion can be prevented by either changing the metal or altering the environment or by separating the metal from the environment. In addition, corrosion can also be prevented by changing electrode potential of the metal. The above discussions are pictorially represented in Figure – 10.

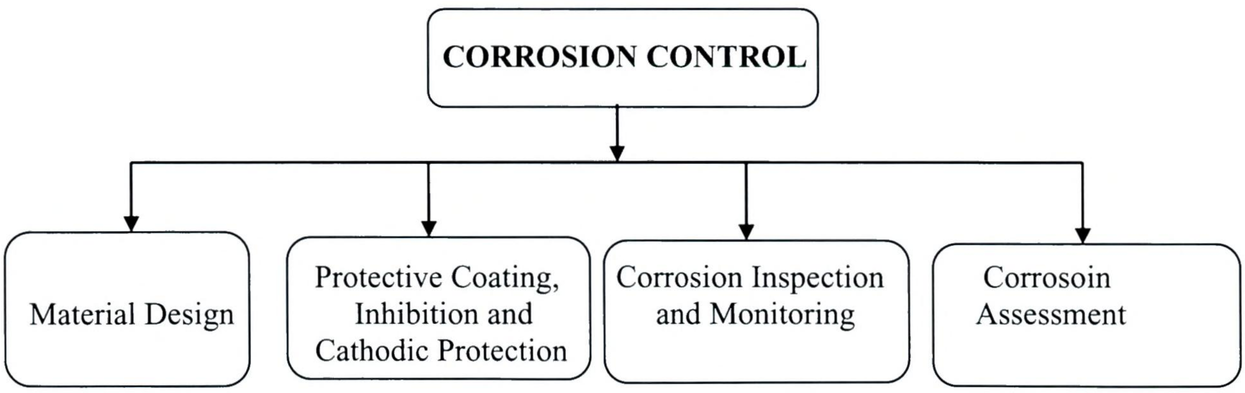

Figure – 10 Corrosion Control Methods

1.8.3 Use of Inhibitors

1.8.3.1 Inhibitors – A Boon for Corrosion Chemists

"An inhibitor is a chemical substance which when added in small concentration to an aggressive environment decrease the corrosion of the exposed metal".

"Inhibitors are substances which when added in small quantity to a corrosive environment lower the corrosion rate. They reduce corrosion by either acting as a barrier by forming an adsorbed layer or retarding the cathodic and / or anodic process"

Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitors reduce corrosion processes by either:

- Increasing the anodic or cathodic polarization behavior (Tafel slopes)
- Reducing the movement or diffusion of ions to the metallic surface
- Increasing the electrical resistance of the metallic surface.

1.8.3.2 Types of inhibitors

One of the very important methods of minimizing corrosion today is the use of corrosion inhibitors. Much of the development work on corrosion inhibitors was accomplished from the late 1940s to the late 1960s and is still used today.

Corrosion inhibitors are extensively used in various applications and many plant operations are dependent on their successful application. The major use of inhibitors in acid solution is in pickling processes, for removal of rust , scale and corrosion products.

The inhibitive practices of iron and its alloys in acidic solutions are increased by the fact that iron and its alloys constitute the bulk of exposed metals in industrial and other environments and iron is more susceptible to attack in the acidic pH range.

Depending upon the mechanism and mode of protection, inhibitors can be classified under the following group

Inhibitors are classified into

- Adsorption Inhibitors
- Vapour phase Inhibitors
- Film forming Inhibitors

❖ Chemical Passivators

1.8.3.3 Requirement for selection of inhibitors:

Selection of inhibitors with following properties (Figure-11) will enable good inhibition.

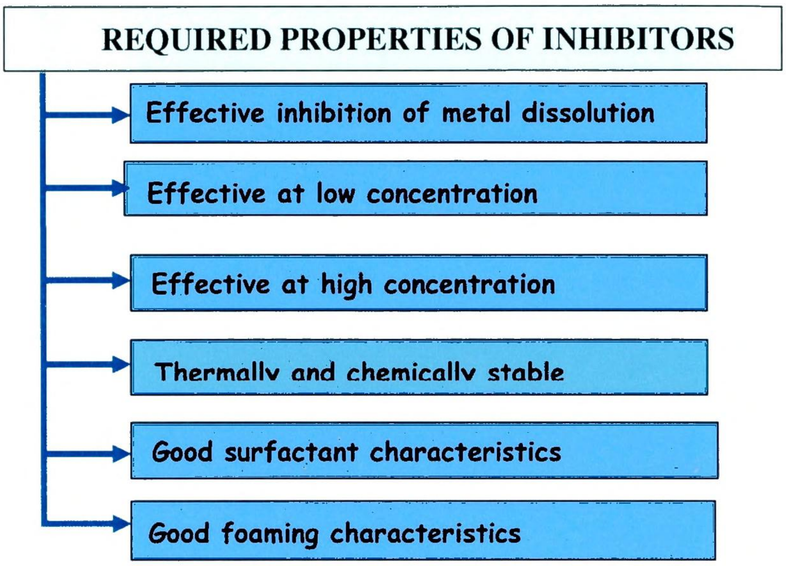

Figure – 11 Required Properties of Inhibitors

1.8.3.4 Richness of organic inhibitors

The richness of organic Inhibitors depends upon

1. The size of the organic molecules
2. Aromaticity or conjugated bonding
3. Chain length
4. Strength of bonding to the metal substrates
5. Type of number of bonding atoms or groups in the molecule
6. The ability to become cross linked
7. The ability to complex with the metal atoms as a solid with in the metal lattice
8. Adequate solubility in the environment
9. Ability to form film, prevents uniform corrosion attack
10. Organic Inhibitors increase the activation energy on the metal surface (Passivation)
11. Organic Inhibitors have been shown to eliminate corrosion over wide range of pH.

Acid pickling baths are employed to remove undesirable scale from the surface of the metal. Once the scale is removed, the acid is then free to attack the metal surface. Because of the general aggressive nature of the acid solution, metal dissolution takes place leading to corrosion.

One way to protect the metal against corrosion is to add certain organic molecules, which can adsorb on the surface and form a protective layer. Most of the acid corrosion inhibitors are organic compounds, such as those containing N, S, O and aromatic ring. The efficiency of these inhibitors mainly depend on their ability to be adsorbed on the metal surface, which results with replacement of water molecules at the corroding surface. The adsorption of inhibitors on the metal/solution interface is influenced by i) nature and surface charge of the metal ii) type of aggressive electrolyte iii) chemical structure of inhibitors.

Many N-heterocyclic compounds such as triazole derivatives, tetrazole derivatives, pyrrole, pyridine derivatives, pyrazole derivatives, indole derivatives, quinoline derivatives have been used for the corrosion inhibition of iron and steel in acidic media. As an important N-heterocyclic compound, imidazoline derivatives are non-toxic and biodegradable. This makes the investigation of their inhibiting properties significant in the context of the current priorities to produce eco-friendly inhibitors.

The present investigation has been conducted using the following synthesized imidazoline derivatives on mild steel corrosion in 0.5 M H_2SO_4 and in 1 M HCl.

- 2-**phenyl imidazoline (P2I)**
- **2-(3',4',5'-trimethoxyphenyl)-imidazoline (TMP2I)**
- **2-(3',4'-dimethoxyphenyl)-imidazoline (DMP2I)**
- **2-(2'-chlorophenyl)-imidazoline (OCP2I)**
- **2-(4'-N,N- dimethylaminophenyl)-imidazoline (PNDMP2I)**
- **2-(4'-nitrophenyl)-imidazoline (PNP2I)**

Search of literature reveals that the inhibition effect of the above mentioned imidazoline derivatives have not been reported so far and hence the imidazoline derivatives are selected and investigated for the present study.

The research work aims at establishing the effectiveness of the synthesized imidazoline derivatives as corrosion inhibitors in 0.5 M H_2SO_4 and 1 M HCl media.

The scheme of current investigation is given in Figure - 12,

12 Inhibitior system

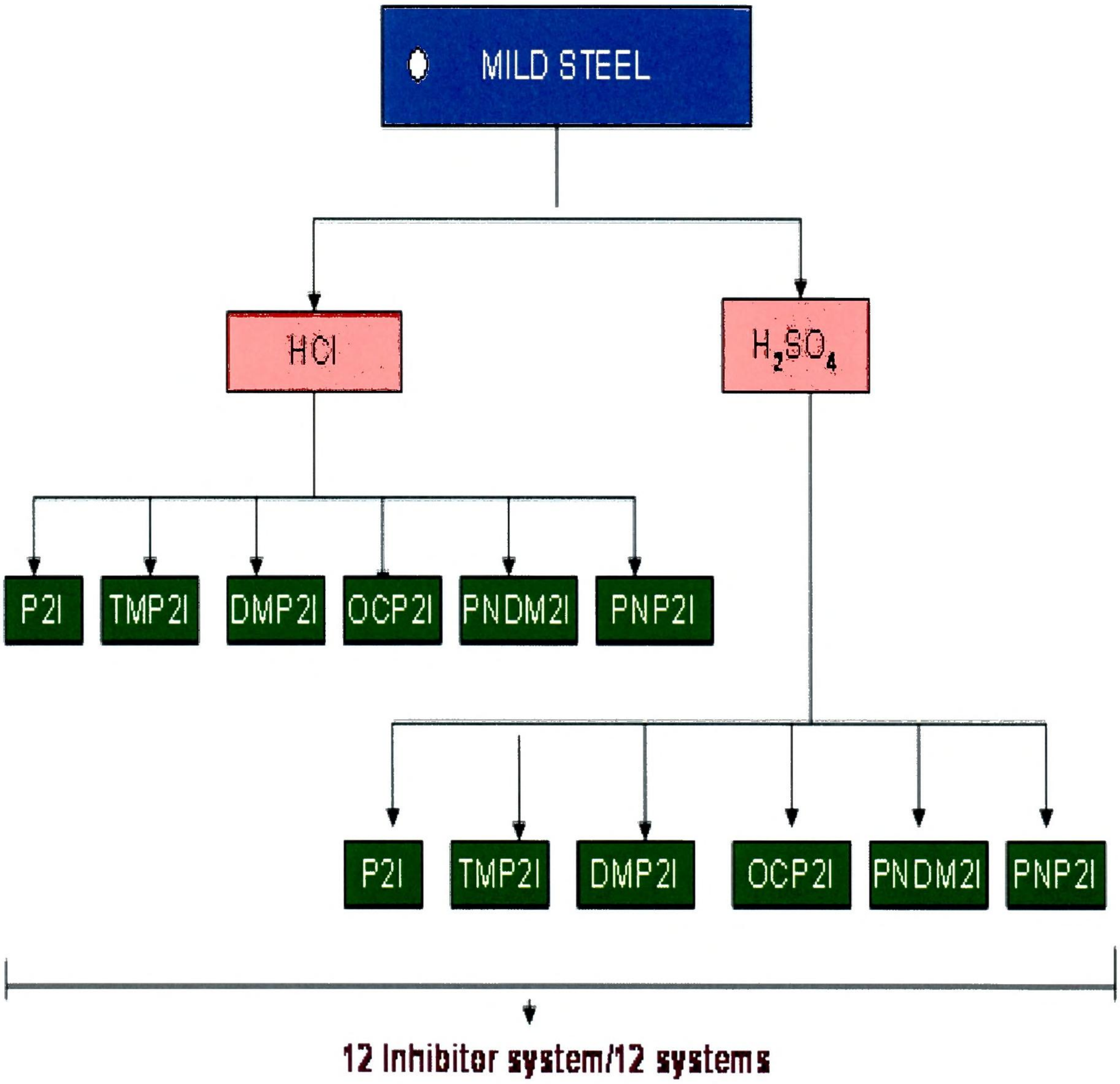

Figure - 12

1.9 OBJECTIVES

1. To synthesize the organic compounds - 2- phenyl imidazoline (P2I), 2-(3',4',5'-trimethoxyphenyl)-imidazoline (TMP2I), 2-(3',4' dimethoxyphenyl)-imidazoline(DMP2I), 2-(2'-chlorophenyl)-imidazoline (OCP2I), 2-(4'-N,N-dimethylaminophenyl)-imidazoline (PNDMP2I), 2-(4'-nitrophenyl)-imidazoline (PNP2I), from ethylene diamine and their respective aldehydes and characterize the synthesized compounds by IR spectral studies.
2. To study the inhibitive action of synthesized imidazoline derivatives for mild steel corrosion in the presence of Sulphuric acid and Hydrochloric acid medium by weight loss and electrochemical measurements.
3. To find out the optimum concentration and the optimum period immersion for maximum inhibition efficiency by weight loss studies a room temperature and at higher temperatures.
4. To fit the experimental data into various adsorption isotherms like Langmuir, Temkin, Freundlich, Flory Huggins and Frumkin isotherms using Statistical Package SPSS 17.
5. To calculate thermodynamic parameters for adsorption process and activation energy for corrosion process.
6. To understand the mode of action of inhibitors by Linear polarization technique, Potentiodynamic polarization studies and Electrochemical Impedance Spectroscopic technique and to suggest a suitable mechanism.
7. To investigate the morphology of mild steel surface in the presence of investigated inhibitors using IR spectroscopy, UV-VIS spectroscopy and Scanning Electron Microscopy.
8. To investigate the dependence of inhibition efficiency of P2I, TMP2I and DMP2I on theoretical chemical parameters such as the energies of the highest occupied molecular orbital (E_{HOMO}), the energy of lowest unoccupied molecular orbital (E_{LUMO}), the energy difference, dipole moments (μ) and total energies using **Gaussian 03 W** code of programs using 6-311G(d,P).

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