CHAPTER – 1

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CHAPTER – 1

GENERAL INTRODUCTION TO CORROSION AND NATURE OF THE PRESENT PROBLEM

1.1. Introduction

Ecology of civilized man revolves around material used by him; so much so, that we speak of Stone Age, Bronze Age, and Iron Age etc. with the tremendous growth of artefacts and possible limitation of the supply of mineral resources, economic and efficient use of materials has become extremely important. With regards to this, the effect of environment on materials forms an important aspect.

Although man is not an aquatic organism, he has become increasingly dependent on the aquatic environment to satisfy his technological and social needs. The water present on the surface of the earth is put to multifarous use. Water bodies form a resource of man's domestic, agricultural and industrial use. After being used the water containing the residuals of the activities is allowed to flow down into the stream or the Rivers. These waste waters are loaded with organic and inorganic chemicals, which are not only harmful to plants, animals and man, but also to metal structures in the water body namely pipelines, communication cables, bridges, boats, etc.

The interaction can not be ignored. One particular interaction of metal with its environment is that of corrosion. Corrosion kills people, waste resources and costs money we can ill afford.

All materials (Metals) are extracted from their ores which is the most stable condition of matter. As such to regain stability, metals resort to corrosion by way
of reacting with oxygen, water and other non-metallic substances in the earth’s environment.

The film so formed on the surface, no doubt is a boon in disguise to the later. This thin layer of oxide cuts off further contact between atmospheric oxygen and the metal and protects the metal as long as it stays intact. This is nature’s own way of protecting metals from the onslaught of environmental agencies. The actual problem, however, arises when this film barrier is breached. This may be affected by a number of factors like corrosive environment, mechanical stress, high temperature, etc. The materials degrade with time due to exposure to the environment in addition to the wear and tear of use. From the initial handling of materials by human agencies to the ultimate demise of a store, the materials experience wastage by spillage, chemical attack by the constituents of environment or by biological degradation from rodents, pests and fungi. Corrosion is the fate of metals and alloys exposed to the environment. The material surface degrades when exposed to radiation, moisture, erosive flows, heat and temperature cycles, microorganisms and chemical action of gases and contaminants, etc.¹.

The pollution in air or in water or in the ground due to material pollutants, caused by the disintegration of chemicals, insecticides, fertilizers or by the effluents and wastes from industries, power, motor exhausts or by foul smells from sewage treatment plants is all due to the abuse of materials.

1.2. Corrosion and its Mechanism

Corrosion is naturally occurring phenomenon commonly defined as the deterioration of substance (usually a metal) or its properties because of reaction with its environments ⁶.
The mechanism of the metallic corrosion can be described as follow. When a piece of a metal is immersed in a salt solution, it starts dissolving and forms its ions in the solution (Fig.1.1). The reaction takes place as follows,

\[ M \rightarrow M^{2+} + 2e^{-} \quad \text{................................. (1)} \]

Where M denotes a divalent metal. On the other hand, the ions already present in the solution may tend to deposit on the metal surface and that of positive ions close to the metal surface (an electrical double layer) (Fig.1.2) giving rise to an electric field. This attainment of equilibrium develops an electric potential. The electrode potential of metal at the equilibrium stage is denoted by \( \rho \). Above this value of potential, metal ions are stable and below this value, metal atoms are stable. The e.m.f. series is an orderly arrangement of the standard oxidation or reduction potentials for all metals. The more positive oxidation values or more negative reduction values correspond to the more reactive metal. The e.m.f. series of the standard oxidation potential for some metals are shown below.

<table>
<thead>
<tr>
<th>Electrode reaction</th>
<th>Standard oxidation potential ( \rho ) (V) at ( 25^\circ \text{C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^- )</td>
<td>1.66</td>
</tr>
<tr>
<td>( \text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- )</td>
<td>0.763</td>
</tr>
<tr>
<td>( \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- )</td>
<td>0.440</td>
</tr>
<tr>
<td>( \text{H}_2 \rightarrow 2\text{H}^+ + 2 \text{e}^- )</td>
<td>0.000</td>
</tr>
<tr>
<td>( \text{Cu} \rightarrow \text{Cu}^{2+} + 2 \text{e}^- )</td>
<td>-0.337</td>
</tr>
</tbody>
</table>

This means that if the potential of metal is raised above \( \rho \), it will have tendency to form more metal ions and metal will start dissolving. This phenomenon is called corrosion. In a general sense, any process which causes a
metal to lose its loosely bound electrons in metallic state to generate solvated
cation in solution to form an oxidation product is a corrosion process. Thus for a
metal to undergo corrosion, it is necessary that its potential be raised above \( \rho_o \) value. To achieve this, some other factor must be involved in the corrosion
reaction. The equation 1 is only a half reaction liberating electrons and it
represents the oxidation of the metal \(^6\).
Considering that the salt solution contains plenty of hydrogen ions and oxygen,
the second half reaction by hydrogen is as follow,
\[
2H^+ + 2e^- \rightarrow H_2 \text{(gas)} \quad \text{... (2)}
\]
And the reaction caused by oxygen is
\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \\
\text{Or}
\frac{1}{2}O_2 + H_2O + 5e^- \rightarrow 2OH^- \quad \text{... ... ... ... ... ... ... ... ... ... ... (3)}
\]
Reaction (2) and (3) are electron consuming represent the reduction
process. The overall net reactions are:
(1) + (2), \( M + 2H^+ \rightarrow M^{2+} + H_2 \) (g) \( \quad \text{... ... ... ... ... ... ... ... ... ... ... (4)} \)
(1) + (3), \( M + \frac{1}{2}O_2 + H_2O \rightarrow M^{2+} + 2OH^- \quad \text{... ... ... ... ... ... ... ... ... (5)} \)
The electrode at which there is liberation of electrons or oxidation occurs
(or electricity leaves the electrodes and enters the electrolyte) is called as ‘anode’
and the electrode at which there is an acceptance of the electrons or reduction
occurs (or current enters in the electrode from the electrolyte) is called ‘cathode’.
The corrosion process is accompanied by the transfer of electrons from anode to
the cathode. In general, during corrosion, the metal undergoes oxidation while
easily reproducible impurities or constituents act as the cathode.
1.3. Forms of Corrosion

Metal corrodes in different ways depending on the environment to which it is exposed. Different forms of corrosion are described below\textsuperscript{7-10}.

1.3.1. Uniform Corrosion

This is the most common form of corrosion in which the entire metal surface degrades but with a near uniform rate. It is characterized by a chemical or electrochemical reaction and caused due to heterogeneity in metal. This type of corrosion leads to greatest amount of damage to the metal but draws least attention, since it can be well predicted and remedied in time. By choosing proper material and by providing adequate thickness of the metal for the desired life, this type of corrosion can be got over.

1.3.2. Pitting Corrosion

This is caused by the highly localised electrochemical reaction and commonly observed in the case of stainless steels, aluminium alloys and metals which form passive films. This is the most serious form of corrosion because it takes place with great rapidity and the failure of metal occurs spontaneously due to perforations of metal surface. It is difficult to predict and replacement of material depending on the severity of pitting is the only remedial measure. In general, pitting is very destructive.

1.3.3. Stress Corrosion Cracking

Corrosion resulting from very high tensile stress is known as stress corrosion and is marked by cracks. Failure of metal surface occurs due to the combination of stress and the corrosion taking place simultaneously. It is equally serious form of corrosion as failure occurs suddenly. Usually, the more severe the corrosion medium and higher the stress faster the occurrence of cracking. In
some cases, failure of metals occurs due to fatigue and rupture of protective film as a result of combined action of corrosion and stress. Occasional check-up of metallic surface and replacement wherever necessary is the only remedial measure.

1.3.4 Galvanic Corrosion

It is the result of dissimilar metals exposed to the fluids which are electrically conductive.

An electrochemical reaction sets in at the junction of the two metal surfaces and an electric potential is established causing galvanic current to flow from the least noble metal to the more noble metal resulting in the metal ion migration causing the failure.

This type of corrosion is found to be more serious when a large surface area of the noble metal is joined to a small area of the less noble metal.

1.3.5 Erosion Corrosion

This is caused by the damage of the passive film by the turbulent flow of the fluid; it is different from abrasion caused by the mechanical damage to the metal surface by solids or solid suspended in a fluid. Cavitations and impingement caused by the formation and collapse of gas bubble in regions of fluids which are in turbulence due to localised pressure fluctuation lead to erosion corrosion.

1.3.6 Intergranular Corrosion

This is caused by a localized attack at the grain boundaries of the metal resulting in a loss of strength and ductility. Grain boundary material of limited area acts as anode and is in contact with large area of grains acting as cathode.
The attack is often rapid penetrating deeply into the metal and sometimes causing catastrophic failure.

1.3.7 Concentration Cell Corrosion

Many cases of failures of metal occur due to concentration cells which form on the surface of metals exposed to portions of a solution of varying composition and are electrochemical in nature. The variation in composition may be due to fluctuations in temperature and insufficient agitation. This type of corrosion sometimes termed as crevice corrosion, differential aeration corrosion, or lodgement corrosion.

1.3.8 Fretting Corrosion

This is the rapid deterioration of metals at joints when their surfaces are bolted, clamped or press fitted and subjected to pressure and vibrating motion. The mechanism and cause for this corrosion is not completely known. The corrosion may occur because of small metal particles being torn off from the metal surface by small relative movements which are subjected to oxidation by the surrounding atmosphere.

1.3.9. Microbiological Corrosion

Corrosion occurs due to activity of bacteria, fungi and algae which may be aerobic or anaerobic. Several instance of such corrosion have been reported in recent year\textsuperscript{11–18}. The metabolic activity of micro-organisms can cause deterioration by direct or indirect processes. The most common micro-organisms which bring about the corrosion are sulphate reducing bacteria.
1.3.10. Underground Corrosion

This is also known as soil corrosion. The various bacteria and microorganisms present in the soil can greatly accelerate the rate of corrosion of the materials. The corrosive properties of soil depend upon the degree of aeration, amounts of salts present, moisture content, and resistivity of soil and pH of the medium.

1.4. Factors Affecting Corrosion

Corrosion is characterized by the anodic and the cathodic changes in the system and hence it is quite essential to know the role played by both of them during the corrosion process.

From the anodic point of view Champion\textsuperscript{19} has stated the following factors affecting corrosion:

- a) Electrode potential of the metal in the system under consideration.
- b) State of aggregation of metal including crystal size and character, the presence of pores and cracks and the nature of the surface film or scale including those formed during corrosion.
- c) The freedom from the internal or external strain.
- d) Over voltage of the metal.
- e) The nature and the concentration of the elements in the solid solution in the metal.
- f) The presence of different phases in the metal and their distribution (solid solution or inclusions).
- g) Temperature and its gradient.
- h) Irreversible electrode potential.
From cathodic point of view, following are the factors affecting the corrosion rate.

a) Characteristics of the ions formed by the ingredients in the electrolyte oxidizing or reducing nature.
b) Over voltage of the gas evolved, i.e. normally hydrogen.
c) Mobility of the ions.
d) pH of the electrolyte.
e) Solubility of the corrosion products formed within the electrolyte and on metal surface.
f) Over voltage of the insoluble corrosion products with respect to the metal.
g) The nature of chemical reaction e.g. exothermic and endothermic.

1.5. Corrosion Control

Corrosion of metal occurs when they come in electrical contact with a corrosive environment. Therefore metallic corrosion can be prevented by either changing the metal, or altering the environment of by separating the metal from the environment. In addition, corrosion can also be prevented by changing electrode potential of the metal. The most effective and cheap method; however is to deal with the corrosion problem at the design stage itself. A large number of corrosion failures are due to improper design and failure to use available knowledge. Many costly corrosion failures can be prevented at the cost of pencil and eraser used properly at the design stage.

Thus corrosion control could be based entirely on i) the selection of a particular metal (or alloy) or rejection of metals in favour of non-metallic material, e.g. by a glass reinforced polymer or fiber reinforced polymer, ii) the use of corrosion resistant material and reduction of the aggressiveness of the
environment by changing composition, removing deleterious impurities, lowering
of temperature and velocity and by adding corrosion inhibitors, etc\textsuperscript{19}.

Vernon\textsuperscript{20} has outlined the Scheme of “Methods of Preventing Corrosion”
in 1957. Tomashov\textsuperscript{21,23-26} has produced a detailed Scheme of control based on
the electrochemical mechanism and the methods have been classified
considering the principles involved.

Corrosion control can be achieved in a number of ways. Some methods
include protection of metal by using plasma spraying, spray painting, chemical
electroplating, vacuum coating etc. However, most of these methods can be
advantageous by only under specific conditions. The following are some of the
methods which are used to minimize corrosion.

1.5.1. Protection by Purification and Alloying of metals.

Surface alloying is widely employed to impart adequate corrosion
resistance; however, conventional methods of alloying involve bulk processing
using large quantities of expensive precious metals to be consumed into the body
of the material. Corrosion being essentially a surface phenomenon, bulk
processing is not only wasteful it may deteriorate the other properties of the
material. Because of these limitations, non-equilibrium techniques involving
surface modification have been developed. Amongst the different non-equilibrium
techniques used for controlled modifications of surface properties\textsuperscript{27-29}, ion
implantation is perhaps most useful.

Extra-pure metals exhibit corrosion resistance, particularly the
electronegative metals, such as aluminium and magnesium. Even the minute
traces of impurities decrease the corrosion resistance by a factor of 100 to 500
because of the increase in the number of local action couples. Purification of
metals is advantageous only if corrosion occurs purely by electrochemical mechanism.

1.5.2 Protection by Design.

The best possible means for controlling and preventing corrosion is to select the proper material to design it properly taking into consideration the fundamental principles which govern corrosion phenomenon. The contact of two dissimilar metals leading to galvanic couples in presence of an electrolyte is avoided. To prevent exposure of the joints of welds to an electrolyte, an insulating coating may be applied.

1.5.3 Protection by Conditioning the Environment.

An environment can be made less corrosive either by removal of the harmful constituents or by the addition of a substance that neutralizes or minimizes the effect of corrosive constituents e.g. de-humidification and purification of atmosphere, deaeration of water etc.

1.5.4 Use of Inhibitors.

Inhibitor is a chemical compound that, when added in small concentration stops or slows down corrosion of metals and alloys. It is well known in surface chemistry that surface reactions are strongly affected by the presence of foreign molecules. Corrosion processes, being surface reactions, can be controlled by compounds known as inhibitors which adsorb on the reacting metal surface. The term adsorption refers to molecules attached directly to the surface, normally only one molecular layer thick, and not penetrating into the bulk of the metal itself. The technique of adding inhibitors to the environment of a metal is a well known method of controlling corrosion in many branches of technology. A corrosion inhibitor may act in a number of ways: it may restrict the rate of the anodic
process or the cathodic process by simply blocking active sites on the metal surface. Alternatively it may act by increasing the potential of the metal surface so that the metal enters the passivation region where a natural oxide film forms. A further mode of action of some inhibitors is that the inhibiting compound contributes to the formation of a thin layer on the surface which stifles the corrosion process.

Inhibitors are classified in variety of ways\textsuperscript{7, 24, 25, 26}. The classification used herein closely follows the discussion given in literature \textsuperscript{27}. Types of inhibitors includes: a) anodic, b) cathodic, c) organic d) precipitation, and e) vapour-phase inhibitors.

(a) Anodic Inhibitors

Passivating or anodic inhibitors produce a large positive shift in the corrosion potential of a metal. There are two classes of anodic inhibitors which are used for metals and alloys where the anodic shift in potential promotes passivation, i.e., anodic protection. The first class includes oxidising anions that can passivates a metal in the absence of oxygen e.g. chromate.

The second class of anodic inhibitors contains ions which need oxygen to passivates a metal e.g. tungstate and molybdate. The concentration of the anodic inhibitor is critical for corrosion protection. Insufficient concentrations can lead to pitting corrosion or an increase in the corrosion rate. The use of anodic inhibitors is more difficult at higher salt concentrations, higher temperatures, and lower pH values and in some cases, at lower oxygen concentrations \textsuperscript{27}.

(b) Cathodic Inhibitors

Cathodic inhibitors retard or poison the cathodic reaction or selectively precipitate onto cathodic areas producing diffusion barriers to cathodic reactants,
thereby reducing the rate of the cathodic reaction. There are three types of cathodic inhibitors, such as hydrogen poisons, oxygen scavengers and cathodic precipitates. Hydrogen poisons are chemical species such as arsenic or antimony that retard the hydrogen reduction reaction.

Oxygen scavengers prevent corrosion by tying tip the oxygen in solution, thereby making it unavailable for the cathodic reaction e.g. sulphur dioxide and sodium sulphate. Cathodic precipitate inhibitors such as calcium carbonate or magnesium carbonate precipitate onto the cathodic areas producing a film that reduces the cathodic activity.27

(c) Organic Inhibitors

Generally, organic inhibitors adsorb on the entire metal surface impede corrosion reactions.27 Organic inhibitors consist of broad classes of organic compounds. For example, aliphatic organic amines adsorb by the surface active group which forms a chemisorptive bond with the metal surface. The hydrocarbon tails orient away from the interface toward the solution, so that further protection is provided by the formation of a hydrophobic network which excludes water and aggressive ions from the metal surface.28

(d) Precipitation Inhibitors

Precipitation inhibitors are film-forming compounds that produce barrier films over the entire surface. Phosphates and silicates, which are the most common, do not provide the degree of protection afforded by chromate inhibitors, but are useful in situations where nontoxic additives are required. Two main drawbacks to the use of phosphates and silicates are the dependence on the water composition and the control required to achieve maximum inhibition.27,28

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(e) Vapor-phase Inhibitors

Vapor-phase inhibitors are volatile compounds that adsorb onto metal surfaces, and retard or prevent corrosion by a variety of mechanisms\textsuperscript{27}. Inhibitors such as dicyclohexamine nitrate can protect a variety of metals such as steel-aluminium and tin-plate. A number of vapour-phase inhibitors are commercially available as powders or tablets. The system to be protected must be closed to maintain the volatile compound. The objects as large as the interior of an ocean-going tanker have been treated by this technique.

1.5.5 Cathodic and Anodic Protection

Most effective method of corrosion control in an electrolyte is the cathodic protection. It can be achieved in two ways, viz, by applying power impressed current or by using sacrificial anodes. Cathodic protection using external power supply, current leaves the auxiliary anode and enters both cathodic and anodic areas of the corrosion cells, returning to the source of D.C. current. External current polarizes the cathode areas to the open circuit potential of the anodes thereby bringing the entire metal surface at the same potential so that local action current no longer flows. The metal surface, therefore, cannot corrode as long as the external current is maintained.

When the sacrificial anode is attached to the protected structure, a galvanic couple is set up. To utilize this method the sacrificial anode must have a potential i.e. more electronegative than that of the protected structure. When connected, the structure is polarised cathodically and the sacrificial anode is polarised anodically. This polarisation explains the behaviour of the sacrificial anode in cathodic protection.
Anodic protection is a method of reducing the corrosion rate of immersed metals or alloys by controlled anodic polarisation which induces passivity. The chief advantage of anodic protection is that it can be applied to metals and alloys in mild electrolytes as well as in very corrosive environments, including strong acids and alkalis in which cathodic protection is not normally suitable.

1.6 Corrosion Testing Techniques

The extent and progress of corrosion can be evaluated in a number of ways which include weight change, change in the mechanical strength, increase in electrical resistance of a metal, depth of pitting, consumption of oxygen, evolution of hydrogen etc. The choice of the technique depends upon the particular type of corrosion being investigated. Some of the commonly used techniques are described below.

1.6.1 Weight Loss Method

The loss in the weight of the metal during the corrosion process is determined by electrochemical test and immersion test.

a) Electrochemical Test

A current of known density is applied in the system and the metal is made an anode. The loss in weight of the metal is measured after a definite time and then the metal piece is removed from the electrolyte. The corrosion products formed on the metal surface are removed by suitable chemical means. The loss in weight of the metal is determined by weighing before and after the test period. It is desirable to note the loss in weight at different time intervals by frequent replacement of the solution. The loss in weight in this method is expressed as mg cm⁻² hr⁻¹ or µg cm⁻² hr⁻¹ or kg m⁻² s⁻¹ or mg dm⁻² day⁻¹ (mdd).
b) Immersion Test

Instead of applying current, the piece of metal is immersed in the test solution for particular time and the weight loss is determined as mentioned in electrochemical test.

1.6.2 Kohen’s Test

If the corrosion reaction is exothermic then the rate of the reaction is proportional to the rise in temperature during the corrosion process; but there are limitations to this test and it is extremely dependent on the surface preparation of the metal specimen.

1.6.3 Polarisation Test

The cathodic and anodic changes occurring during corrosion are the liberation and acceptance of electrons which cause the rise in the potential of the anode and drop the potential of the cathode. These changes are accelerated by applying currents of various densities in the system and recording corresponding potentials of cathode and anode. The data provide certain electrochemical parameters for the rapid assessment of the initiation and the propagation of the corrosion reaction. This test is carried out by galvanostatic and potentiostatic techniques.

(a) Galvanostatic Technique

In this technique, the current is held constant and the steady state potential is measured. As a result, the information about passivation potential. The steady state current is lost and with increase in current, directly the transpassive nature is obtained.
(b) Potentiostatic Technique

Here a constant potential is applied to the metal solution interface and its electrochemical behaviour is measured with time. It gives an idea of passivation or repassivation potentials.

These techniques are quite commonly used in the study of inhibitors for metallic corrosion. The natural corrosion of the metal in the aqueous environment can also be studied without applying any current in the system and by plotting potential time curve for the metal in that medium but it becomes a time taking task.

1.6.4 Electrical Resistance Monitoring

The ER probe is comprised of a sensing element that is basically a loop of material made from a wire or strip which is used to conduct an electrical signal. When exposed to a corrosive environment, the cross section of the loop (probe) is reduced which increases the resistance of the sensing element thus produces a charge in output of the ER meter.

ER technique can be utilized in continuous on line process monitoring.

1.6.5 Electrochemical Impedance Spectroscopy

EIS monitors the electric response of the metal / environment interface to the applied AC signal over a frequency spectrum usually in the range of 10 KHz to 50 micro Hz. In EIS measurements a small AC potential excitation of different frequencies is applied to the electrode at the free corrosion potential to determine Rs as the high frequency limit and (Rs + Rp) as the low frequency limit. The polarisation resistance, Rp, and the corrosion rate can then be calculated.
1.6.6 Eudiometric Method

During corrosion process the cathodic reaction results in the formation of gases, normally hydrogen is liberated. The equipment is designed to collect the gases by displacement of the electrolyte in the measuring tube. The volume of the gases evolved is proportional to the rate of the corrosion. This test provides relative data for the determination of the corrosion rate.

1.7 Importance of Corrosion Study

Corrosion in metals can be compared to cancer in a human body. Both act very slowly without being easily visible and by the time one notices it the irreparable damage has been done. Corrosion is a word, widely used for various forms of attack on metals such as chemical, electrochemical, erosion, cavitations, impingement, graphitization etc. Engineers, industrialists, metal producers, suppliers and municipalities all face corrosion problem because the life of the equipment or plant is very much reduced due to corrosion. It is very difficult to assess exactly the loss incurred due to corrosion. This varies from country to country, from industry to industry and process to process. In India, due to tropical climate, the corrosion problem is more serious than that exists in cold countries. The 2004 global direct cost of corrosion, representing costs experienced by owners and operators of manufactured equipment and systems, was estimated to be $ 990 billion United State dollars (USD) annually, or 2% of the $ 50 trillion USD world gross domestic product (GDP)\(^{30}\). The 2004 global indirect cost of corrosion, representing costs assumed by the end user and overall economy, was estimated to be $ 940 billion (USD)\(^{30}\). On this basis, the total cost of corrosion to the global economy in 2004 was estimated to be approximately $ 1.9 trillion (USD) annually, or 3.8% of the world GDP. The largest contribution to this
cost comes from united state at 31%. The next largest contributions were Japan 6%, Russia 6%, Germany 5%, and New Zealand 2.5% (Fig.1.3). In India direct cost of corrosion is estimated to be around $364 billion USD of 3.1% of GDP as of 2004.

The importance of corrosion studies is threefold. The first area of significance is economic including the objective of reducing material losses resulting from the corrosion of piping, tanks, metal components, bridges, ships, marine structures etc.

The second area is improved safety of operating equipment which through corrosion may fail with catastrophic consequences. The examples are pressure vessels, boilers, metallic containers for radioactive materials, turbine blades and rotors, bridge cables, airplane components and an automotive.

Third is conservation applied primarily to metal resources the world’s supply of these is limited, and the wastage of them includes corresponding losses of energy and water reserves associated with the production and fabrication of metal structure, not least important is the accompanying conservation of human effort entering the design and rebuilding of corroded metal equipment, otherwise available for socially useful purposes.

Currently the prime motive for research in corrosion is provided by the economic factor. Losses sustained by industry, by the military and by municipalities’ amount to billions of dollars annually.

Economic losses are divided into direct losses and indirect losses.

1.7.1 Direct Losses

By direct losses are meant the costs of replacing corroded structures and machinery or their components, such as condenser tubes, mufflers, pipelines and
roofing, including necessary labour. Other examples are repainting of structures where prevention of rusting is the prime objective and the capital costs plus upkeep of cathodically protected pipelines. Direct losses include the extra cost of using corrosion-resistant metals and alloys instead of carbon steel where the latter has adequate mechanical properties but not sufficient corrosion resistance.

The total combined losses of this kind to the United States alone is estimated conservatively to be about $276 billion annually \(^{31,32}\).

1.7.2 Indirect Losses

Indirect losses are more difficult to assess but brief survey of typical losses of this kind compels the conclusion that they add several billion dollars to the direct losses already outlined. Examples of indirect losses are shut down, loss of product, loss of efficiency, contamination of product and over design \(^{5,32,33}\).

1.8 The Study Area

1.8.1 Demographic Features and Industrialisation.

Thane (formerly Thana) is a city in Maharashtra, India, part of the Mumbai Conurbation northeast of Mumbai at the head of the Thane Creek. It is the administrative headquarters of Thane District (Fig.1.4). Other major cities in the district near to Thane City are Navi Mumbai, Kalyan, Dombivali, Ulhasnagar, Ambernath, Badlapur Mira-Bhyander, Bhiwandi, Vasai and Virar. The city of Thane was ruled by Maratha and Portugeese in 1660-1800. Later on till independence the city was ruled by Britishers. Thane is also known as city of Lakes. The first railway train in India ran from Bombay VT (Now Mumbai CST) to Thane in 1853. Thane City is also marked with the rapidly growing residential area
Thane is the third most industrialized district in the state. First planned industrial estate was set up by M.I.D.C. in 1962 at Thane to promote and develop planned growth of industries in Maharashtra. There are 1548 large and medium scale 18,480 small scale industries in the district. The main products of these industries are drugs, textiles, adhesives, plastic, rubber, pharmaceuticals, engineering, fertilizers, electronics, chemicals, iron and steel. The Thane-Belapur-Kalyan industrial belt is the centre of highly sophisticated modern industries. All the industries are mainly concentrated in the Trans-Thane Creek and Belapur road industrial area. Currently as per the MPCB records, there are about 5449 industries in Thane region.

Because of rapid industrialization, the population of Thane in 1941 which was only 29,751. It reached 803,389 in 1991 and in 2001 it reached to 12,61,517 and currently the metropolis has approximately 13 Lakhs populations and it is expected to increase to 50 Lakhs in next 25 years.

1.8.2 Climate

There are two distinctly different climates in the district, one on the western coastal plains and the other on the eastern slopes of Sahyadri. The Climate on the western coastal plains of Thane, Vasai, Palghar and Dahanu Talukas is tropical, very humid and warm. The climate on the plains at the foot of the slopes of Kalyan, Bhiwandi, Ulhasnagar, and Ambernath talukas and on the eastern slopes of Sahyadri Murbad, Shahapur, Jawhar and Mokhada talukas is comparatively less humid. Temperature variation is also more in the eastern part of the district composing to west coastal areas. Climatically the district has four distinct seasons in a year. The winter season is from December to February followed by summer season from March to June. The south west monsoon
season is from June to September, October and November months constitute the past monsoon season, which is hot and humid in the coastal areas. The average rainfall is 1500 to 200 mm beginning of June to end of September. Average temperature is in the range of 25-37°C. In April and May the maximum temperature often rises to above 38°C to 44°C. Humidity is 45% to 87% highest in the month of August.

1.8.3 Soil

Thane is a part of Konkan area. Konkan as a distractive soil zone is characterized by a high monsoon rainfall, which decreases from 2671 mm in Vengurla in the south of 1759 mm in Dahanu in the north, by the relief, by the presence or absence of Laterites and by the past and present influence of the sea including coastal deposits. The coastal zone of southern Konkan consists predominantly of laterites along with some coastal saline lands and some alluvial soils along the Rivers. The Texture of the lateritic soils ranges from Sandy, silty to clayey loams. Coastal saline soils have a high salinity total dissolved salts being around 0.6%. The alluvial soil is freely drained silty loams and resembles in many aspects of brown soils.

1.8.4 Physiography and Drainage Pattern:-

The Topography of Thane city is scenic. On one side it has the higher altitude like Yeor hills and the other side’s coastal areas like Kalwa, Mumbra, and Diva etc. Ulhas River and its tributaries, Bhatasi and Kalu, in the northern part of the region, Panvel River in the central area; and Patalganga, Amba, Balganga, Bhogeshwari and Bhogwati in the south are the main Rivers draining the region. Tansa in the north forms the northern limit of the region. The details of the important Rivers in the region are as follows; Ulhas River, about 135 km. long,
rises in the rainy ravines of the Bhor Ghats and bound by the steep scarps of the Sahyadri and Matheran ridge, flows northwards after leaping over a depth of 90 meters in two waterfalls one below the other. The valley opens out steadily as the River flows past Karjat toward the north. Near Badlapur, the River is dammed and used for a drinking water reservoir. It supplies drinking water to Badlapur, Ambernath and Kalyan. After its confluence with Kalu and Bhatasai, east of Kalyan, the River turns west and flows through Mumbra ridge, later it turns northwards to flow for about 10 km. through a picturesquely forest-clad hill country and then turning west again to develop an estuary. About 3 km. wide, joins the sea south of Vasai. An island, namely Panju Island, just east of the estuary on the River is used by the Western Railway for a bridge to connect Salsette with Vasai. The River is distinctly tidal as far as Kalyan, which is reported by historians as a port during the historic past. Tansa River rises in the Shahapur uplands beyond the limits of the region and has a westward flow till it cuts through Bhiwandi hills. Thereafter, it turns north and joins Vaitarna River before the latter develops its estuary. Panvel River is a small stream rising in the northern parts of the Matheran hills and flowing through the Panvel flats before joining the Thane Creek west of Panvel.

1.8.5 Geology

Geologically, the region falls in the Deccan lava country. Basalt, popularly known as Deccan Trap constitutes predominant formations. They are generally characterized by step-like terraces formed by successive layers of basalt flows. The main types of rock occurring in the Region are basalts and other rocks, such as, trachytes, shells, volcanic breccias and tuffus in small quantities at isolated locations. Some fossiliferous sediment mainly of tufaceous
origin partly of fresh water, rich in fauna, is also found in Mumbai area. In Thane area acid differentiates, namely Rhyolytes and Trachytes do not occur. The area is chiefly made up of basalt volcanic breccias and tachytylic basalts. These have been intruded by numerous basaltic and doleritic dykes. In the southern part of the Region, namely in the areas of Panvel, Pen, Khopoli, Uran and Alibag tehsils both compact and amygdaloidal basalt predominates. They are intruded by a number of dykes. In some places in this area, the soil over burden is found to be 5 to 8 meters deep. No minerals of economic importance are found in the Region, except bauxite deposits in the Tungar hill ranges at a height of 665 meters. Reserves are estimated to be 1.3 million metric tonnes with mineral content varying between 40 to 60 percent. Basalt rock found in the Region makes good construction material. Both compact basalt and amygdaloidal basalt can be used for variety of construction purpose such as masonry works, road works or aggregate in concrete. Trachytes with fine grains and brownpink and greenish colours found only in and around Mumbai (Malad, Uttan, Dongri) are also used extensively as building material. Quarrying activity on a very extensive scale is witnessed in the Region.

1.9 Literature Survey

1.9.1 Corrosivity of Surface and Groundwaters

Metals when immersed completely or partly in water tend to corrode because of thermodynamic instability. The total amount of dissolved salts in waters varies from 40 ppm in very soft water to 35,000 ppm in sea water. The main ions present in surface groundwaters are cations, such as calcium, magnesium, sodium and anions like chloride and sulphate. Chloride and sulphate ions are highly aggressive from corrosion point view and their concentrations are
of importance in this connection. The rates of corrosion of metals are, however, controlled by the amount of dissolved oxygen in water. In surface water chloride content is low, but groundwater may contain sufficient quantity to give rise to corrosion.

Water containing different constituents affect in different ways and the effects of particular constituent in water on corrosion of more commonly used metals and alloys are discussed. A description given to water quality criteria and effluent guidelines as well as EPA programs related to corrosion are also discussed.

The Problem of corrosion as a result of the quality of metropolitan water supplies is investigated to establish general relation between water, common metals and alloys. A comparison of the components of some Australian water is given special attention to Adelaide water and its effects in typical corrosion problems. Corrosion by city water and characterization of natural water in Japan have been examined.

Many workers have carried out corrosion studies on different metals and alloys which are commonly used in domestic water piping, municipalities and industrial components; the corrosion problems with its various forms and the factor such as dissolved oxygen, chloride, sulphate, hardness, pH etc. and their mechanisms are discussed in detail in various aggressive environments. Similarly in the drinking water system the use of chlorine dioxide, free chlorine, bleaching powder (calcium hypochlorite) as disinfectant and its effect on water treatment systems and drinking water pipe lines are well documented with respect to pipe service age, loss of water, leaching of lead, iron and copper from pipe line.
By using corrosion rate data measured during 4 month experiment, the effect of aqueous silica on corrosion of iron is discussed. High levels of silica caused more iron release to the water and decreased the size of suspended particles\textsuperscript{56}. Long term tests (6-8 months) in a synthetic, microbially stable soft tap water confirmed that lower pH and higher temperatures increased copper release to water \textsuperscript{57}. The effect of sulphide on the corrosion behaviour of carbon steel in natural waters is investigated, study reveals that the presence of sulphide accelerate the corrosion rate of carbon steel No.20 \textsuperscript{58}.

A long term field based immersion test in ground water using corrosion coupons was undertaken at 24 sites across Australia. The general corrosion rate of mild steel after 9 month were found to range from 0.018 to 0.624 mm per year while stainless steel was found to have minimal corrosion under same conditions\textsuperscript{45}.

Corrosion of concrete and steel underground structures by natural and waste waters of various physico-chemical properties has been studied. Their corrosiveness is proved on the basis of pH, salt content, carbon dioxide, organic matter, chlorides, and sulphate content\textsuperscript{59, 67,121} studies on corrosion of mild steel in concrete was carried out. It was shown that sea salts can accumulate in a building wall exposed to airborne sea spray in quantities sufficient not only to deteriorate the concrete but also to cause the reinforcing steel to rust \textsuperscript{62, 68}.

Many workers studied the corrosion of copper in aqueous media, the corrosion of copper is a complex multiparameter phenomenon, which is influenced by the organic and inorganic constituent in waters operational conditions, temperature, metal homogeneity and surface characteristics\textsuperscript{69- 72}. 
J. Datta \textsuperscript{49} reported the influence of Cl\textsuperscript{−}, Br\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, and SO\textsubscript{4}\textsuperscript{2−} ions on the corrosion behaviour of 6061 Aluminum alloy through immersion test, polarization studies, microscopic analysis. From the evaluated corrosion parameters it was found that the dissolution matrix was extensively reduced in presence of aqueous solutions containing Br\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, and SO\textsubscript{4}\textsuperscript{2−} ions while Cl\textsuperscript{−} ions aggravated corrosion by penetrating into the barrier oxide Film on the surface of material. The maximum corrosion rate in presence of chloride ions is indicative of high penetrating power of these aggressive ions into the barrier oxide film as well as their ability to retard the film repair kinetics in the experimental condition.

Mine atmospheres and mine waters occupy a unique place in corrosion study in view of their highly complex nature and widely varying composition from mine to mine. Hoey \textsuperscript{73, 74} have analyzed some Canadian mine waters and have studied their corrosivity. In another report, the causes of corrosivity of mine atmospheres and mine waters have been described in detail \textsuperscript{75}.

The use of high purity water is more aggressive than less pure water in the corrosion of iron and steel particularly if dissolved oxygen is present \textsuperscript{6}. In distilled water the critical-concentration of oxygen above which corrosion decreases is stressed. In deaerated water iron does not corrode appreciably. Moreover, the corrosion rate in some natural environments is found to be abnormally high. These high rates have been traced to the presence of sulphate-reducing bacteria \textsuperscript{71-72}. Detail study of bacterial corrosion was also carried out by Friend \textsuperscript{76} and Von \textsuperscript{77}.

Campbell \textsuperscript{78} classified fresh water corrosive to copper into two categories. Soft waters in the first category contain small amounts of manganese salts. In that case corrosion occurs at hottest part of the system. In the second category
hard waters are included and corrosion occurs at the cold portions of the system. Corrosion products are Cu$_2$O and small amount of chloride. Copper is found to be resistant to sea-water, fresh water (hot or cold), deaerated hot or cold, dilute H$_2$SO$_4$, H$_3$PO$_4$, CH$_3$COOH and other mono-oxidising acids.

The corrosion of iron and steel influence by sulphate reducing bacteria, manganese oxidizing microorganisms, methanogen bacteria and halothiobacillus neapolitanus DSM 15147 bacteria have been discussed in detail 79-92.

1.9.2 Corrosivity of Soils

Soils are known to promote corrosion of buried metallic structure like pipe lines for waters, gas, oil transmission, tanks, power cables etc. 93-100. Factors attributed to this are the presence of moisture, air, and electrolytes. Corrosion is also caused by the formation of differential aeration cell, compositions and textures present along the metal structures 101-104.

Many workers have also demonstrated a correlation between corrosion occurring in soils due to various influencing factors. For example, the resistivity has been correlated with corrosiveness 105, 106. Booth 37, 107 investigated soil corrosivity on the basis of resistivity and redox potential.

Romanoff 108 has shown that poor aeration, high acid value, high electrical conductivity, high moisture and salt content are the characteristics of the corrosive soils. Dry, sandy and low conductivity soils produce little corrosion.

Markovic 109 reported that texture and electrolyte content of the soils play a significant role in to corrosivity of soils. Its permeability to air and water is dependent on its particle size. The capillary porosity of the soil causes retention of water and non capillary porosity causes retention of the air in the soil.
It was reported that under field conditions the resistivity of the same soil varies due to seasonal fluctuation\(^\text{109}\). Variations up to 50 percent have been noticed on account of precipitation and 20 percent due to temperature changes.

However, some factors associated with soil environments which can have an impact on the corrosion rates of metal and alloys include soil texture, internal drainage, resistivity, redox potential, moisture content, permeability, chloride ion content, sulphide and sulphate ion content, presence of corrosion causing bacteria, oxygen content, pH, total hardness and hardness as calcium carbonate of soil moisture, and stray direct currents (DC)\(^\text{110–112}\).

A. Benmoussat\(^\text{96}\) said that relationship between soil corrosivity and physico-chemical parameters is very complex, therefore the soil corrosivity appraised by these parameters is often unreliable. The electrochemical parameters such as corrosion current density and polarization resistance (Rp) can serve as the parameters for evaluation of soil corrosivity with accuracy and ease.

A great deal of work has been reported by National Bureau of Standards, America, on the corrosion behaviour of metal pipes in representative types of soils\(^\text{113–116}\).

Growth of underground gas and oil pipeline lines in Soviet Union has made it necessary to develop rapid and precise method for evaluation of soil corrosivity. Accordingly many workers have reported a classification of soils, their distribution, factors affecting corrosion and corrosivity of soils\(^\text{117–119,121,122}\).

Fourteen types of Indian soils were analyzed for their mechanical, physical, chemical and potential corrosion causing micro organisms\(^\text{120}\). Anaerobic sulphate reducing bacteria mainly belonging to the genus Desulfovibro...
perform the role of cathodic depolarizer by removing the hydrogen from the metallic surface with the help of enzyme hydrogenasa and thus promote the process of corrosion. 12, 123, 124.

Bajendra Nath Tripathi et al. 97 studied on corrosion of ferrous metal (mild steel) in typical Indian soils, employing Schwerdtfeger's soil corrosion cell. The study reveals that the rate of corrosion in non acidic soils is maximum at the beginning and gradually decreases with time. The soils of moisture equivalents ranging 25–30% are most corrosive. Direct chemical corrosion has been found to be very predominant in acidic soil. Recent research results have suggested that 125 corrosion of steel in soil environment can be maintained by thin film electrical resistance sensor to predict long term corrosion behaviour of steel within a short period. Moreover, the effect of soil resistivity on corrosion rate measurement can be eliminated by using this sensor.

Corrosion of agricultural equipments in soil caused by chemicals used on farmlands, grain and silage preservatives. Pests and weed control and as proprietary acid solutions for cleaning dairy equipment. In addition to these, farm wastes and slurries contain many chemicals on the whole; these various chemicals frequently damage farming machinery and ancillary structures 126.

1.9.3 Corrosion in Industrial Effluents

Industrial effluents can cause a variety of problems in treatment plants and in municipal sewer systems such as plugging of the sewer, corrosion of pipe materials and plant equipment, health hazards and explosion risks 127. Out of these, corrosion is very frequent and affects economy directly or indirectly. A comprehensive account of corrosion in effluent treatment and waste water treatment plants, its forms, importance of water analysis, factors affecting the
corrosion process, the suitability of different metals and alloys including stainless steels in plant environment along with the cathodic protection. Inhibition and use of different corrosion resistant non-materials is given in detail \textsuperscript{127-131}. The economic losses and hazards also reported in industrial environment when treated and biologically purified waste waters are reused in the processing, cooling towers and boiler purposes \textsuperscript{132-134}.

The various type of attack encountered with natural and treated waters are examined in relation to the composition of the water. The examples given are taken from a large number encountered in dealing with enquiries from industrial and private organizations, mainly in the U.K. The composition and chemical equilibrium of water and their variation with source of supply are discussed. \textsuperscript{135}.

Complete or substantial closing of the system in paper machine section leads to considerable loading of process water i.e. higher temperature, higher acidic conditions and higher concentration of ions. Those conditions result in increased corrosion of various machinery part viz, pipelines, stock and back water lines and the wire pits etc. \textsuperscript{136}. A detail review of corrosion in pulp and paper industry, its causes, forms, factors affecting the corrosion and control and management is discussed by various workers \textsuperscript{137-141}.

Sugar machinery is very much affected by corrosion. The increasing cost of equipment and machinery on one side and the high expenditure involved in over-hauling and maintenance of the plant on the other, have made the author stress that the major over - hauling cost of the sugar plant is mainly due to the need to replace the equipment and part of the plan that get rusted or corroded during the coarse of operation of the plan. Forms of corrosion and main factors
which influence the corrosion are also reviewed\textsuperscript{142-143}. Localized corrosion of high alloy steels in cane sugar juice has been investigated\textsuperscript{144}.

A wide literature is available on corrosion in chemical industries such as wineries, chlor-alkali, acid manufacturing, lasing dyes and some organic solvents such as phenol, benzene etc.; the forms of corrosion, losses due to corrosion as well as the resistive materials have been described along with a prevention and control\textsuperscript{145-148}.

Dairy industry equilisation is discussed in relation to corrosiveness of materials used. Milk is corrosive to various types of metal containers and, therefore, can become contaminated with Sn, Cu and Fe. Solutions used in the processing of milk or cheese containing Cl\textsuperscript{-} or chlorinated disinfecting agents can caused corrosion of metals. Whey, which has a low pH, can also cause pitting of ordinary stainless steel and special types must be used to prevent corrosion\textsuperscript{149-152}.

Most materials are inherently unstable at waste water treatment plants because of the presence of corrosive compounds (chlorides, sulphates, hydrogen sulphide, corrosive bacteria etc.) in air or in waste streams. Also, irregularities in industrial waste may cause more rapid rates of corrosion\textsuperscript{131}.

1.9.4 Inhibition of Corrosion

The Inhibition of corrosion of aluminium and its alloy in alkaline media is now a day’s fairly well known and number of inhibitors has already been described, such as alkali silicates\textsuperscript{152}, potassium permanganate\textsuperscript{153}, glucose\textsuperscript{154}, sodium silicate\textsuperscript{155}.

A number of organic compounds have been introduced as aluminum corrosion inhibitors in acid media\textsuperscript{156, 157}. Investigations of various aliphatic and
aromatic amines as well as nitrogen-heterocyclic compounds \(^{158-162}\) showed that their inhibitory action is connected with several factors such as (i) structure of molecules, (ii) the number and type of adsorption sites (iii) electron density on the adsorption sites and (iv) the type of interaction between organic molecules and metallic surface. The efficiency of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pairs, the \(n\) orbital character of free electrons, and electron density around nitrogen atoms.

Another interesting system is based on sodium silicates and has been known for quite a long time \(^{163}\). Many workers \(^{164-168}\) studied the inorganic corrosion inhibitors in aqueous solutions and showed that certain substances posses high inhibition efficiency. Similarly, the efficiency of various organic inhibitors has been reported in the literature \(^{169-171}\). A few classes of organic compounds have been studied as corrosion inhibitors in hot and concentrated Hydrochloric acid \(^{172-174}\). Because of toxic nature and high cost of some chemicals currently in use it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered as a good source for this purpose \(^{175}\). Natural products of plant origin contain different organic compounds e.g. alkaloids, tannins, pigments, organic and amino acids and most are known to have inhibitive action \(^{176-177}\). Corrosion Inhibition mechanism was suggested on the basis of physiosorption of Inhibitor on the metal surface.

Epoxy Resins such as Aradur 450, Aradur 3986, are the recent inhibitors provide thick non-porous and highly chemical resistant films with inherent porosity. These inhibitors are free from pollution hazards and fire and best suitable for corrosion inhibition of marine equipments \(^{178,179}\).
The corrosion inhibition of mild steel embedded in concrete by using nanomaterials such as EPCO KP-200 (concrete corrosion inhibitor) are well documented\textsuperscript{180, 181}.

The corrosion inhibition of steel in a closed system containing sodium sulphite, sodium nitrite at room temperature has been studied\textsuperscript{182, 183}. The functions of these inhibitors are to maintain the oxide film, formed by the reaction of dissolved oxygen with the steel surface. The corrosion rates of mild steel as function of chromate chloride concentration at various temperatures have been investigated\textsuperscript{184}.

Various attempts have been made to study the corrosion inhibition of copper by triethyl and triphenyl phosphate in chloride solution\textsuperscript{185}. The mechanism of these inhibitors explained on the basis of adsorption and formation of self-assembled monolayer (SAMs). Most of compounds forming self assembled monolayer contain nitrogen, sulphur or oxygen\textsuperscript{186}. A lot of research has been done with n-alkanethiol SAMs\textsuperscript{187-189}. The role of carbazole, N-vinyl carbazole, several kinds of Schiff bases and surfactants has been investigated by various workers in the corrosion inhibition of copper\textsuperscript{190, 191}. Lusk and Jennings\textsuperscript{192} investigated the SAMs formed by series of sodium S-alkyl thiousulphates, which are water soluble inhibitors. The use of thiazole derivatives in the corrosion inhibition of copper in 0.1M Na$_2$SO$_4$ has been investigated\textsuperscript{193}.

The inorganic oxidizing substances such as chromates, nitrites, and molybdates are known to passivate the metal and shift the corrosion rate to very low values. For optimum inhibition, the concentration of passivator must exceed a certain critical value. Below this concentration, passivators behave as active depolarizers and increase the corrosion rate at localised areas. The critical
concentration for CrO$_4^{2-}$, NO$_2^-$, MO$_4^{2-}$ inhibitors is about 10$^{-3}$ to 10$^{-4}$ M $^{194-197}$. Some substances indirectly facilitate passivation of iron and some other metals by making conditions more favourable for adsorption of oxygen. In this category the compounds are alkaline e.g. NaOH, Na$_3$PO$_4$, Na$_2$B$_4$O$_7$. These are all non-oxidising substances requiring dissolved oxygen in order to inhibit corrosion, hence oxygen is considered as a passivating substance.

Various attempts have been made to study the effect of inorganic inhibitors on corrosion of different engineering materials such as steel, aluminium and titanium in different acidic as well as in alkaline environments. The corrosion of mild steel in aqueous sodium sulphate and sodium chloride containing potassium chromate as an inhibitor is reported $^{197}$. It was observed that the life of the passive film increases with the increase in the concentration of inhibitor $^{198}$. The formation of passive film on iron in chromate solution has shown the presence of Cr$_{3}^{3+}$, Fe$_3^{3+}$ and O$_2$ on the surface on the basis of XPS $^{199}$ The role of different phosphates such as Na(PO$_3$)$_6$. Na$_3$PO$_4$ as corrosion inhibitors for steel in various concentrations of surfactant has been reported $^{200}$.

Several attempts have been made to control the corrosion of aluminum in acid media. Singh et al. $^{201}$ have tried sodium chromate and di-sodium hydrogen phosphate individually as well as in the form of mixture to study the corrosion rate of some commercial aluminum alloys. This study has shown the low concentrations of these compounds used individually accelerate the corrosion rate while the mixture of the two completely arrested the corrosion even if the impression period is extended upto 500 days. Hundred percent efficiency of the mixture has been attributed to the absorption of Al-phosphate and Al-chromate at the active sites of the metal. Brett $^{202}$ has studied the corrosion of roughened and
polished aluminum in aerated and deaerated solutions. Suhybani \(^{203}\) has compared the effectiveness of some amines on the corrosion of aluminum in hydrochloric acid. The inhibitor efficiency increases in the order: methylamine < ethylamine < n-propylamine < n-butyl amine < octylamine < benzyl amine.

Kamel \(^{204}\) observed the non corrosive action of the tertiary phosphate ion on aluminum in sodium hydroxide solution but they have observed that the addition of some small amounts of trisodium phosphate decreases the corrosion rate and corrosion potential in very dilute solution due to the adsorption of Na\(^+\) on the metal surface accelerating cathodic reaction. Moustafa et al. \(^{205}\) have reported the corrosion of aluminum in trichloro acetic acid using thermometric method. They have found that the corrosion rate increases with the increase in the concentration of the acid. Various anions such as SCN\(^-\), CN\(^-\), N\(_3\)^- have been found \(^{205}\) to inhibit the reaction which was due to the complexation reaction of these anions with the aluminum. The formation of the anodic passivating films of sodium dihydrogen phosphate on zinc at different temperatures was reported \(^{206}\). The passivity film was found to be due to the inclusion of phosphate in zinc oxide.

1.10 Nature of the Present Problem

The proposed work was undertaken to study corrosion and corrosion inhibition of metals and alloys by natural waters (i.e. surface and groundwaters), effluents and by the soils of Thane region. Thane area is chosen because it has undergone considerable industrialization and urbanization in recent years and especially after the establishment of Maharashtra Industrial Development Corporation which sponsored the development of industrial areas in and around the city.
There has been large scale migration of people from rural areas to seek jobs in Thane. Thane used to be described as a sleepy city when compared to Mumbai till the early 90s. But the size of city has increased manifold in recent years, spurred by residential boom due to people moving away from the Mumbai city to find affordable and good homes as well as amenities in Thane.

Along with the developments of large multistoried residential complexes, large numbers of hutment colonies have come up all over the Thane and in nearby suburbs. It is evident that the pollution of waters and soils within its environments is largely due to effluents from newly developed industries and from domestic wastes especially those emanating from the slum areas.

The work done that is carried out is divided into eight chapters. The CHAPTER - 1 deals with the introduction to the subject and the review of the work done in the area of interest followed by the scope of the present work.

CHAPTER - 2 is devoted mainly to the experimental part. It summarises the procedures used for the analysis of surface water, groundwater, and soil and effluent samples in the study area. The physico-chemical parameters such as pH, electrical conductivity, total dissolved solids, total hardness, total alkalinity, dissolved oxygen, chemical oxygen demand, chlorides, sulphates, nitrates, phosphates, calcium, magnesium, sodium, and potassium are determined from samples collected at 68 sites. In addition to this, moisture content, resistivity and texture of soils as well as oils and grease in the effluents are also estimated. The detail procedure for corrosion as well as corrosion inhibition studies and heavy metal analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy are also outlined in this Chapter.
CHAPTER - 3 summarises the corrosion of metals and alloys in surface and groundwaters. Ten surface waters and twenty-two groundwater samples are collected from the area under investigation. A brief description of various physico-chemical parameters in post-monsoon and pre-monsoon seasons are given in this Chapter. Ferrous alloy such as mild steel, SS-304, SS.-316, S.S.- 430 and non ferrous metals such as copper, aluminum and non ferrous alloy such as brass are used for corrosion studies. The various factors responsible for corrosion of metals and alloys in such waters are presented.

CHAPTER - 4 presents the results of corrosion of metals and alloys in soil environment. Twenty different soil samples are collected from the study area. The physical, mechanical and chemical parameters are used to characterize the soil. A probable correlation of corrosivity of metals and alloys and type of soil is proposed.

The corrosion of metals and alloys in industrial effluents is investigated and results are presented in CHAPTER - 5. Effluents from sixteen different industries around the Thane city are collected. The physico-chemical characteristics of these samples are determined and the influence of various parameters on the corrosion rates is determined.

CHAPTER - 6 deals with the results of corrosion inhibition of metals and alloys in surface, groundwaters and effluent samples. For this study, the selected water samples and effluent samples are used. Potassium dichromate, phosphoric acid, ethylenediamine, sodium sulphite, potassium oxalate, and sodium nitrite are tried as corrosion inhibitors. The data are analyzed in the light of the inhibition efficiency to metals and alloys under investigation.
CHAPTER - 7 reports the heavy metal analysis of selected surface and groundwater, effluent and soil samples. Heavy metals such as arsenic, copper, cobalt, cadmium, iron, mercury, nickel, zinc, lead and chromium are determined by Inductively coupled plasma atomic emission spectroscopy. The accumulation patterns of these metals in soil and their indirect effect on the surface and groundwater aquifers are discussed.

CHAPTER - 8 compiles the conclusions drawn from the present investigation by the candidate.
FIGURE 1.1 METAL DISSOLUTION AND FORMATION OF AN ELECTRIC DOUBLE LAYER

FIGURE 1.2 ARRANGEMENTS OF IONS AT METAL SOLUTION INTERFACE (HELMHOTZ MODEL)
FIGURE 1.3 GLOBAL COST OF CORROSION