CHAPTER ONE
INTRODUCTION

Corrosion is the damage to metal caused by the reaction with its environment. The word corrosion comes from the Latin word corrodere— to gnaw away. It is gradual deterioration of a material caused by the chemical or electrochemical reaction with its environment.

According to the general definition given above, decay, damage and deterioration of materials other than metals, such as ceramics, plastics, rubber or concrete, may also be called corrosion. Losses due to corrosion could be direct or indirect. Inability to use otherwise desirable materials, over design to allow for corrosion and the cost of repair or replacement of the corroded component or equipment, cost of anticorrosive painting or other protection methods are direct losses. Indirect losses may be either economical or social. These include: Contamination of the product, loss of valuable product from a container that has corroded through, damage of equipment adjacent to that in which corrosion failure occurs, loss of production, man power, efficiency, time and energy, loss of safety and accidents and dull appearance of the metal surface.

It is not possible to give any exact data but a rough estimate, made by Rajgopalin in 1984, shows that the total annual cost of corrosion was approximately 4000 crores of rupees. By the year 1996, this cost should easily go up to at least 15,000 crores of rupees per annum. It is possible to avoid about 30% loss due to corrosion if suitable measures are taken to control the corrosion. From national economy point of view, it is therefore, necessary for scientists and engineers to adopt various ways and means to reduce the loss due to corrosion.

1.1 Why do Metals Corrode?

Except for the noble metals such as gold, metals occur in the earth’s crust as certain stable compounds, usually oxides, hydrated oxides or sulphides, some
times basic sulphates basic chlorides or carbonates etc. In reducing the 'ore' to metallic state, energy must be expanded to overcome the affinity between the metal and the non metal. The metal, thus produced represents an energy rich state and if, as usually happens in service, it is exposed to oxygen and/or water, or to sulphur compounds etc. they return to the lower energy state in which they originally occurred in the earth through the reactions involving decrease of free energy i.e. an operation which will occur spontaneously. It is not surprising to find that iron when heated in air acquires a scale of oxides, that iron exposed to air and water produces rust (hydrated oxide) or that copper exposed to an atmosphere containing a trace of certain sulphur compounds develops tarnish films. Since the earth is surrounded by oxygen and water vapours, it would be sensible, instead of asking the question 'why do metals corrode?' to enquire how under these circumstances metals manage to escape corrosion.

The amount of energy required and stored up varies from metal to metal. Some noble metals like gold, platinum & silver require least energy to convert their ores to metals (Most corrosion resistant), where as for the metals like magnesium, aluminium, iron, it is relatively high. Metallic materials of general use are iron, nickel, chromium, copper, zinc, aluminium etc. Some of the metals or alloys corrode heavily in certain environments in which other remain unaffected. Iron when left to an industrial atmosphere, forms a reaction products layer or rust (Fe₂O₃·H₂O), which is unable to protect the metal by formation of a protective barrier. But in similar corrosive atmospheres copper forms an adherent green patina CuSO₄·(3Cu(OH)₂) which protects the metal by isolating it from the environment. Both metallurgical structure and environmental conditions are important factors in the study of corrosion phenomenon.

1.2 Electrochemical Theory of Corrosion

Wallaston² produced first-paper in the year 1801 regarding the mechanism of corrosion. The most acceptable electrochemical theory of corrosion was given by Whitney³ in 1903. Various other theories namely acid theory⁴,⁵, direct chemical
attack theory⁶, colloidal theory⁷ have also been put forwarded but they are mainly restricted to specific systems only. The electrochemical theory of corrosion is the only theory which is universally accepted and is applicable to most of corrosion processes.

Evans⁸ has explained the role of ions in the corrosion and dissolution of metals and alloys under the influence of exchange of ionic charges. This laid down the basis of electrochemical theory of corrosion. When a metallic object is immersed in a corrosive medium the metallic surface gets divided into areas having different potentials under the influence of various metallic phases, grain boundaries, stress and strain, impurities etc. In all cases, in the presence of an electrode⁹, one of the metals or an area of the metal (anodic metal or anodic area) undergoes dissolution essentially through electrochemical reactions resulting in the formation of an electrochemical cell.

Anodic reaction in this case is

$$\rightarrow \text{M} \rightarrow \text{M}^{n+} + ne^- $$

(i)

This represents oxidation of metal. Various cathodic reactions are possible depending upon the pH of the system. The most common cathodic reactions are:

$$2H^++2e^- \rightarrow H_2 \uparrow$$  \hspace{1cm} \text{Hydrogen evolution} \hspace{1cm} (2)

$$\rightarrow O_2+4H^++4e^- \rightarrow 2H_2O$$  \hspace{1cm} \text{Oxygen reduction/oxidation} \hspace{1cm} (3)

$$O_2+2H_2O+4e^- \rightarrow 4OH^-$$  \hspace{1cm} \text{Oxygen reduction} \hspace{1cm} (4)

(neutral and alkaline solution)

$$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$$  \hspace{1cm} \text{Metal ion reduction} \hspace{1cm} (5)

$$\text{Cu}^{2+}+2e^- \rightarrow \text{Cu}$$  \hspace{1cm} \text{Metal deposition} \hspace{1cm} (6)

Thus for corrosion to occur anodic reaction and one or more of the above mentioned cathodic reactions should occur simultaneously. The essential concept⁹ of the electrochemical mechanism is; the corrosion of metal is a redox reaction,
occurring at a metal/solution interface with consequent transfer of electrons through
the metal and ions through the solution; the position and the distance of separation
of the anodic and cathodic sites are immaterial to this concept.

1.3 Forms of Corrosion

Damage due to corrosion takes many forms depending on the nature of
the metal or alloy, the presence of inclusions or other foreign matter at the surface,
the homogeneity of its structure, the nature of the corrosion medium, the incidental
environmental factors such as the presence of oxygen and its uniformity,
temperature, velocity of movement and such other factors as stress, oxide scales,
porous or semi porous deposits on surfaces, built in crevices, galvanic effects
between dissimilar metals and the occasional presence of 'stray' electrical currents
from external sources. As many as 57 different forms of corrosion have been
recognised but many of them are found rarely and under very specific conditions.
The common types of corrosion forms classified with respect to the outward
appearance or altered physical properties of metals are as follows:

1. Uniform or general corrosion
2. Pitting corrosion
3. Intergranular corrosion
4. Crevice corrosion
5. Galvanic corrosion
6. Stress corrosion cracking
7. Corrosion fatigue
8. Hydrogen embrittlement
9. Selective leaching
10. Fretting corrosion
11. Erosion corrosion
12. Cavitation corrosion
13. Microbial corrosion
1.4 Protection Against Corrosion

To minimize the losses occurring due to corrosion various preventive measures have been developed. Some of the main techniques are:

1. **Modification in the design of the metallic structure**: The most effective and economical method of reducing losses due to corrosion starts at the designing stage. The metallic structure should be designed in such a manner so as to cause minimum corrosion. Care should be taken to avoid sharp bends, flat surface, contact with soil etc.

2. **Change of metal**: Corrosion resistance of a metal can be greatly improved by change of its composition, change of micro structure, elimination of residual tensile stresses, introduction of surface compressive stresses.

3. **Change of environment**: Corrosion can be effectively controlled by changing or modifying the corrosive environment. The change in the corrosive environment can be done by removing moisture, oxygen, chloride ions, by adding inhibitors and changing the operating variables like temperature, pH and velocity.

4. **Electrochemical technique**: In most of the cases corrosion can be prevented by changing the electrode potential of the metal. This can be achieved by I) lowering the potential of the metal in the negative direction. This is called cathodic protection. II) Increasing the potential of the metal in the positive direction in the domain of passivity. This is called anodic protection.

5. **Isolation of the metal from corrosion environment**: Corrosion of metals which occurs due to chemical or electrochemical reaction of the environment can be prevented by separating the metal from the environment. This separation can be achieved either by metallic or non metallic protective coating on the surface of metal.
1.5 Corrosion Inhibitors

Corrosion inhibitor is a chemical substance which when added to a corrosive environment, decreases the rate of attack by the corrosive environment on the metal surface. Inhibitors have a critical concentration that must be reached or exceeded for them to be effective and in some cases to prevent them from making corrosion worse. Corrosion inhibitors are commonly added in small amounts to acids, cooling waters, steam and other environments either continuously or intermittently to prevent serious corrosion. An inhibitor useful for a particular corrosion system may be harmful to another under certain situations. Some inhibitors retard corrosion by adsorption to form an invisibly thin film only a few molecules thick; others form visible bulky precipitates which coat the metal and protect it from attack. Another common inhibition consists of causing the metal to corrode in such a way that the combination of adsorption and corrosion products forms a passive layer. In addition, these are substances which when added to an environment, retard corrosion but do not interact directly with the metal surface. This type of inhibitor causes conditions in the environment, to be more favourable for the formation of protective precipitates or it removes an aggressive constituent from the environment.

The passivating type of inhibitors are mainly inorganic oxidizing chemicals (e.g. chromate, nitrite, nitrate etc.) which can passivate steel in absence of oxygen and when added to the corrodent, facilitate the anodic process of oxide film formation by retarding the cathodic current density or by increasing the fade potential value to more negative value and subsequently promoting the anodic process. The other passivating type of inhibitors are inorganic non-oxidizing chemicals (e.g. phosphate tungstate, molybdate, etc.) which require the presence of oxygen to passivate steel. Passivating inhibitors are most effective of all inhibitors because they can stifle corrosion almost completely. Passivating inhibitors are also dangerous inhibitors because under certain conditions they can accelerate corrosion.
Organic inhibitors, usually nitrogen or sulphur containing organic compounds, like thiourea, amines, azoles etc are classified in the category of non passivating inhibitors which have slight effect on corrosion potential and act mostly by adsorption.

Inorganic precipitation inhibitors are the compounds including many of the indirect passivators which react with environment to precipitate insoluble products that give general coverage to the metal. Bicarbonate ions ($\text{HCO}_3^-$) for example, form insoluble carbonate in alkaline solution. Phosphates are most widely used for precipitating ferrous and ferric phosphates ($\text{FeHPO}_4$ and $\text{FePO}_4$) on steel.

An alternative method of protecting steel components during transport and storage is to use vapour phase inhibitors (VPIs). They spread through the free space in a container and form a water-repellent (hydrophobic) film on to exposed surfaces. While VPIs are beneficial towards ferrous metals, they can increase the rate of attack on other materials. Carbonate and nitrite are the anions in two typical VPIs. For steels and aluminium, two common VPIs are dicyclohexylamine nitrite and cyclohexylamine carbonate.

The study of corrosion processes in recent years has been almost entirely based on the so called Evans diagrams. The Evans diagram\textsuperscript{10} is a graphical presentation in semilogarithmic coordinates of the anodic and cathodic reaction rates expressed as partial current dependent on potential. When the metal is freely corroding the partial reactions proceed with equal reaction rates. In order to express the reaction rates in terms of current the conversion per time is multiplied by the Faraday constant according to the following equation:

$$J = Q \cdot F \cdot n.$$ \hspace{1cm} (7)

Where $J$ is current, $n$ is number of electrons transferred per molecule, $F$ equals Faraday constant and $Q$ is the rate of the reaction expressed in terms of moles per unit time. If the above equation is divided by the surface area the current density can be expressed as follows:

$$\frac{J}{A} = i = Q \cdot F \cdot n/A.$$ \hspace{1cm} (8)
The partial anodic \( i_a \) & cathodic \( i_c \) current densities are then expressed as exponential functions of the over potential \( \eta \) which is the difference between \( (E_a, E_c) \) of the particular partial reaction. These relationships are shown graphically and explicity in Fig 1.1. Thus by defining the anodic and cathodic current potential relationship for a corroding system and by plotting them as shown in a potential vs \( \log i \) diagram, one quickly finds the point where the two lines intersect, which is the potential at which anodic and cathodic reaction rates are equal. The current at this point becomes corrosion current or corrosion rate while the corresponding potential is the corrosion potential.

1.5.1 Classification of Inhibitors

Attempts to classify inhibitors according to their chemical composition and structure are known. Such schemes are undoubtedly for developing methods of synthesizing new inhibitors and for identifying the actual inhibiting substances in the complex mixture. On the basis of mechanism of inhibition, inhibitors can be classified as

- Anodic inhibitors
- Cathodic inhibitors
- Mixed inhibitors

1.5.1.1 Anodic Inhibitors: Those substances which reduce the anodic area by blocking the anodic sites and polarize the anodic reactions are called anodic inhibitors. They displace the corrosion potential in the positive direction and reduce the corrosion current, thereby retard anodic reaction and suppress corrosion rate.

Fig 1.2 (a) Anodic inhibitors are primarily inhibitors of oxidizing action. As oxidants they have a two fold nature VIZ (i) they act as good depolarizers and thus accelerate cathodic processes and (ii) they also lead to the formation of protective film on the anode.

1.5.1.2 Cathodic Inhibitors: Those substance which reduce the cathode area by acting on cathodic sites and polarize the cathodic reaction are called cathodic inhibitors. They displace the corrosion potential in the negative direction
Fig. 1.1 Polarization curves for a corroding electrode

$E_{corr} =$ Corrosion potential

$i_{corr} =$ Corrosion current
and reduce corrosion current, thus retard cathodic reaction and suppress the corrosion rate Fig 1.2 (b). Cathodic inhibitors may be divided into three categories viz (i) those that absorb oxygen (ii) those that reduce the area of cathode (iii) those that increase the hydrogen over potential of the cathode process.

1.5.1.3. Mixed Inhibitors: Mixed inhibitors affect both anodic and cathodic reactions. Gelatin, glue and other high molecular weight substances fall in this category. Mixed inhibitors are concentrated or coagulated at the metal liquid interface providing shield to the metal surface. Action of mixed inhibitors may also be due to the formation of electrical resistance of the surface layer.

In the classification of corrosion inhibitors, it has been considered that the cathodic inhibitors do not participate in the anodic reaction nor do the anodic inhibitors interface with cathodic reactions. Although such an assumption is valid theoretically but in number of practical cases cathodic inhibitors do cause to some extent anodic polarization and vice-versa. Such compounds are still considered as anodic or cathodic inhibitors depending upon the electrode at which their action is more dominant.

1.5.2 Mechanism of Inhibition

Till to date there is no single generally accepted view on the mechanism of the protective action of inhibitors. There exists a multitude of ideas, often diametrically opposed, regarding the protective action in acid media and neutral aqueous solutions, and hundreds of investigations have been devoted to the elucidation of this problem during the past decades. The controversy, however, continues to the present time. Several workers who have examined inhibitive action in acid solution have suggested that in presence of inhibitors the hydrogen over voltage is increased and consequently the dissolution of the metal is retarded.

The protective properties of the inhibitor in the presence of which the medium become less corrosive, can be explained as being due to their combination with substances causing corrosion. For example in the corrosion of copper by nitric
Fig. 1.2. Mechanism of action of corrosion inhibitors based on polarization effects.
acid, urea, phenyl hydrazine and other substances acts as inhibitors of this type by combining with nitrous acid, which is always present in nitric acid and is highly corrosive towards copper.

The protective action of inhibitors most frequently consists of passivation of the metal surface, i.e. formation of a protective film which is nearly insoluble in the surrounding medium. Films of passivators can be considered to form an intermediate phase between the metal and the corrosive medium, isolating one from the other.

The corrosion reactions in the presence of organic inhibitor may sometimes involve the formation of adsorbed intermediate species with the surface metal atoms. Such participation by organic inhibitor is generally characterized by the change of Tafel slopes observed for the process. Investigations on the anodic dissolution of iron in the presence of some inhibitors e.g. aniline and its derivative\(^1\) benzoate ions\(^2\) and fluorate ions\(^3\) have indicated that the adsorbed inhibitor 'In' participates in the reaction probably in the form of a complex of the type Fe(\(In\))\(_{ads}\) or Fe(\(OH-In\))\(_{ads}\). Anodic dissolution proceeds less readily via the adsorbed inhibitor complex than via (Fe-OH)\(_{ads}\) and so anodic dissolution is inhibited and change in Tafel slope is observed for the reaction. Heuslar and Bockris\(^4\) postulated the mechanism that the dissolution of iron in sulphuric acid solution is accompanied by formation of an intermediate adsorption product MOH which is in equilibrium with OH\(^-\) ions. In contrast to iron and cobalt the reaction

\[
M+OH^-\rightarrow(MOH)_{ads}+e^- \tag{9}
\]

on nickel during anodic dissolution is virtually irreversible and is the limiting stage of the dissolution process. No appreciable accumulation of the intermediate compound NiOH occurs on the metal surface.

### 1.5.3 Adsorption Isotherm

As adsorption is key to the mechanism of corrosion inhibition action in the presence of organic inhibitors, it is certainly important to study the nature of adsorption of these inhibitors on metal surface at various temperatures and thereby
to study the kinetics and thermodynamics of interaction between the surface active
group on metal and the corrosion inhibitors. An adsorption isotherm gives the
relationship between the coverage of an interface with an adsorbed species at a
particular temperature\textsuperscript{15,16}. In electrochemical corrosion, corrosion processes
coverage depends also on the potential difference at the interface.

1.5.3.1 Langmuir adsorption isotherm

Langmuir put forward the first quantitative theory of the adsorption. If one
assumes that in the absence of inhibitor blank corrosion rate ($I^\circ_{\text{corr}}$) represents the
total number of ‘active sites’ on the surface of a corroding metal and that in the
presence of inhibitor, inhibited corrosion rate ($I^\text{inh}_{\text{corr}}$) represents the total number of
active sites minus the inhibited sites, then an expression for the fraction of the
surface which is covered by inhibitor molecules is given as:

$$
\theta = \frac{I^\circ_{\text{corr}} - I^\text{inh}_{\text{corr}}}{I^\circ_{\text{corr}}}
$$

(10)

Where, $\theta$ stands for the fractional coverage of the surface with inhibitor
and is, of course, equal to the percent protection. The dependence of coverage $\theta$
on the concentration of the inhibitor, is given by the adsorption isotherm of a
particular inhibitor. A typical adsorption isotherm was derived by Langmuir and is
given as follow -

$$
\theta = \frac{KC_{\text{inh}}}{1 + KC_{\text{inh}}}
$$

(11)

where $k$ is the Langmuir adsorption constant. Rearranging equation 10
and 11 gives equation 12 which shows the relationship between the percent
protection and inhibitor concentration

$$
\frac{\theta}{1 - \theta} = KC_{\text{inh}}
$$

(12)
It is based on the assumption that all sites are energetically equal, i.e. the heat of adsorption is independent of coverage. It can be seen from equation 12 that, if logarithm of the inhibitor concentration is plotted against the logarithm of $\frac{\theta}{1 - \theta}$, a straight line with unit slope should result.

The Langmuir adsorption isotherm has been found to be obeyed by a number of systems at low and high surface coverage but fails in the intermediate region. Determination of the heat of adsorption of clean metal surfaces shows that it frequently decreases markedly with increasing surface coverage, an observation that is indicative of surface non uniformity due to intrinsic heterogeneity of the surface and to the repulsive forces between adsorbed atoms of molecules. Consequently the slope of Langmuir adsorption isotherm plot will not remain unity.

1.5.3.2 Freundlich Adsorption Isotherm

Another adsorption isotherm was derived by Freundlich and is shown in equation (13). Here the logarithm of coverage is directly proportional to the logarithm of the inhibitor concentration. This isotherm is only valid at low coverage. It assumes exponential dependence of adsorption energy on coverage.

$$\log \theta = K \log C_{inh} + K'$$  \hspace{1cm} (13)

1.5.3.3 Tempkin adsorption Isotherm: Tempkin suggested that the deviation of Langmuir adsorption isotherm at high coverage could be accounted for by regarding the surface of the metal as being composed of small patches of equal size, at each of which the Langmuir isotherm holds independently with a characteristic local standard free energy of adsorption that depends on patch distribution. He assumes a linear dependence of the adsorption on fractional coverage.

$$\theta = \frac{1}{a} \log C_{inh} + \text{Const}$$  \hspace{1cm} (14)

Thus a plot of $\theta$ vs $\log C_{inh}$ yields a straight line.
1.5.4 Influence of Inhibitor Concentration on the rate of Corrosion.

The dependence of corrosion rate of steel in acids upon the concentration of organic inhibitors was first systematically investigated by Sieverts and Lueg. According to them, to be fully effective, all inhibitors require to be present above a certain minimum concentration. Although, the direct relationship between inhibitor concentration and inhibitor efficiency may not be applicable everywhere, it was found that at low inhibitor concentration the effectiveness of inhibitor species in retarding the corrosion process may be greater than that at high surface coverage whereas in other cases, at low concentration of inhibitor, stimulation of corrosion occurs and inhibition takes place only at higher concentration. In many cases the corrosion that occurs with insufficient inhibitor may be more severe than in the complete absence of inhibitor. Such inhibitor are known as 'dangerous' inhibitors. The dependence of the inhibitor efficiency on the concentration of the additive is shown in an increase of inhibiting power when the concentration is increased.

Nevertheless cases have been reported in which decomposable substances such as thioureas cause stimulation at relatively low concentrations, generating depolarizing agents under conditions of inadequate coverage of the electrode. At higher concentration, inhibition is obtained because of the favourable change in the ratio of decomposed materials to inhibiting materials and because of the increase in surface coverage. When the additives under consideration are enable of forming soluble complexes with the ions of the metal, a stimulation effect may appear at higher concentration.

It has also been seen that many organic substances retard corrosion to a lesser extent at higher concentration and sometimes become accelerators of the process. For examples the protective power of thiodiglycol in 5N hydrochloric acid decreases above 20m mole/l, and at concentration greater than 150m mole/l thioglycol substance accelerates the corrosion of steel in this medium. This falling off of
protective power was first explained by suggesting that aldehydes are hydrogen acceptors i.e. they play the part of hydrogen depolarizers, by virtue of their property to be reduced to alcohols.

1.5.5 Effect of the structure of inhibitors on their inhibiting properties

The use of inhibitors to protect metals from corrosion is associated with chemical adsorption, involving a change in the charge of the adsorbed substance and a transfer of charge from one phase to other. Hence molecular structure of inhibitors assumes special significance. The electron density at atom of functional groups constituting a reaction centre affects the strength of the adsorption bond. The strength of the bond also depends on the properties of the metal as well as on the polarizability of the functional group. According to the theory put forward by Heckerman and co-workers the inhibiting properties of many compounds are determined by the electron density at the atom constituting the main reaction centre. With an increase in the electron density at the reaction centre, the chemisorption bonds between the inhibitor and metal are strengthened. Heckerman revealed that the inhibiting properties of pyridine and its derivatives are increased at higher electron densities around the nitrogen atom following the sequence.

Pyridine <3-picoline <2-picoline <4-picoline

Similar trend is observed for aliphatic and cyclic amines, the higher the electron density at the nitrogen atom, the more effective will be the inhibitor. Cyclic amines are better inhibitors than aliphatic amines, for which the electron density at the nitrogen atom is considerably lower.

Trabanelli and his co-workers studied alicyclic amines and their derivatives and found that the effectiveness of the inhibitor increases considerably for a higher electron density at the nitrogen atom, the factor determining the electron-repulsive effect of the substituent.

The effectiveness of the functional atom in adsorption process for similar stability of the compounds varies according to the following sequence.

Selenium > Sulphur > Nitrogen > Oxygen
This indicates that the electronic structure of organic compound undoubtedly plays a definite role in phenomena of adsorption and corrosion inhibition.

Aliphatic compounds of different classes can be ranked as given below according to their adsorptivity i.e.

acids > amines > alcohols > ethers.

Molecules of organic substances containing electron donating active groups like CN, -CNS, -CNO, =CO, -CHO, -NH₂ are chemically adsorbed on surfaces of metals having unshared electron orbitals. The adsorption of surface active organic substances increases with molecular weight and dipole moment of the substances.

According to Mann et al²¹ the difference in activity between inhibitors of identical molecular weight but differing in structure is due to the fact that the ions of these inhibitors screen the metal surface to different extent since they cover greater or smaller areas of the surface when adsorbed.

The ability of organic substances of a given homologous series to be adsorbed is known to increase with increasing molecular weight of the compounds. The observed increase of protective power of aliphatic amines as the carbon chain is lengthened has been cited as an argument in favour of the adsorption theory hence methylamine < ethylamine < propylamine etc. For aldehydes, however, which are also effective inhibitors of acidic corrosion Kemkhadze and Balezin²² found a reverse trend:

formaldehyde > acetaldehyde > propionaldehyde etc. which cannot be explained in terms of adsorption theory of inhibitive action.

1.5.6 Chemical change of the adsorbed inhibitors during electrode process

Organic inhibitors adsorbed on the metal surface may undergo electrochemical reduction and thus form products which may also have inhibition properties. Inhibition caused by these substances whose stoichiometry is not changed from the beginning is called primary inhibition and secondary inhibition is caused by those substances which are generated during the electrode reaction and
by electrochemical or chemical reaction competing with the basic electrode reaction\(^3\). The inhibition efficiency may increase or decrease with time according to whether the secondary inhibition is more or less effective than the primary inhibition. Sulphoxides are reduced to sulphides which are efficient inhibitors\(^4\). Quaternary phosphonium and arsenium compounds have been found to be reduced to phosphine and arsine with little change in inhibition efficiency.\(^5\) Acetylene compounds can undergo reduction followed by polymerization forming multimolecular protective films.\(^6\) Thioureas are known to produce its ions which act as stimulators of corrosion.\(^7\)

### 1.5.7 Thermodynamics and Corrosion Kinetics in presence of inhibitors

An increase in temperature leads to different effects depending upon the nature of inhibitor. Belezin\(^8\) reported that the rate of corrosion of metal could be accelerated by increasing temperatures particularly in media in which evolution of hydrogen accompanied corrosion. Speller\(^9\) found that in a closed system the corrosion rate was linearly related to temperature while in open systems this linear relation was limited up to a certain temperature above which the corrosion rate falls with the rise of temperature owing to linear concentration of dissolved oxygen. The influence of temperature on reactions between metals and acids was studied by Calcott and Whetzel.\(^10\) They found that between 20°C and 100°C the logarithm of the corrosion rate \(p\) is a function of temperature \(t\) as 

\[
\log p = a + bt - (15)
\]

where \(a\) and \(b\) are empirical constants and \(t\) is temperature in °C. Putilova et al\(^11\) established a relationship between the logarithm of the corrosion rate and the value of \(1/T\) (\(T\) is in Kelvin) and obtained a linear relationship.

\[
\log p = A/T + B \quad (16)
\]

This relationship resembles Arrhenius equation. Gorbachov et al\(^12\) proposed a similar relationship between corrosion current density (I) and temperature in the electrochemical corrosion reaction as

\[
\log I = A/T + B \quad (17)
\]
where $A$ and $B$ are characteristic constants for a given reaction. Comparing equation 16 with equation 17 it can be seen that the $\rho$ is proportional to the rate constant of the reaction. Gorbachov et al showed that the constant $A$ has the value

$$A = -\frac{E_{\text{eff}}}{2.3R}.$$  \hspace{1cm} (18)

Where $E_{\text{eff}}$ is the effective activation energy given by the slope of function $\rho = f(1/T)$, and $R$, is the universal gas constant. For the corrosion process the value of $E_{\text{eff}}$ can be written as

$$E_{\text{eff}} = -2.303 \times 1.987 \frac{d (\log \rho)}{d(1/T)} \text{cal/mole}.$$  \hspace{1cm} (19)

The value of the effective activation energy for various acid corroding metals in the presence and absence of inhibitors have been calculated by many authors. The rate of corrosion of metals in acid solution containing inhibitors were shown by them to rise rapidly with increasing temperature.

Sieverts and Lueg remarked that desorption of inhibitors when temperature is raised must lead to a loss of protective activity. On the other hand Machu came to the conclusion that in the presence of powerful inhibitors, the temperature coefficient as well as the corrosion rate is lowered.

According to Putilova the relation $\log \rho = f(1/T)$ is not always linear in the presence of inhibitors. Three different types of behaviour can be seen. In the first case the activity of the inhibitor which retards corrosion at lower temperatures, decreases at higher temperature. In this case activation energy of the reaction rate is higher in the presence of inhibitors than its absence. Behaviour of such inhibitors can be compared with the behaviour of unstable catalytic poison.

The second group of inhibitors do not change the effective activation energy of the process when the temperature is raised. In this case corrosion rate remains unchanged at low as well as at elevated temperatures in the presence of inhibitors. These inhibitors resemble in behaviour with the stable poisons in heterogeneous catalysis which, as Taylor has shown do not affect the temperature coefficient of the reaction.
The compounds belonging to the third group of inhibitors for which the effective activation energy of the process is lower in the presence of inhibitors than in its absence. Such inhibitors are of great interest from the practical point of view, when the reduction of corrosion at elevated temperature is desired. Such inhibitors are firmly held on the metallic surface. It may be presumed that they are bound to the surface by specific adsorption forces or by chemisorption, as a result of which a surface film of the reaction product is formed. In such cases specific adsorption of the products of reaction between the inhibitors and the metal salt formed in the acid may occur as well as adsorption of the inhibitors itself. Dibenzyl sulphide, dibenzyl sulphoxides and iodides belong to this category.

1.6 Techniques For The Study Of Corrosion:

There are several methods to study the corrosion behaviour of metals and alloys in corrosive environments. In recent years, weight loss methods, electrochemical and microscopic methods have been frequently employed to study the corrosion phenomenon of metals and alloys.

1.6.1 Weight Loss Method:

This is a direct method of corrosion rate measurement in corrosive environment. Weight loss can be determined by weighing the samples before and after exposure. Weight loss measurement is valid only if corrosion is perfectly uniform. One major drawback in this method is that the corroding metal has a film of corrosion products. At the time of weighing (after exposure) it is necessary to remove the corrosion products from the surface without removing any of solid metal.

Weight loss is frequently expressed as loss in weight per unit area per unit time. By introducing the density of the metal into the calculation, the loss in thickness per unit time can be determined. Corrosion rates are usually expressed either in mg/dm².day i.e. mdd or in mpy (mils per year) where 1 mil is 1/1000 of an inch. The corrosion rate in mpy is readily calculated from weight loss of metal specimen after the exposure of the specimen to the corroden by the formula:

\[ \text{Corrosion rate (mpy)} = \frac{534 \ W}{\text{DAT}} \] (20)
where,
\[ W = \text{weight loss in mg} \]
\[ D = \text{density of specimen (g/cm}^2) \]
\[ A = \text{area of specimen in square inch} \]
\[ T = \text{exposure time in hours} \]

Some other similar methods used are:

i) Oxygen consumption\(^{44}\) and hydrogen evolution\(^{45}\)

ii) Loss of metal thickness\(^{46,47}\)

iii) Loss of electrical conductivity\(^{48}\)

iv) Loss of tensile strength\(^{49}\)

v) Loss of reflectivity\(^{50}\)

vi) Change in conductivity of corroding liquid\(^{51}\)

These methods are used only in certain specific studies and do not have universality of the weight loss method.

1.6.2 Electrochemical Techniques

As most of the corrosion processes are electrochemical in nature hence electrochemical techniques can be used to study the corrosion rates as well as the mechanism involved. The main requirements for the application of such techniques are that (a) the environment should be continuous and fairly conducting, (b) the oxidation state of the metal in the particular environment must be known and (c) the measuring instruments and the techniques adopted should not disturb the normal corrosion process in a manner that may make the result meaningless. The electrochemical method of testing involves the determination of specific properties of the electrical double layer formed when a metal is placed in contact with a solution. The following techniques are generally employed to study the corrosion by this method:

1.6.2.1 Electrode potential measurement:

The electrode potential of a metal and alloy sample is measured with respect to a reference electrode as a function of time. In general such measurements can be used to explain corrosion behaviour, as they can furnish information on whether the cathodic or anodic process or both are controlling corrosion. A shift in
the electrode potential in the cathodic direction could be due to either depolarization of the cathode or increased polarization of the anode. In a similar manner a shift of electrode potential towards anodic direction would indicate either increased polarization at the cathode or depolarization at the anode. Such measurements can also provide useful information about film breakdown or film repair.

This method is qualitative and is employed in evaluation of inhibitors, conversion coatings and organic coatings and also in underground corrosion of pipelines. This method has the limitation that it can be applied only to the systems whose electrode potential characteristics are known.

1.6.2.2 Polarization measurement:

When a net current flows to or from the surface of an electrode, it remains no longer in equilibrium. The equilibrium potential of such an electrode is altered to an extent that depends on the magnitude of the external current and its direction. The potential always change in a direction so as to oppose the flow of current, whether the current is of galvanic or is impressed externally. The extent of potential change caused by the net current to or from an electrode measured in volts, is called polarization. In potentiostatic polarization technique, the potential is kept constant until the current reaches a stable value. The values of the steady state current are then recorded for successive input potentials and the curve of potential-dependent current is obtained. The corrosion rate is determined from the polarization data either by extrapolation of Tafel lines of the anodic or cathodic reaction to the corrosion potential or by linear polarization tests using Stern-Geary equation.52

(a) Tafel Extrapolation method:

Corrosion rate determination by Tafel-line extrapolation method53 is based on the theory of rate equation which predicts that under activation control, the overvoltage greater than $RT/nF$ is related to the applied current according to the Tafel equation.53

$$\eta = \pm \beta \ln \frac{i}{i_0}$$  \hspace{1cm} (21)
where,

\( \eta \) is the overvoltage,

\( \beta \) is the Tafel slope in volts per decade,

\( i \) is the applied current density

\( i_0 \) is the exchange current density at equilibrium potential.

Over-voltage for anodic and cathodic reactions are plotted against the logarithm of applied current density. (Fig. 1.3) The point of intersection of the extrapolation of the two Tafel-lines corresponds to the corrosion potential \( E_{corr} \) and the corrosion current density \( I_{corr} \) using corrosion current density, corrosion rate can be calculated with the help of following relation:

\[
\text{Corrosion Rate (mpy)} = 0.1288 \frac{I_{corr} \cdot E}{D} \quad (22)
\]

where \( I_{corr} \) = corrosion current density (\( \mu \) A/cm²)

\( E \) = Gram equivalent weight of metal

\( D \) = Density of metal (g/cm²)

However, this method is time consuming and considerable polarization from the steady state condition, of the order of hundreds of millivolts, may disturb the system and make the results meaningless unless the applied currents are of the order of the corrosion current.

(b) Linear Polarization (Resistance) method:

The linear polarization method is based on the fact that within 10 to 20mV of the corrosion potential, the overvoltage varies linearly with applied current. Steam and Geary derived the following mathematical relationship necessary for the application of the experimental data to calculate the corrosion rate:

\[
I_{corr} = \frac{|\beta_a| |\beta_c|}{2 \cdot 30.3 (|\beta_a| + |\beta_c|)} \times \frac{\Delta I}{\Delta E} \quad (23)
\]

where,

\( |\beta_a| \) = Anodic Tafel slope

\( |\beta_c| \) = Cathodic Tafel slope

\( \frac{\Delta I}{\Delta E} \) = Admittance (reciprocal slope of the potential versus current line)
The $\frac{\Delta i}{\Delta E}$ has the dimensions of resistance and it is generally called the polarization resistance. Many investigators$^{54-56}$ have used linear polarization technique. Corrosion rates can be calculated immediately, if good values for the constants $\beta_0$ and $\beta_c$ are available. In case where great precision is not required, the values which are reported in literature for these constants can be used for the calculation of corrosion rate. If more accuracy is required, the constants could be derived from the polarization curve. The advantage of the linear polarization method is in the ability to complete a large number of determination in a few minutes. It is particularly useful in situations where relative rather than absolute corrosion rates are required. Such cases could be evaluation of inhibitors or screening a variety of alloys for a particular service.

1.6.3 Surface studies

The surface study of metals and alloys before and after corrosion is used to estimate the mechanism and rate of corrosion. X-ray and electron diffraction techniques are successfully used to study the structure of the corrosion product film on the metal surface responsible for the passivation$^{57,58}$. The electron probe analysis is used for the surface topography$^{59}$. Here, an electron probe down to 50Å in diameter is scanned in a rectangular raster across the surface to be studied. Secondary electrons emitted at the point of impact of the beam are accelerated by an auxiliary electrode close to the surface into a scintillation counter and the electrical signal so generated is amplified and used to modulate the brightness of a cathode ray tube, the time base of which is synchronized with the probe scanning this base. In this way, a picture of the surface is built up with the contrast determined largely by the surface topography and also to some degree by differences in the chemical composition. The electron probe analysis combined with electron microscopy and diffraction is used now-a-days for microstructural studies of their films and surfaces$^{60}$. Several new surface analysis techniques like Auger electron
spectroscopy (AES), Electron spectroscopy for chemical analysis (ESCA), secondary ion mass (SIMS) and scanning electron microscopy (SEM) are being used frequently to investigate surface films on metals and alloys.

1.6.3.1 Auger Electron Spectroscopy (AES):

In Auger Electron spectroscopy a specimen is excited with an electron beam causing inner shell electrons to be removed from the atoms present. Through a relaxation mechanism, outer shell electrons fill the created vacancies and so called "Auger electrons" are ejected from the material. An Auger spectrum is obtained by plotting the derivative of the electron energy distribution vs energy. The typical depth analysis with AES is of the order of 10 Å or less and elemental concentrations as low as 0.1% of a monolayer can be detected and identified. Both qualitative and quantitative information can be obtained for all elements above helium.

The inner core vacancy is created by electron bombardment of the surface with electrons having energies in the range of 1-5 keV. Auger electrons are generated having energies in the range of 0 to 2000 eV and only those electrons coming from within few monolayers of the surface escape with characteristic energy. The depth profiles of the surface films are obtained by sputtering the surface away slowly by Ar+ ions. The absolute thickness of the surface film cannot be determined but the information about the thickness relative to the sputtering of Ta$_2$O$_5$ can be easily obtained.

1.6.3.2 Electron Spectroscopy For Chemical Analysis (ESCA)

Electron spectroscopy for chemical analysis (ESCA) also referred to as X-ray photo-electron spectroscopy (XPS) bears much in common with AES. In ESCA a specimen under vacuum is irradiated with monochromatic X-ray causing electron with kinetic energies characteristics of the parent atoms and the incident X-ray energy to be ejected from the specimen. A spectrum containing distinguishing peaks for each constituent element is obtained by plotting the total number of ejected electrons vs kinetic energy. ESCA is a surface analysis technique with a typical analysis depth of the order of 20Å or less, and ultimate sensitivity is sufficient to
allow fractions of a monolayer to be detected and identified. It can also provide chemical binding information about the atoms on the surface of a material. An ESCA signal is obtained for all elements in the periodic table above helium and adjacent elements are clearly distinguished. AES and ESCA techniques have their own relative advantages while they both provide a surface composition analysis. AES offers superior spatial resolution and higher sensitivity for a given analysis time than ESCA. It is a preferred technique for rapid elemental analysis of specimens that are not easily damaged by electron bombardment. ESCA is the preferred analysis technique when electron radiation damage is of concern, since x-ray excitation causes very little radiation damage to most of the specimens. ESCA also provides more detailed chemical information than AES.

1.6.3.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is very useful technique to study the morphology of corroded surface of the specimen. In SEM the specimen is scanned with a timely focused electron beam that traces out a line raster pattern. The essence of this technique which is characteristic of all electron probe scanning instruments, is that there is a point to point corresponding between object and image at any moment.

Sometimes, other techniques like radiotracer, nuclear magnetic resonance, ultrasonic Mossbauer technique, etc. are also used to study the corrosion behaviour of metals and alloys in certain specific investigations.
1.7 Review of past work on inhibitors

The growth of industry and new technical developments makes the problem of protecting metals against corrosion more important. When various methods of protecting metals, such as plating or lacquering are either ineffective or inapplicable, corrosion inhibitors can be employed to advantage. This makes possible preservation of hundreds of thousands of tons of ferrous and nonferrous metals and often leads to considerable improvement in working conditions and a rise in productivity. The results of the industrial application of inhibitors can be made known more widely through the technological literature, since problems concerning protection of metals against corrosion by means of inhibitors are attracting a growing amount of attention from workers in the most diverse professions. A large number of organic compounds have been studied as corrosion inhibitors for various metals and alloys by many workers. A brief description of the work done about inhibitors for corrosion protection of metal and alloys by various workers is summarized below.

Heckerman et al. have compared the adsorption characteristics and the inhibition efficiencies of 4-ethylpyridine with those of polyvinylpyridines having different degrees of polymerization. The authors have shown that adsorption of the polymers takes place through several points of the molecules and the surface area of the metal inhibited in solution of hydrochloric acid containing polyvinylpyridine is considerably greater than the area physically covered by the adsorbed molecules.

Afanas'ev et al. carried out comprehensive studies of industrial inhibitors designed for pickling metals. Their purpose was to find the most effective modes of application of these inhibitors under industrial conditions since during pickling in a bath iron sulphates tend to accumulate. They observed that if ferrous sulphate is added to sulphuric acid, the rate of dissolution of steel is greater by a factor of 1.1 to 1.7.

Antropov studied the behaviour of pyridine derivatives as inhibitors of the acid corrosion of iron, coming to the conclusion after an examination of the
variation in coverage as a function of the molecular structure that the compounds examined are adsorbed on the metal surface in the form of cations and not as neutral molecules with nitrogen atoms as the active centre.

Miskirham et al.\textsuperscript{70} studied the protective properties of halides of substituted ammonium compounds. Of the compounds studied by them, the most effective in 6N sulphuric acid were benzylallylamine hydriodide, allylpiperidine hydriodide, allylebenzylamine hydrobromide and triallylamine hydrobromide. The good protective properties of these compounds were attributed to the enhanced adsorptivity of iodine and bromine. It was also found that compounds studied proved to be effective in hydrochloric acids as well. These compounds also show the protective properties at higher temperatures, showing that the inhibitors act according to a chemisorption mechanism.

Organic derivatives of phosphorous with sulphur or selenium in the molecule, were studied by Smialowska\textsuperscript{71}. The results of the electrochemical and gas volumetric measurements showed adsorption of inhibitors following the Freundlich isotherm. The inhibition efficiency of the compounds containing the same aliphatic substituent was higher in the presence of selenium than in the presence of sulphur in the molecule.

Antropov and his co-workers\textsuperscript{72} carried out systematic studies of individual organic compounds as corrosion inhibitors, as well as studies of their mechanism of action. The nitrogen containing compounds in the pyridine series included the following: pyridine, 2-picoline, 2,4,6-lutidine, aniline, ethylaniline etc. Compounds of this series slightly inhibit the corrosion of iron in sulphuric acid. The protective effect in hydrochloric acid is even less. However, they found that the inhibiting properties are greatly enhanced when we pass salts of pyridine bases. Quaternary salts of pyridine bases also manifest an inhibiting effects for zine in 1N H\textsubscript{2}SO\textsubscript{4}.

Aronslen et al.\textsuperscript{73} investigated the inhibiting action of amines of the fatty and aromatic series, as well as of the heterocyclic nitrogen containing substances. They found good protective properties only for quaternary pyridine salts of halogen
hydracids. N-cetylpyridine chloride, N-cetylpyridine bromide, n-cetylpyridine iodide. It was also established that the inhibiting effect of urotropine is increased when it is mixed with sulphur containing compounds like thio carbamide, diphenyl thio carbamide and thiophene.

Machu\textsuperscript{74} and many others\textsuperscript{75-78} showed that organic substances containing atoms of both nitrogen and sulphur in the molecule found application in pickling treatments. These compounds were thiourea and its derivatives substituted on the nitrogen atom with aliphatic chains or aromatic rings.

Balezin et al\textsuperscript{79} investigated the protective properties of sulphur containing compounds in dilute sulphuric acid. Derivatives of 2-mercapto imidazole were found to have the best protective properties. The optimum inhibiting effect was for unsaturated compounds mixed with granulated 2-mercaptobenzimidazole. A mixture of propargyl alcohal with 2-mercaptobenzimidazole lowered the corrosion rate of iron by a factor of 500 to 1000 at 70°C.

Petrova and Klyuchnikov\textsuperscript{80} studied the protective properties of alcohols of the acetylene series. For steel propine-1-ol-3 and hexine-1-ol-3 are reported to be effective inhibitors. They found that the protective action of a secondary alcohol was enhanced with a rise in temperature. Tertiary alcohols were weak inhibitors, and with an increase in molecular weight, their inhibiting effect falls off. The mechanism of action of alcohols of the acetylene series is evidently an adsorption mechanism. For non ferrous metals, nickel and cobalt in particular, these compounds are less effective.

Kurbanov et al\textsuperscript{81} investigated the protective properties of propargyl esters of alkylphenols with regard to steel. The best inhibiting effect was shown by propargyl ester of unsubstituted phenol. The protective effects was found to increase for higher degrees of non saturation of the phenol esters, which according to authors indicates a definite role of the triple bond.
Smilowski and Smialowska\textsuperscript{82} showed that fatty acid decreases the density of the critical anodic current of a 13 cr steel in \( \text{H}_2\text{SO}_4 \). The inhibition efficiency increases when the number of carbon atoms in the additives is increased in the following sequence: acetic acid, propionic acid, \( n \)-butyric acid, \( n \)-valeric acid, \( n \)-caporic acid and \( n \)-capric acid. An explanation of the phenomenon by the authors is based on adsorption of the anions of these fatty acids on the metal surface with subsequent reduction of the active zones for through anodic dissolution.

Kurbanov et al\textsuperscript{83} studied amino derivatives of thioesters as inhibitors of corrosion for steel in 1.0N hydrochloric, sulphuric and citric acids. In synthesizing these compounds, Kurbanav et al based themselves on the assumption that introducing into a molecule of a propagyl thioesters an amino group capable of being adsorbed on a metal surface enhances the inhibiting effect of the compounds. They concluded that the main role in the process of corrosion inhibition by propargyl ether is played by the final acetylene bond and that its shielding by the heteroatom impedes adsorption.

Foroulis\textsuperscript{84} studied the effect of \( n \)-butylanmine, aniline cyclohexylamine and pyridine on nickel monel and copper while Trabanelli, Zucchi and Zucchine\textsuperscript{85,86} used carbon monoxide in comparative measurements of inhibition on iron and nickel in solutions of hydrochloric and sulphuric acids.

\( \alpha \)-alkenylphenones as a new class of corrosion inhibitors for steel in strong HCl is reported by Fremier et al\textsuperscript{87}. It was found that when formulated with small amounts of surfactants, \( \alpha \)-alkenylphenones provide excellent protection for oil field steel in contact with strong HCl (up to 28\%). The protective levels are similar to, and some times superior to those provided by alkynols. All the four alkenylphenones namely benzoylallyl alcohol, benzoyl dioxane benzoyldimethoxy propane and benzoylmethoxy propene used provide protection to the corrosion of steels.

A series of compounds having the N-acylamino acid or related structure were investigated by DeBerry and Viehbeck\textsuperscript{88} as potential inhibitors of localized
corrosion of 304 L stainless steel. The compounds which showed the greatest inhibition effects have both a long hydrocarbon group and a polar region containing a carboxylic acid group and other polar functional groups.

Chaudhary et al have investigated various organic compounds as corrosion inhibitors for many metals and alloys in different acids. They used o-, m-, p-tolyl thioureas, \textsuperscript{89}1[(5-mercapto)-1, 3, 4-thiadiazolyl] 3-0-tolyl, \textsuperscript{90}paratoludine, para anisidine, parachloro aniline, paramino benzoic acid and paraphenetidine\textsuperscript{91} for corrosion protection of 1060 aluminium in nitric acid solution. It was observed that p-tolyl thiourea was more efficient than its other two isomers at all the three temperatures studied. All the three tolyl thioureas were found to be mixed type of inhibitors. In the case of p-substituted aromatic amines, paraamino benzoic acid showed maximum efficiency and the efficiency decreases in the following order. Para-amino benzoic and >para-anisidine >paraphenetidine >para toluidine>parachloro aniline.

Inhibitive effects of some azoles\textsuperscript{92} such as 2 mercapto benzothiazole, sulphatriazole and 1,2,3-benzotriazole and substituted urea\textsuperscript{93} compounds for corrosion of aluminium in nitric acid have also been reported. Azoles were found to be most effective at 200 ppm concentration. At 250 ppm concentration, the inhibition efficiency of the compounds decreases, which is probably due to the formation of corrosion promoting species like S\textsuperscript{2-} and HS\textsuperscript{-}. Chaudhary et al\textsuperscript{94} have also reported the inhibitive effect of 2-picoline, 3-picoline and 4-picoline on the corrosion behaviour of aluminium alloys in one percent hydrochloric acid. The inhibitors were found to retard the corrosion by predominantly acting on local cathodes. Corrosion protection properties of azoles\textsuperscript{95} amines\textsuperscript{96} and pyridine and its derivatives\textsuperscript{97} towards the corrosion of 70/30 in brass in sulphuric acid are also reported by Chaudhary et al. The inhibition efficiency of azoles for the corrosion of \alpha-brass has been found to decrease in the following order 2 - mercaptobenzothiazole > benzotriazole > benzimidazole. All the three azole compounds used were mixed inhibitors and inhibitive action is due to the formation of a protective complex film mainly with copper metal ions on the surface of the alloy. All the amine compounds studied
showed a poor efficiency and are anodic inhibitors. Pyridine, 2-picoline, 3-picoline and 4-picoline were also reported to decrease the corrosion rate of brass in 1% H$_2$SO$_4$. The inhibitive efficiency of these compounds may be arranged in the following order: 2-picoline > 4-picoline > 3-picoline > pyridine. The relative inhibitive efficiencies of these compounds are dependent on the relative position of N and -CH$_3$ group in the pyridine ring and the effective electron density which affects the surface adsorption characteristics. Malachite green, congo red, crystal violet, alizarin and methyl orange along with benzotriazole have been reported to provide better protection from corrosion and dezincification of 63/37 brass in 1% H$_2$SO$_4$ solution than in the presence of benzotriazole alone.

Chaudhary and Chaturvedi investigated the inhibitive action of some azoles and hexamethylene tetramine towards the corrosion of mild steel in sulphuric acid solution. The effectiveness of the investigated azole compounds was found in the order: 4-amino -5-ethyl -3-mercapto-1,2,4-trizole > 4-amino -3-mercapto -5-methy-1,2,4-triazole > 4-amino -5H-3-mercapto- 1,2,4-triazole. Low value of heat of adsorption is reported for all the azoles studied. They also used pyridine and 3-picoline for the corrosion protection of mild steel in perchloric acid solution. 3-picoline provided better protection than pyridine.

The inhibitive action of resorcinol and pyrogallol for the corrosion of mild steel in 1N sulphuric acid solution has been studied by Gurmeet Singh and Jha. They reported that these compounds are predominantly anodic inhibitors and inhibition efficiencies upto about 82% can be obtained. The inhibition was found to occur via chemisorption.

Sethumadhavan et al. have investigated 1, 10-phenanthroline as a corrosion inhibitor for mild steel in sulphuric acid solution. They concluded that 1, 10-phenanthroline is a good inhibitor for the corrosion of mild steel at lower temperature but at a higher temperature (50 and 60°C) the compound at 10$^{-8}$ M concentration rather acts in a catalytic manner.
J.D. Talati et al\textsuperscript{104} investigated the effects of some dyes on the difference effect for aluminium-copper alloy in hydrochloric acid. The inhibitive efficiency increases in the following order.

Catechol Violet (~11\%) < dimethyl yellow < fast sulphan black F < acridine orange < methyl red < alizarin red S < rhodamine B < bromo cresol purple < bromo cresol green < eriochrome black T (~90\%). With an impressed anodic current the Al-4\% cu alloy shows a negative difference effect in plain as well as inhibited HCl. The DE increases linearly with cd in the case of uninhibited acid and also to a certain extent in inhibited acid.

The effect of triphenylmethane dyes as inhibitors for Al-copper alloy in phosphoric acid solution has been studied by J.D. Talati et al\textsuperscript{105}. The inhibitive efficiency of triphenylamine dyes for B 26S aluminium in phosphoric acid has been found to increase with increase in inhibitor concentration but decrease with acid concentration. At 0.5\% inhibitor concentration in 0.033M H\textsubscript{3}PO\textsubscript{4}, the efficiency increases in the order: Methyl violet 6B (15\%) < crystal violet < fuchsine acid < fuchsine base (36\%) < malachite green (68\%) < victoria blue (75\%) < light green < fast green (88\%).

The inhibitive effect of these dyes for aluminium copper alloy has also been investigated in sulfuric acid solution by J.D. Talati et al\textsuperscript{106}.

They observed that inhibitive efficiency increases with inhibitor concentration whereas at constant inhibitor concentration the efficiency first decreases with increase in acid concentration up to 1.0M and then decreases; the increase in efficiency in 4M acid being in the order methyl violet < fuchsine base < victoria blue < fuchsine acid < light green < crystal violet < malachite green < fast green. The inhibitors appear to function through general adsorption following Langmuir adsorption isotherm.

Gurmeet Singh et al\textsuperscript{107} investigated the synergistic effect of halide ions on the corrosion inhibition of mild steel in presence of ethylenediamine in IN sulphuric acid. They observed that addition of halides increases the corrosion in general but
iodide and to a certain extent bromide reduces the corrosion rate at certain concentration. In general the inhibition efficiency of ethylenediamine increases by the addition of halides and the effect is in the order I\(^{-}>Br\(^{-}>Cl\(^{-}\). The synergistic effect is explained due to Co-and overlap adsorption of halide ions and inhibitor molecules and/or cations. They also studied the corrosion behaviour of mild steel in sulphuric acid medium in presence of acrylamide, methylacrylamide and dimethylacrylamide at 25\(^\circ\)C. It was observed that these compounds are anodic inhibitors and inhibition efficiency up to 85\% can be obtained. The inhibitors appear to function through Langmuir adsorption. It is concluded from the depth analysis of the specimen surface that the adsorption of the additives on mild steel surface is in order of acrylamide methylacrylamide dimethylacrylamide.

Jha studied the corrosion inhibition of mild steel by anisidenes in 1.0M HCl solution. The inhibition is assumed to occur via chemisorption of the additive molecules. P-anisidine has been found to be less effective than o- and m-anisidine. XPS results showed that N 1s electron is responsible for complex formation between o-anisidine and mild steel.

Corrosion of mild steel in sulphuric acid solution with D-galactose thiosemicarbazone, 1-phenyl thiosemicarbazide and 4-phenyl thiosemicarbazide as inhibitor was studied by Khamis. Results reported elucidate the effect of temperature and the molecular structure on the inhibition efficiency. The inhibitors acted as mixed type inhibitors and obeyed Tempkin adsorption isotherm.

Ismail and Sanad recently studied the corrosion inhibition effect of hexamine, quinoline and thiourea on different types of stainless steel in 1.0M hydrochloric acid solution. These compounds acted as mixed type inhibitor. Hexamine and quinoline were found to be more effective for stainless steel type 430 and 440.

Aldehydes as inhibitors of corrosion of mild steel in HCl, H\(_2\)SO\(_4\), HClO\(_4\) acids have been reported by Balakrishnan and Devarajan. They used benzaldehyde, o- and p-hydroxybenzaldehyde, o- and p-tolualdehyde, anisaldehyde,
vanilline, cinnamaldehyde, crotonaldehyde and furfural and concluded that adsorption is not the only process that determines inhibition but inhibition also depended on how the adsorbed molecules interact with metal surface. In some cases like cinnamaldehyde the adsorbed molecules form surface complexes with the metal which is responsible for high inhibition efficiency.

Abdel aal and Assaf\textsuperscript{113} studied the corrosion inhibition of tin and cadmium in IN H\textsubscript{2}SO\textsubscript{4}, solution using aniline, o-toluidine, m-toluidine, p-toluidine, 2-chloroaniline, 3-chloroaniline, 4-chloroaniline, pyridine, 2-picoline, 3-picoline, 4-picoline, 2-amino pyridine and 3-aminopyrididine. The structural inhibition correlation indicated that -CH\textsubscript{3} substitution in aniline decreased its inhibition efficiency for tin, while Cl substitution increased the efficiency. Substitution of -CH\textsubscript{3} in the ortho and para position of pyridine improved the inhibition efficiency for tin but decreased it in case of cadmium. Amino group in the ortho position of pyridine increased its efficiency for both tin and cadmium but it had no effect when it was in the meta position.

The work on corrosion inhibition of zinc in hydrochloric acid solution by several pyrazole derivatives namely, 3(5) amino 5(3) phenylpyrazole, 3(5) amino-5(3) [4'methylphenyl] pyrazole, 3(5) amino-5(3) [4'methoxyphenyl] pyrazole and 3(5) amino -5(3) [4'chloro-phenyl] pyrazole was reported by Allah et al\textsuperscript{114}. Their efficiencies were 77\%, 85\%, 87.8\% and 89\% respectively and they acted as anodic inhibitors. The adsorption process of additives was observed to obey Temkin isotherm.

M.N. Desai et al\textsuperscript{115} examined the seven Schiff bases as corrosion inhibitors of mild steel in 1.0-6.0N solutions of HCl. They observed that all these compounds were predominantly cathodic inhibitors and protective action of the inhibitor increases with increase in HCl concentration. All these compounds seem to function as inhibitors by being adsorbed on metal surface. They obey Freundlich adsorption isotherm and efficiency improves with an increase in temperature.
Banerjee et al. studied the synergistic effects of some surface active compounds like tetramethyl ammonium iodide, formaldehyde, thiourea and potassium chromate with methyl amine, cyclohexylamine, aniline in corrosion inhibition of mild steel in sulphuric acid solution. They observed that following mixed inhibitor systems were found to have highly synergistic effect in inhibition of corrosion of mild steel in sulphuric acid.

Thiourea+aniline, Thiourea+cyclohexylamine, Thiourea+methanolamine, Formaldehyde+aniline, Potassium chromate+aniline.

H.M.Wahdan et al. investigated the effects of polyvinylacetic acid ether as inhibitors for corrosion of mild steel in H₂SO₄. They concluded that dissolution of mild steel greatly reduced in the presence of polyvinylacetic acid ether as a result of adsorption and formation of thin layer of these polymers on the surface of mild steel electrode and these were anodic inhibitors. Moreover, the inhibition efficiency was found to be increased with increase in the concentration of polymers and it reaches 90% at the concentration of 1% by weight.

N. Rajendran et al. studied the effect of diphenylthiourea (DPTU) on the corrosion of mild steel in stimulated flue gas desulphurization (FGD) environment. They concluded that DPTU can be used as a potent inhibitor to prevent corrosion of mild steel in FGD environment, the inhibitive action of DPTU was attributed to metal-sulphur bond formation proving that it function as an anodic inhibitors. It has been investigated that though the inhibition efficiency decreases with increase in temperature, it is more than 91% at 323±2K which is the normal operating range of FGD system.

Inhibition of corrosion of mild steel in aqueous solution of chloride by chromate has been studied by Somnath et al. They observed that corrosion of mild steel decrease as the concentration of chromate is increased, chromate remained effective at high temperature (up to 80°C). The mechanism of the action of inhibitor indicate the anodic nature of inhibitor.
Corrosion inhibition of mild steels by pyridine derivatives in 0.1M HCl solutions has been investigated by Mehta et al. The results show the order of inhibition efficiency as pyridine < Lutidine < collidine < nicoitinamide.

N.C. Subramanyam et al. studied the effect of substituted Tertiary arsines, phosphines and stibines as corrosion inhibitors for mild steel in hydrochloric acid. A significant decrease in corrosion rate was observed in presence of these inhibitors, these compounds act as mixed inhibitors.

Inhibition by Zinc molybdate mixtures of corrosion of mild steel in chloride solution has been studied by Qian et al. It was concluded that better inhibition obtained with mixtures than with the individual components was due to the mixture acting as cathodic inhibitor.

An ellipsometric study has been made on the effect of the inhibitors indole, thiosemi carbazide (TSC) and thioacetamide (TAA) on the surface of mild steel in hydrochloric acid by Brakenburg et al. Lower corrosion rates were obtained with indole and TSC if the specimens immersed were cathodically polarized whereas with TAA no significant difference was observed.

Tripathi et al. studied the influence of ascorbic acid on the corrosion of mild steel in brackish water. It was observed that the presence of ascorbic acid (>0.05M) influence the formation of usual corrosion products like β,α-FeOOH and ferrihydrite and retard the rate of rust formation.

The corrosion inhibition of mild steel by ascorbic (AA) and folic acids (FA) in 0.3% NaCl solution has also been studied by Isao Sekine et al. They observed that AA and FA show good corrosion inhibition in comparatively low concentrations, the maximum inhibition effect by AA at 30-80°C was shown at 200ppm, while that by FA was shown at 500ppm concentration in the range of 30-40°C and in 100ppm at 60-80°C, both AA and FA were considered to inhibit by chemical adsorption and obey Langmuir adsorption isotherm. The effect of thiourea and its derivatives on the anodic dissolution of mild steel in HCl has been studied by K.ChandraSekara Pillai. He found that thiourea and N-substituted derivatives show maximum anodic
polarization when present at low concentrations. The anodic Tafel slope show an abrupt change in the intermediate concentration range i.e. 4-40mM, which has been explained in terms of protonated species taking part in metal dissolution. S-substituted derivatives exert increasing anodic polarization with increasing concentration.

The adsorption of thiourea on mild steel in 1N H₂SO₄ has been studied by Ateya et al. Degree of surface coverage was found to increase with temperature and concentration. It was shown that at 20°C the adsorption behaviour follows Frumkin type isotherm, and at 30-50°C the adsorption behavior follows a Flory-Huggins isotherm.
1.8 Justification and objectives of the present work

Since mild steel is widely used in various industries and is highly reactive in the presence of aggressive environment, it is therefore, necessary to understand the corrosion behaviour of mild steel in different acids and to develop suitable methods to prevent the corrosion of mild steel. Aim of the present investigation was to investigate the corrosion behaviour of mild steel in sulphuric acid, hydrochloric acid, perchloric acid and phosphoric acid and to control its corrosion by using some organic dyes as inhibitors. Dyes have been selected for investigations on the basis of the following points:

I. Literature survey shows that organic dyes have not been investigated to control the corrosion of mild steel in acidic solutions.

II. During the recent years there has been a trend in industries to add dyes to acid solutions to give acids a particular colour so that it may be easier for the industry to educate its workers to handle acids carefully.

III. The selected dyes are cheap and easily available in the market.

Keeping in view the above factors various dyes Viz. methylene blue, auramine O, methyl red, rhodamine B, and turquoise blue have been used in the present work to investigate their influence on the corrosion behaviour of mild steel in different acid solutions, with the following objectives:

I. To employ weight loss, potentiostatic polarization, linear polarization resistance, scanning electron microscopy and ESCA techniques to carry out experiments for investigating the corrosion behaviour of mild steel in sulphuric acid, hydrochloric acid, perchloric acid and phosphoric acid solutions in presence and absence of dyes.

II. To evaluate various corrosion parameters like corrosion potential, corrosion current density, corrosion rate, Tafel slopes, inhibition efficiency etc.

III. To carry out investigations with different concentrations of various dyes in the corroding systems.
IV. To study the mechanisms by which various dyes reduce the corrosion rate of mild steel.

V. To find the influence of temperature on the efficiency of the dyes.

VI. To determine the adsorption mechanism of the dyes by computing the data for various adsorption isotherms.

VII. To evaluate heat of adsorption and activation energy values in presence of dyes as inhibitors.

VIII. To study the morphology of corroded specimens in the absence and presence of various dyes by scanning electron microscopy.

IX. To find the elemental composition of the surface film present on the corroded samples in the presence of various dyes by ESCA technique.