CHAPTER (1)

INTRODUCTION

1.1- *Definition of Corrosion*

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. The vast majority of metals occur naturally in the combined state (commonly as oxides or sulphides) They are only won from these ores by a high energy input. Thermodynamically, the return of a metal to the combined state by corrosion is, therefore, expected to be a spontaneous process. The corrosion products of this reaction may be solid, liquid or gas. Both the physical and chemical natures of the products are important since they frequently influence the subsequent rate of corrosion. Corrosion is a complex process and its study is still more complex due to various and varying conditions of environment.(1)

The majority of metal-corroding processes taking place in electrolytes are electrochemical in nature. The rate of any given electrochemical corrosion process depends on the rates of two conjugate reactions proceeding at the metal surface, anodic reaction consisting in the transfer of metal ions from the lattice to the solution with an attendant liberation of electrons, and a cathodic reaction consisting in the assimilation by some depolarizer of the electrons liberated during the anodic reaction.

$$\mathrm{Ox} + ne \longrightarrow \mathrm{Red} \qquad (1.1)$$

Many researches(2-5) have contributed for the understanding of the Process of corrosion and its prevention.(6-10)

1.2- Corrosion of Iron

The most familiar and costly example of corrosion is the formation of rust on iron. Iron and steel structures are highly susceptible to corrosion, and their protection costs billions of dollars annually. The chemistry of corrosion under atmospheric conditions is extremely complex and is catalyzed by $H^+_{(aq)}$, explaining why increased acid precipitation causes increased rates of corrosion. Oxygen gas and water must also be present for iron to rust.

Rusting is a redox reaction, involving the loss and gain of electrons between reactants. An electrochemical cell is created with impurity sites in the iron acting as cathodes for the reduction of O_2 gas and a region of the metal surface serving as the anode, where the oxidation of iron occurs:

$$2Fe(solid) \rightarrow 2Fe_2 + (aq) + 4e^-$$

The electrons given up by the iron reduce atmospheric oxygen to water at the cathode:

$$O_{2(gas)} + 4H+(aq) + 4e^- \rightarrow 2H_2O_{(liquid)}$$

Note: this reduction half - reaction occurs in an acidic medium. The $H^+_{(aq)}$ are provided, along with the water required, by acid rain. Oxygen and water are obviously abundant therefore the rusting of iron is limited to the availability of $H^+_{(aq)}$ from acid precipitation.

The $Fe^{2+}_{(aq)}$ ions formed at the anode are further oxidized by oxygen the overall redox equation:

$$4Fe^{+2}(aq) + 3O_{2(gas)} + 6H2O_{(liquid)} \rightarrow 2Fe_2O_3 .6H_2O_{(solid)}$$

This hydrated form of iron (III) oxide is known as rust. The amount of water associated with the iron oxide can vary. Since this precipitate does not adhere tightly yon the metal it allows further corrosion to take place.

Galvanized steel, protected with zinc is also subject to accelerated corrosion under acidic conditions, 5- year exposure tests indicate that in heavily industrialized areas, galvanized steel may last as little as 5 - 20 years.

1.3- Corrosion Process

Humans have most likely been trying to understand and control corrosion for as long as they have been using metal objects. The most important periods of prerecorded history are named for the metals that were used for tools and weapons (Iron Age, Bronze Age). With a few exceptions, metals are unstable in ordinary aqueous environments. Metals are usually extracted from ores through the application of a considerable amount of energy. Certain environments offer opportunities for these metals to combine chemically with elements to form compounds and return to their lower energy levels.

Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals. Metals will also corrode when exposed to gaseous materials like acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases.

Corrosion specifically refers to any process involving the deterioration or degradation of metal components. The best known case is that of the rusting of steel. Corrosion processes are usually electrochemical in nature, having the essential features of a battery .When metal atoms are exposed to an environment containing water molecules they can give up electrons, becoming themselves positively charged ions, provided an electrical circuit can be completed. This effect can be concentrated locally to form a pit or, sometimes, a crack, or it can extend across a wide area to produce general wastage. Localized corrosion that leads to pitting may provide sites for fatigue initiation and, additionally, corrosive agents like sea water may lead to greatly enhanced growth of the fatigue crack. Pitting corrosion also occurs much faster in areas where micro structural changes have occurred due to welding operations.

Corrosion is the disintegration of metal through an unintentional chemical or electrochemical action, starting at its surface. All metals exhibit a tendency to be oxidized, some more easily than others. A tabulation of the relative strength of this tendency is called the galvanic series. Knowledge of a metal's location in the series is an important piece of information to have in making decisions about its potential usefulness for structural and other applications.

The electrons (e^- in this figure) produced by the corrosion reaction will need to be consumed by a cathodic reaction in close proximity to the corrosion reaction itself. The electrons and the hydrogen ions react to first form atomic hydrogen, and then molecular hydrogen gas. If the acidity level is high (low pH), this molecular hydrogen will readily become a gas as it is demonstrated by exposing a strip of zinc to a sulfuric acid solution.

As hydrogen forms, it could inhibit further corrosion by forming a very thin gaseous film at the surface of the metal. This "polarizing" film can be effective in reducing water to metal contact and thus in reducing corrosion. Yet it is clear that anything which breaks down this barrier film tends to increase the rate of corrosion. Dissolved oxygen in the water will react with the hydrogen, converting it to water, and destroying the film.

High water velocities tend to sweep the film away, exposing fresh metal to the water. Similarly, solid particles in the water can brush the hydrogen film from the metal. Other corrosion accelerating forces include high concentrations

Of free hydrogen ions (low pH) which speed the release of the electrons, and high water temperatures, which increase virtually all chemical reaction, rates. Thus a variety of natural and environmental factors can have significant effects on the corrosion rate of metals, even when no other special conditions are involved.

1.4- Costs of Corrosion

Millions of dollars are lost each year because of corrosion. Much of this loss is due to the corrosion of iron and steel, although many other metals may corrode as well. The problem with iron as well as many other metals is that the oxide formed by oxidation does not firmly adhere to the surface of the metal and flakes off easily causing "pitting". Extensive pitting eventually causes structural weakness and disintegration of the metal. (It should be noted, however, that certain metals such as aluminum, form a very tough oxide coating which strongly bonds to the surface of the metal preventing the surface from further exposure to oxygen and corrosion).

Corrosion occurs in the presence of moisture. For example when iron is exposed to moist air, it reacts with oxygen to form rust,

$$Fe_2O_3 \cdot X\,H_2O$$

The amount of water complexes with the iron (III) oxide (ferric oxide) varies as indicated by the letter "X". The amount of water present also determines the color of rust, which may vary from black to yellow to orange brown. The formation of rust is a very complex process which is thought to begin with the oxidation of iron to ferrous (iron "+2") ions.

$$Fe \rightarrow Fe^{+2} + 2\,e^-$$

Both water and oxygen are required for the next sequence of reactions. The iron (+2) ions are further oxidized to form ferric ions (iron "+3") ions.

$$Fe^{+2} \rightarrow Fe^{+3} + 1\,e^-$$

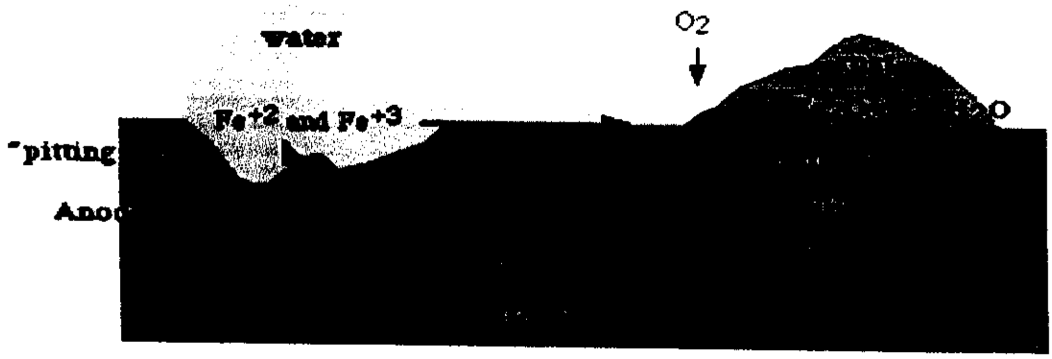
The electrons provided from both oxidation steps are used to reduce oxygen as shown.

$$O_2\,(g) + 2\,H_2O + 4e^- \rightarrow 4\,OH^-$$

The ferric ions then combine with oxygen to form ferric oxide [iron (III) oxide] which is then hydrated with varying amounts of water. The overall equation for the rust formation may be written as :

$$4\,Fe^{+2}(aq) + O_2\,(g) + [4 + 2\,X\,H_2O\,(l)] \dashrightarrow 2\,\underset{\text{"rust"}}{Fe_2O_3 \cdot X\,H_2O\,(s)} + 8H^+\,(aq)$$

The formation of rust can occur at some distance away from the actual pitting or erosion of iron as illustrated below. This is possible because the electrons produced via the initial oxidation of iron can be conducted through the metal and the iron ions can diffuse through the water layer to another point on the metal surface where oxygen is available. This process results in an electrochemical cell in which iron serves as the anode, oxygen gas as the cathode, and the aqueous s solution of ions serving as a "salt bridge" as shown below.



The involvement of water accounts for the fact that rusting occurs much more rapidly in moist conditions as compared to a dry environment such as a desert. Many other factors affect the rate of corrosion. For example the presence of salt greatly enhances the rusting of metals. This is due to the fact that the dissolved salt increases the conductivity of the aqueous solution formed at the surface of the metal and enhances the rate of electrochemical corrosion. This is one reason why iron o r steel tend to corrode much more quickly when exposed to salt (such as that used to melt snow or ice on roads) or moist salty air near the ocean.

1.5- Classification of Corrosion

Corrosion of metals can also been classified as:

(1) Dry or chemical corrosion.

In which the metal is converted into oxide when the metal is exposed to a reactive gas or non-conducting liquids.

(2) Wet or electrochemical corrosion.

The formation of hydrous oxide film occurs when the metal is immersed in a conducting liquid containing dissolved reactive substance. The reaction is Considered to take place at the metal-solution local anodic cathodic sites on the metal surface.

The nature and extent of corrosion depend on the metal and environment.

The important factors influencing corrosion are:

(i) Nature of metal.

(ii) Nature of the environment.

(iii) Electrode potential.

(iv) Nature of the corrosion products formed.

(v) Hydrogen over potential.

(vi) Concentration of various ions in solution.

(vii) pH of the solution.

(viii) Amount of dissolved oxygen.

(ix) Temperature.

(x) Conditions of flow of solution.

1.6- Electrochemical Nature of Corrosion

Corrosion (or) cancer of metals arises from the thermodynamic unstability. During the production of iron ,ores such as haematite (Fe_2O_3) is reduced with carbon in the form of coke(11)

$$2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2 \qquad (1.2)$$

Energy is expended in this process and consequently steel, when exposed to Moisture and air, tends to revert to its original form of lower rust energy state as indicated blew.

$$4Fe + 3O_2 + 2H_2O \longrightarrow 2Fe_2O_3.H_2O \qquad (1.3)$$

In the presence of moisture and oxygen, the poor protective film present on the metal surface breaks and corrosion occurs. Micro galvanic cells with local anodes and cathodes are formed on the metal surface due to heterogeneities in the metal composition. Heterogenities are due to defects, grain structures and variations in composition of solution such as differential aeration and differential concentrations. The above process is basically electrochemical in nature and can be written as follows

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad \text{(anodic reaction).} \qquad (1.4)$$

The cathodic reaction can be either hydrogen evolution or oxygen reduction

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow \qquad \text{(acid solutions)} \qquad (1.5)$$

$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O \qquad \text{(aerated acid solutions)} \qquad (1.6)$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4\,OH^- \qquad \text{(neutral solutions.)} \qquad (1.7)$$

1.7 -Thermodynamic Principles of Corrosion

For a reaction to occur spontaneously there must be a free energy change, ΔG, and since the energy, in the case of spontaneous reaction , is given out, the sign is negative.

The magnitude of the ΔG and its sign are of great importance, since it indicates whether or not the corrosion reaction will take place. For example the following reaction of iron in hydrochloric acid

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2 \qquad (1.8)$$

This reaction is thermodynamically favorable, i.e. free energy change , ΔG, must be negative. This reaction can be divided into anodic and cathodic half reactions as follows:

anodic half reaction $Fe \longrightarrow Fe^{2+} + 2e^-$ (1.9)

cathodic half reaction $2HCl + 2e^- \longrightarrow H_{2(g)} + 2Cl$ (1.10)

These two half reactions have associated free energy change, thus overall, the sum of the two free energy changes must be negative, i.e.

$$\Delta G_{an.} + \Delta G_{cath.} < 0 \qquad (1.11)$$

where, ΔG_{an} and $\Delta G_{cath.}$ represent free energy change for anodic iron dissolution and cathodic hydrogen evolution, respectively.

The electrical potential, measured in corrosion studies, can be related to the free energy change by the following equation :

$$\Delta G = - nFE \qquad (1.12)$$

where n is the number of electrons transferred in the half cell reaction, F is the charge transported by 1 mole of electrons and has the value of 96494 coulombs/mole and E is the measured potential (volts) (vs. SHE).

Similarly,

$$\Delta G^{o} = - nFE^{o}$$

where, ΔG^{o}, n and F have the usual meanings, E^{o} is the standard electrode potential and can be obtained from thermodynamic tables. Under nonstandard conditions, i.e., the respective ions not at unit activity, the electrode potential is related to the standard electrode potential by Nernst equation(12).

$$E = E^\circ + \frac{RT}{nF} \ln a_{ox} / a_{Red} \qquad (1.13)$$

As can be seen from this equation the activity of the oxidized species increases as the electrode potential becomes more positive. In aqueous environments the thermodynamic consideration of electrochemical corrosion was the basis of the construction of E – pH diagrams which are also known as Pourbaix diagrams.(13) such diagrams are essentially isothermal phase diagrams which represent meta- ion /oxide equilibria plotted with potential and pH as coordinates(14).

The major uses of Pourbaix Diagrams are :(15)

1- To predict the spontaneous direction of reactions.
2- To estimate the composition of any corrosion products that can be formed at particular potential or pH.
3- To predict environmental changes (solution composition, potential or pH) which accelerate or reduce corrosion rate.

The thermodynamic treatment of the corrosion process, which includes the use of potential –pH diagrams, does not provide any indication of the rate at which the corrosion process proceeded, but only the tendency to do so.

1.8- Kinetics of Corrosion Processes

The study of kinetics of corrosion reaction is very important, since it is necessary to determine the corrosion rate. Thermodynamic (discussed in the previous part) assumes the metal is in equilibrium with its own ions and, thus, at its equilibrium potential. Corroding systems however, are not in equilibrium since they are under an irreversible electrode potential which deviates considerably from the equilibrium potential of the metal with its ions. The new potential is accompanied by electrode reaction consisting of charge transfer, mass transport and other related phenomena. The current accompanying such a reaction, the corrosion current $i_{corr.}$ is a measure of the rate of corrosion process .

1.9- Mixed potential theory

when an electrode or metal sample is freely immersed in electrolyt, there are two or more oxidation – reduction systems with different equilibrium potential, $E_{eq.}$, and different exchange current densities.

For example, an iron electrode in acid solution produces the following half cell reactions.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1.14)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (1.15)$$

Since, the hydrogen evolution (cathodic reaction) takes place on the iron substrate, the result is a mixed potential between the equilibrium potential of Fe^{2+}/Fe electrode and the equilibrium potential of H^+/H_2 electrode.

For corrosion reaction to proceed the rate of both reactions must be equal with no accumulation of charge during the electrochemical reaction. By plotting the current density on a logarithmic scale for example, the two half reactions (1.14) and (1.15) against the applied potential, polarization lines will be linear, in accordance with Tafel equation.(16&17) this diagram is very important since it considers both, the thermodynamics (represented by the potential E) and the Kinetics of corrosion reaction (represented by current density i).

1.10 - Methods of Preventing Corrosion

Methods of preventing corrosion have been conveniently summarized as follows.(18&19)

1. Methods based on modification of procedure.

a) By attention to design.

b) By application of cathodic protection.

2. Methods based on modification of the environment.

a) By de-aeration or adjusting the pH of the environment.

b) By purification or de-humidification of air.

c) By addition of corrosion inhibitors.

3. Methods based on modification of the metal.

a) By addition of alloying elements.

b) By heat treatment.

4. Methods based on protective coatings.

a) Coating by reaction production (chemical or electrochemical treating of metal surface)

b) Organic coatings (paints, resins,etc.).

c) Inorganic coatings (enamels, cements).

d) Metallic coatings.

e) Temporary protectives.

1.11 -Inhibition of Corrosion of Metals in Acids

The NACE defines inhibitor as a substance which retards corrosion when added to an environment in small concentrations.(20)

1.11.1-Classification and Mode of Inhibition

Inhibitors are classified as acid, neutral, alkaline and vapour phase inhibitors depending upon the environment in which they are used. Based on the mechanisms they are classified as anodic, cathodic or mixed type of inhibitors.

As we are interested only in acid inhibitors other inhibitors are not discussed here.

1.11.2- Acid Inhibitors

Acid inhibitors are those chemical substances which are used to prevent corrosion in aqueous acid solutions. They are further classified into inorganic inhibitors and organic inhibitors.

1.11.3- Inorganic Inhibitors

Inorganic compounds such as As_2O_3 and Sb_2O_3 have been reported as inhibitors in acid media. The action of these compounds has been attributed to the deposition of the metal on the corroded metal surface and rise the hydrogen overvoltage and there by reducing the corrosion.(21) In strong acid solutions, Br^- and I^- ions have been found to be effective inhibitors(22). This is due to more stable chemisorption of these ions because of the easy deformability of their electron shells(23). Recently it is shown that the addition of heavy metal ions such as pb^{2+}, Ti^+, Mn^{2+} and Cd^{2+} are found to inhibit the corrosion of iron in acids. This effect is attributed to the under potential deposition of metal ions leading to complete coverage of metal-adsorbate on the iron surface(24).

1.11.4- Organic Inhibitors

A large number of organic compounds have been found to be effective in acid media. Studies on the relation between the organic structure of inhibitors and their effectiveness in acid system have been made by many workers and summarized by Eldredge et al(25) and Douty.(26) It has been found that these inhibitors have O, N or S atoms in their structure which will donate electrons for bonding with metal surface.

1.12- Factors affecting inhibitor adsorption on metal

a) *Electrostatic forces:*

Adsorption may take place due to electrostatic forces between the adsorbed species, e.g, ions or dipoles and the electric charge on the metal surface, which, is expressed by its potential with respect to zero- charge potential rather than hydrogen. The size and magnitude of this potential (Φ - potential) is very important with respect to adsorption, as Φ potential becomes more negative, cation, adsorption is favoured, and as Φ potential becomes more positive, anion adsorption is favoured. In addition Φ potential affects the orientation of dipoles and molecules adsorbed on the metal surface. At the same Φ potential Antropov (27) has shown that adsorption of inhibitors on mercury can be related to the adsorption and inhibitive effect of those inhibitors on iron. This may be related to the difference in Φ potential.

b)*Functional group and structure of the inhibitors:*

Some inhibitors can form a co-ordinate type of link with the metal by electron transfer to the metal. Organic compounds, of functional groups containing elements of group V and VI of periodic table, having suitable lone pair electrons occur in these functional groups for co-ordinate bonding. The tendency, to stronger adsorption by these elements, increase with decreasing the elecronegativity in the order $O < N < S < Se$.(28) It also depends on the nature of the functional group and the rest of the molecules since they affect the electron density on the functional group, which is generally to increase the efficiency of an inhibitor as it increases. So, with increasing electron density on the functional group stronger co-ordinate bonding with metal surface produced, hence greater adsorption.

c)*Interaction of the inhibitors with water molecules:*

Due to adsorption process of an inhibitor, water molecules are being removed from the metal surface. During the adsorption process of a molecule the interaction energy between molecule and water changes as it passes from the dissolved to adsorbed state. This change forms an important part of the free energy of adsorption, i.e., the higher the solvation energy of the adsorbing species, the higher the free energy of adsorption. Increasing the size of the hydrogen portion of an organic molecule will increase the solvation energy(29) of an inhibitor leading to decreasing solubility and increasing adsorbability.

d) *Interaction of adsorbed species:*

Interaction between adsorbed inhibitor may become significant as the Surface coverage of adsorbed species increases. Attractive interaction occur between molecules of the long hydrocarbon chain due to the increase of van der waals attractive forces between adjacent molecules leading to stronger adsorption at higher coverage. On the other hand, repulsive forces occur between ions or molecules containing dipoles leading to weaker adsorption at higher coverage.(30) Synergistic inhibitive effect was observed (31), when a mixture of cationic and anionic inhibitors is used. This is due to the attraction between the inhibitive ions of opposite charge, thus increasing the inhibitor efficiency. With quaternary ammonium cations, presence of halide ions I^-, Br^-, Cl^- significantly increases the inhibitive effect.(32)

e) *Effect of adsorbed inhibitors:*

Adsorbed inhibitors may react and form new products which could be inhibitive forming a secondary inhibition where inhibitive efficiency may increase e.g. sulphoxides can be reduced to sulphides which are more efficient(33) or it may decrease, e.g. thiourea which can reduced to HS- which in turn act as corrosion stimulation (34).

1.13- Adsorption isotherms

An adsorption isotherm is the mathematical expression which relates the bulk concentration of an adsorbing species to its surface concentration at constant temperature. An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution. Various adsorption isotherms have been formulated. A list of various isotherms and the corresponding equations are given in the Table 1.1 (35). A common procedure is to convert isotherm to a linear form and plot the experimental data accordingly. The data can be fitted to any one of the adsorption isotherms from the suitable plot and the free energy of adsorption of the organic inhibitors can be obtained.

Most of the organic inhibitors obey Langmuir's or Temkin's adsorption isotherms. An inhibitor is found to obey Langmuir's isotherm if a plot of $\log \theta/1-\theta$ vs $\log C$ is linear. Similarly for Temkin's plot of θ vs $\log C$, for Bockris Devanathan and Muller (BDM) a plot of $(\log C - \log \theta/1-\theta)$ vs $\theta^{3/2}$ and for the Frumkin's a plot of $\log \theta/(1-\theta)C$ Vs θ will be linear.

Table (1.1):-Adsorption Isotherms

No	Isotherm	Equations
1	**Langmuir**	$\beta C = \frac{\theta}{(1-\theta)}$
2	**Freundlisch**	$\beta C = \theta(\theta < n < 1)$
3	**Frumkin**	$\beta C = \frac{\theta}{(1-\theta)}\exp(-2a\theta)$
4	**Temkin**	$\beta C = \frac{\exp(a\theta)-1}{1-\exp[-a(1-\theta)]}$
5	**Parsons**	$\beta C = \frac{\theta}{(1-\theta)}\exp\frac{2-\theta}{(1-\theta)^2}\exp[-2a\theta]$
6	**Bockris,** **Devanathan and** **Muller (BDM)**	$\log C \pm \log\frac{\theta}{(1-\theta)} = C + \beta\theta^{3/2}$

Note: $\beta = e^{-\Delta G_{ads/RT}}$

a = interaction Parameter

a > o = attraction

a < o = repulsion

1.14- Literature survey on corrosion of Iron :

As known that economic power of a country is determined by its output of iron. So, studies of iron properties in general and electrochemical, specially, have been received a great attention. In such respect, the corrosion and corrosion inhibition of iron in the different media become very interesting and important owing to its wide applicability in industry and domestic life. Corrosion inhibition of Fe using different inhibitors and various factors affecting on it were studied by many authors(36-62). In the following a concise literature servey on the corrosion and corrosion inhibition of Fe by some related organic compounds in hydrochloric acid are collected.

The inhibitive effect of some substituted phenyl N-phenylcarbamates on corrosion of iron in 2M HCl was studied using galvanostatic polarization measurements(63). Studies carried out with different concentrations of the inhibitor indicate that, these compounds act as mixed type inhibitors. The results indicate that the additives reduce the corrosion rate by way of adsorption through the oxygen atom of phenoxy group and nitrogen atom of NH group. The inhibitory character of the compounds depends upon the concentration of inhibitor as well as its chemical composition. The results of electrocapillary measurements are consistent with the electrochemical measurements.

Some synthesized pyrazol compounds were tested as corrosion inhibitors for iron in 1M HCl(64). Polarization measurements showed that the pyrazole compounds inhibit both the anodic and cathodic reactions. The corrosion inhibition of pyrazole compounds studied is regarded by a simple blocked fraction of the electrode surface related to adsorption of inhibitor species according to Langmuir's adsorption isotherm.

The inhibition effect of some cyanoacetylhydrazine derivatives towards iron corrosion in hydrochloric acid solution has been studied using galvanostatic polarization, scanning electron microscopy and electrocapillary measurements(65). The inhibitors appear to function through general adsorption following the Langmuir 's adsorption isotherm. Galvanostatic polarization data suggest that for all inhibitors the cathode and anode are polarized under the influence of an external current.

The corrosion protection of iron during pickling by substituted N-arylpyrroles having carbaldehyde (-CHO) or amine (-NH_2) groups, which can form large molecules by condensation or polymerization of the monomers, was studied by linear polarization technique(66). Pyrroles substituted with carbaldehyde groups show the highest inhibition efficiency at 40°C. The protective characteristics of substituted pyrroles containing a nine groups improve with increasing temperature in the range 20°C- 60°C.

The inhibitive behavior of acetylenic alcohols in 0.1M H_2SO_4 and 1M HCl at high temperatures was studied on iron by combining electrochemical tests and surface analysis(67). The inhibitors tested (octynol and propynol) proved to be efficient at high temperatures. They acted primarily by electrosorption on the iron, then through the formation of a dimmer (in sulphuric medium) or a short-chain polymer (in hydrochloric medium), which remained stable at high temperature. A catalytic effect of the Cl^- ions on the polymerization process was postulated.

The inhibitive action of ortho-methoxy substituted polyaniline, a new class of conducting polymer, on the corrosion of iron in acidic chloride solutions has been evaluated by electrochemical impedance spectroscopy (EIS), linear polarization resistance and weight loss measurements (68). Inhibition efficiencies of nearly 80-88% have been observed even at 25 ppm concentration. Double layer capacitance studies indicate a strong adsorption of polymer following the Temkin 's adsorption isotherm.

The inhibitor effect of some surfactants having the chemical formula 2-(alkyl(C_nH_{2n}+1) dimethylamino alkanol bromides on the corrosion of iron in acid chloride medium was investigated by steady – state electrochemical and gravimetric methods(69). Results obtained show that these compounds are very good cathodic inhibitors and act on the cathodic hydrogen evolution reaction without modifying its mechanism. High inhibition efficiencies are observed around their critical micellar concentrations and the inhibition efficiency increases with the number of carbon atoms in the chain length.

The effect of some hydrazone oxime derivatives on the corrosion of iron in 2M HCl was studied by polarization and weight loss techniques(70). It was found that the compounds under consideration are adsorbed on the iron surface according to the Temkin 's isotherm. The Tafel slopes is approximately constant independent of the concentration of the inhibitor. The results of polarization indicate that all compounds tested were of a mixed type, but the cathodic is more preferentially polarized.

The inhibition performance and effect of concentration of cetyltrimethylammonium bromide and of tetraphenylphosphonium chloride on the corrosion of iron in 1M HCl solution was studied electrochemically(71). The inhibition efficiency reached to 84% with $1x10^{-2}$ M cetyltrimethylammonium bromide and 98% with $1x10^{-2}$M tetraphenylphosphonium chloride. Also, the degree of inhibition for both inhibitors closely followed the adsorption isotherm of the inhibitor on the metal.

Some aminoester organic compounds were tested as corrosion inhibitors for iron in 1M HCl by mass loss and electrochemical polarization methods(72). Both techniques gave the same order of inhibition. Comparison of results among those aminoesters showed that, L-methionine Methylester ($METOCH_3$) was the best inhibitor. Its inhibition efficiency (%In.) reached a maximum value of 95% at 10^{-2}M. Polarization measurements indicated that, $METOCH_3$ acted as a cathodic inhibitor without changing the mechanism of the hydrogen evolution reaction. $METOCH_3$ was found to adsorb on the iron surface according to Frumkin's isotherm model.

The effect of some benzene sulphonyl-hydrazone derivatives on the corrosion of iron in 1M HCl solution at 303 K was investigated using polarization and weight loss techniques(73). A significant decrease in the corrosion rate of iron was observed by the presence of traces of these compounds. The corrosion rate was found to be a function of the nature, concentration of the inhibitor and temperature of the medium. The degree of surface coverage calculated from the results were used to evaluate the free energy of adsorption $\Delta G^o_{ads.}$ of the inhibitors. All the inhibitors follow the Frumkin's adsorption isotherm. The mechanism of inhibitor action was discussed on the basis of adsorption and molecular polarization of inhibitor. The observed experimental data indicated that all compounds tested were of a mixed type but the cathodic is more preferentially polarized.

The corrosion inhibition of pure iron in 1M HCl using 1-phenyl-5-mercapto- 1,2,3,4- tetrazole (PMT) was studied using weight loss and electrochemically steady-state experiments(74). From the comparison of results with those obtained using other tetrazoles. PMT was the best inhibitor and its inhibition efficiency was 98% at $2x10^{-3}$M Polarization measurements show that PMT is a mixed type inhibitor. PMT acts on the cathodic reaction without changing the mechanism of the hydrogen evolution reaction. The PMT appears to function through the general adsorption mode following the Langmuir's adsorption isotherm model. The inhibition efficiency of PMT is temperature independent in the range 20°C-40°C.

The effect of alkyltriazole compounds on iron corrosion in 1M HCl solution has been studied(75). Using weight loss, polarization data and impedance measurements, it has been shown that the compounds studied reduce the iron corrosion. The dodecyl -1,2,4 triazole product was the best inhibitor. The inhibiting effect has been interpreted by inhibitor film formation.

Adsorption and corrosion inhibition characteristics of acrylamide, methacrylamide and dimethylacrylamide towards corrosion of pure iron, were investigated using galvanostatic and potentiostatic polarization techniques in 1M HCl and 1M $HClO_4$ at different temperatures(76). For all the additives, inhibition efficiency is maximum with the highest additive concentration, 10^{-1}M, at 25°C and the inhibition decreases with decrease of additive concentration and increase of temperature. Inhibition efficiency is in the order of acrylamine > methacrylamide > dimethylamide. Adsorption of an additive to metal surface is through the π-electron of nitrogen atom. However, ClO^-_4 and Cl^- ions of $HClO_4$ and HCl, respectively, and $-CH_3$ group of additives played significant role in adsorption phenomena.

Some 3-methyl-1-butyne derivatives was tested as corrosion inhibitors for corrosion of Armco iron in 1M HCl at 70°C(77). The substitution of the acetylenic hydrogen atoms with halogen atoms improves their inhibitive performances and their polymeric surface films act through a blocking effect of the active metal surface. 1-Octyn - 3 - ol is highly efficient and its polymeric surface film acts as a physical barrier for H^+ discharge and markedly hinders also the anodic iron oxidation reaction.

The inhibition effects of bezonitrile (BN), 1,2-dicyanobenzene (1,2-DCB), 1,4 -dicyanobenzene (1,4-DCB) and of 7, 7 , 8 , 8-tetracyanoquinodimethane (TCNQ) on the corrosion of pure polycrystalline iron in hydrochloric acid solution was studied by the electrochemical polarization and impedance spectroscopy techniques(78). The inhibition was found to decrease in the following sequence: BN > 1,4-DCB >1,2-DCB > TCNQ . The polar properties of the molecules, energies and coefficients of the MOS (molecular orbital system) calculated and were taken into account in the discussion.

The inhibition effects of inorganic bismuth (III) compounds towards the corrosion of iron in 1M HCl at elevated temperatures was studied(79). $BiCl_3$ was fairly effective in the temperature region between 30°C and 65°C but ineffective at temperature higher than 80°C. $BiCl_3$ was a good inhibitor for iron corrosion at $1x10^{-8}M$ in 1M HCl at 80°C. A protective film formed on the iron surface was analyzed by X-ray photoelectron spectroscopy.

Some new synthesized pyrazole organic- type compounds have been tested as inhibitors for the corrosion of iron in 1M HCl by weight loss and electrochemical polarization methods(80). Both techniques gave the same order of inhibition. The compound 1,3-bis (3'-chloromethyl-5'- methyl -1'- pyrazolyl) propane was the best inhibitor and its inhibition efficiency increased with increasing concentration reaching 95% at $4x10^{-4}M$ Polarization measurements have shown that the pyrazole substances studied inhibited both the anodic and the cathodic reaction. The corrosion inhibition of pyrazole studied is regarded by a simple blocked fraction of the electrode surface related to adsorption of inhibitor species according to Langmuir's isotherm model on the iron surface. The introduction in the pyrazole ring of substituted such as –OH , $-CO_2H$, $-CO_2CH_3$, and –Cl in the position 3, enhances the inhibiting effect of the pyrazole compounds. The results indicate that the rate of corrosion of iron increases with increasing temperature in the range of 25°C- 50°C.

The inhibitory effect of the quinazol -4- one derivatives on the corrosion of iron in hydrochloric acid was investigated(81). Polarization curves indicated that these compounds act as mixed - type inhibitors, but the cathode is more preferentially polarized. The effect of structural changes in these compounds on their inhibition efficiency has been studied. The inhibitors appear to function through general adsorption following the Langmuir's adsorption isotherm. Results indicate that the rate of corrosion of iron increases with increasing temperature over the range 27°C - 50°C both in absence and in presence of inhibitors.

The effect of sodium salt of ethyl 1,3-indandione 2-carboxylate on corrosion of iron in 2M HCl has been studied using galvanostatic polarization method(82). The observed experimental data indicate that the compound used were of mixed-type inhibitor. The adsorption of the compound was found to follow S- shaped adsorption isotherm.

The inhibition and the effect of concentration of quaternary ammonium salts on corrosion of iron in 1M HCl solution were studied electrochemically (83). The percentage inhibition efficiency increased with the increase of the concentration in each inhibitor and with the increase of the chain length of the alkyl substituent. The efficiency of corrosion inhibition ranged from 89.55% with $1x10^{-2}M$ tetramethylammonium bromide and 99.46% with $1x10^{-2}M$ tetraheptyl-ammonium bromide. Also, the degree of inhibition for all the inhibitors closely followed the adsorption isotherm of the inhibition on the metal surface.

The effect of some 1,5-benzodiazepin -2- one derivatives on the corrosion behavior of 99.5% Fe in 1M HCl has been investigated using gravimetric and electrochemical polarization methods(84). Both techniques gave the same order of inhibitor efficiencies. Polarization data indicate that all of the compounds tested act as mixed-type inhibitors, without changing the mechanism of the cathodic hydrogen evolution reaction. The inhibitor efficiency decreases in the order 7- methyl -4- phenyl -1,5– benzodiazepine -2- one > 4-phenyl-1,5-benzodiazepin-2-one > 3,7-dimethyl-1,5- benzodiazepin-2-one. The protection efficiency decreases slightly with increasing temperature.

Some peptidic organic type compounds such as Boc-Phe-Met-OCH_3 [BPMM] and Boc - Tyr - Gly - Gly - Phe - Met - OCH_3 [BTGGPMM] were synthesized and tested as corrosion inhibitors by weight loss and electrochemical polarization methods(85). Peptidic compounds act as cathodic inhibitors without changing the mechanism of the hydrogen evolution reaction . inhibition efficiencies of BTGGPMM decrease roughly with increasing temperature.

The inhibitory effects of new oxazole derivatives toward the corrosion of Armco iron in 1M HCl are examined by weight – loss and electrochemical methods(86). The weight loss measurements have confirmed the electrochemical trend of 5-chloro 2-(3'-nitrophenyl)1,3 benzoxazole (I) is the best inhibitor and its inhibition efficiency reaches a maximum value of 91% at 10^{-3}M. The effect of temperature indicated that inhibition efficiency of (I) is temperature dependent in the range 30°C - 90°C.

The effect of 4(2-pyridyl)-1-benzaldehyde -3- thisosemicarbazone(4-PBT) derivatives towards the corrosion of iron in 1M HCl solution at 303K was investigated(87). Potentiodynamic and weight loss measurements show that compounds under investigation act as effective inhibitors for the corrosion of iron in 1M HCl. The results showed that these compounds behave as mixed type inhibitors. The obtained results, from potentiodynamic and weight loss techniques, indicate that the inhibition efficiency of the compounds depend on the type of the substituent attached to the (4-PBT) part, which increase the charge density on the adsorption sites. The adsorption of the compounds on the iron surface was found to obey Temkin's adsorption isotherm.

The inhibition and the effect of concentration of benzyl tri-methyl ammonium chloride (BTMAC) and benzyl tri-ethyl ammonium chloride (BTEAC) on the corrosion of iron in 1M HCl were studied electrochemically(88). It was concluded that the percentage inhibition increased with the increase of the inhibitor concentration and with the increase of the chain length of the alkyl substituent. The efficiency of inhibition was 90.28% with 1×10^{-2}M (BTMAC) and 92.25% with 1×10^{-2}M (BTEAC). Compared with the percentage inhibition obtained previously caused by 1×10^{-2}M of tetra-methyl ammonium bromide (TMAB) (85.55%) and tetra-ethyl ammonium bromide (TEAB) (88.79%), it was concluded that the substitution of one alkyl group in the quaternary ammonium salt for a benzyl group only caused an increase in the percentage inhibition at high concentrations (1×10^{-2}M).

The polarization behavior of Armco iron in solutions of HCl with and without inhibitors has been studied by potentiostatic method(89). At lower overvoltage values the dissolution process is controlled by activation, while at higher overvoltage values the dissolution process is controlled by diffusion. The inhibition of this metal corrosion in the aqueous solutions of HCl has been studied using three surfactants. Under the critical micelle concentration, the inhibition of those three surfactants is negligible. At a concentration higher than critical micelle concentration, the inhibiting action of surfactants increases rapidly. The process of inhibition was attributed to the formation of the adsorbed film on the metal surface, that protects the metal against the corrosive agents.

3- Mercapto-1,2,4-triazole derivatives have been tested as inhibitors of the corrosion of iron in 1M HCl, by gravimetric and electrochemical polarization methods(90). Both techniques gave the same order of inhibition. Their inhibition efficiencies reached a maximum value of 90% at 10^{-3} M. Polarization data indicate that all compounds tested act as a mixed-type inhibitors, without changing the mechanism of hydrogen evolution reaction. Compounds tested were adsorbed on the iron surface according to a Frumkin isotherm model. The inhibition efficiency is influenced by the nature of substituted groups in position 4 and 5 in the 1,2,4-triazole ring. The protection efficiency was found to decrease slightly when the temperature increases.

Corrosion of Armco iron in aqueous solutions of hydrochloric acid was studied by potentiostatic method, in the presence of benzyl di-methyl dodecylammonium chloride, benzyl di-methyl alkylammonium chloride, benzyl di-methyl hexadecylammonium chloride and trioctyl methyl ammonium chloride(91). Electrochemical measurements showed that the organic compounds examined had good inhibiting properties at 30°C. At higher concentrations than the critical micelle concentration the inhibition of those four surfactants increases rapidly. The process of inhibition was attributed to the formation of the adsorbed film on the metal surface that protects the metal against the corrosive agents. Each compound exhibits Langmuir behavior and inhibition increases with increasing alkyl chain length. This is attributed to cohesive van der Waal's forces between the positive head groups co adsorbed with chloride ions on the positive charged irons surface.

New bipyrazolic compounds were synthesized and tested as a corrosion inhibitors of Armco iron in 1M HCl medium using weight loss, electrochemical polarization and impedance measurements(92). Comparison of results showed that 1,3 – bis (3,5 –dimethyl pyrazol) propane (I) was the best inhibitor. The maximum inhibition efficiency was reached 93% at 10^{-3} M. (I) adsorbs on the iron surface according to the Langmuir's isotherm model. The inhibition efficiency of (I) increases with the rise in temperature in the range 308-338K. The apparent activation energy for iron corrosion was determined.

Pyrazole compounds were studied as corrosion inhibitors for Armco iron in 1M HCl by weight – loss and electrochemical polarization methods (93).3,5 – dimethyl pyrazole is the best inhibitor studied and its inhibition efficiency reaches 83% at 10^{-3} M. The adsorption of the compound on the Armco iron surface obeys Frumkin isotherm model. The effect of structural changes in pyrazolic ring on the inhibition efficiency was studied. Weight loss measurements indicates that the inhibition efficiency increases with the temperature in the range 308-303 K. The apparent activation energy was determined.

The corrosion accelerating effect of rhenium oxide deposited onto Armco iron surface has been studied in aerated 0.5 M H_2SO_4 and 1M HCl blank solutions and in the presence of 10 and 100 $mgdm^{-3}$ Re_2O_7(94). It has been shown that rhenium has a decisive effect on the acceleration of cathodic hydrogen evolution and, consequently, on the corrosion of iron.

The anodic iron dissolution in 0.5 mol dm^{-3} perchloric acid ($HClO_4$) was investigated by the electrochemical impedance spectroscopy, the potentiodynamic sweep and the scanning electron microscopy measurements(95). The anodic polarization behavior of iron in $HClO_4$ solution showed that the strong current oscillations occurred in a narrow potential region, particularly the pitting corrosion was observed in the active dissolution region. These characteristics were quite different from those of iron in the sulfuric acid (H_2SO_4). At the potentials 82 and 132 mV more positive than the corrosion potential (−482 mV vs. SCE), the impedance spectra for the iron in $HClO_4$ displayed two inductive arcs; however, by gradually increasing potential the lower frequency inductive arc disappeared at −300 mV at first, and then the higher frequency inductive arc changed into a capacitive arc at −250 mV. Based on the impedance display of iron at various potentials, a reaction model involving two adsorbed intermediate species was proposed, in terms of which the impedance behavior at different potentials were described. Occurrence of the pitting corrosion in active dissolution region was explained.

The effect of some new synthesized pyranocoumarins on the corrosion of iron in 0.5 M HCl was investigated. The investigation involved electrochemical polarization methods (potentiodynamic, Tafel extrapolation and the determination of the polarization resistance) as well as weight loss measurements(96). The results showed that these compounds act as mixed type inhibitors, but the cathode is more preferentially polarized.

The inhibition efficiency depends on both the nature and concentrations of the investigated compounds. Compounds are found to adsorb on the iron surface according to the Langmuir adsorption isotherm. Fourier transform infrared (FTIR) spectrophotometry was used to obtain information on bonding mechanism between the metallic surface and the inhibitors.

The inhibitive action of some benzimidazole derivatives namely 2-aminobenzimidazole (AB), 2-(2-pyridyl)benzimidazole (PB), 2-aminomethylbenzimidazole (MB), 2-hydroxybenzimidazole (HB) and benzimidazole (B), against the corrosion of pure iron in solutions of hydrochloric acid has been studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) (97). At inhibitor concentration range (10^{-3}–10^{-2} M) in 1 M acid, the results showed that these compounds suppressed both cathodic and anodic processes of iron corrosion in 1 M HCl by adsorption on the iron surface according to Langmuir adsorption isotherm. The efficiency of these inhibitors increases in the order AB>PB>MB>HB> B. Both potentiodynamic and EIS measurements reveal that these compounds inhibit the iron corrosion in 1 M HCl and that the efficiency increases with increasing of the inhibitor concentration. Data obtained from EIS were analyzed to model the corrosion inhibition process through equivalent circuit. A correlation between the highest occupied molecular orbital E_{HOMO} and inhibition efficiencies was sought.

The inhibitory activity of some *o*-substituted anilines on iron corrosion in hydrochloric acid (HCl) was studied in relation to inhibitor concentration using potentiodynamic and electrochemical impedance spectroscopy (EIS) measurements(98). *O*-substituted anilines were found to act as mixed type inhibitors. The results showed that *o*-substituted anilines suppressed both cathodic and anodic processes of iron corrosion in 1 M HCl by its adsorption on the iron surface according to Langmuir adsorption isotherm. Potentiodynamic and EIS measurements reveal that these compounds inhibit the iron corrosion in 1 M HCl and that the efficiency increases with increasing of the inhibitor concentration. Data obtained from EIS are analyzed to model the corrosion inhibition process through equivalent circuit.

The inhibition effects of tryptamine (TA) on the corrosion behavior of Armco iron in 0.5 M deaerated H_2SO_4 (in the 25–55 °C temperature range) was studied in both short and long time tests (1, 24 and 72 h) by means of potentiodynamic curves (PCM) and electrochemical impedance spectroscopy (EIS)(99). TA was found to be an effective Armco iron inhibitor, even at 55 °C and 72 h, but only at 10 mM. At this concentration the inhibition percentages (IP%), calculated by PCM and EIS, ranged from 90% to 99% and did not diminish over time and as the temperature increased. TA adsorption followed Bockris–Swinkels' isotherm (x=1). The thermodynamic data indicated that, in the more concentrated solutions, TA also chemisorbed on the iron surface.

Inhibitory effect of some new synthesized bipyrazole compounds, namely, *N*, *N*- bis [(3,5 – dimethyl – 1 H - pyrazol -1- yl) methyl 1]- *N* - (4 – methylpheny 1) amine (P1) and methyl - 1 - [((methylphenyl) {[3-(methoxycarbonyl)-5-methyl-1H-pyrazol-1-yl]methyl}amino)methyl]-5-methyl-1H- pyrazole - 3 - carboxylate (P2) on corrosion of pure iron in 1 M HCl solution has been studied using chemicall technique as weight loss and electrochemical techniques as potentiodynamic polarization, linear polarization and impedance(100). The inhibition efficiencies obtained from gravimetric, cathodic Tafel plots, linear polarization resistance and EIS methods are in good agreement. The results obtained reveal that these compounds are efficient inhibitors. The inhibition efficiency increases with the increase of inhibitor concentration to reach 93% for P1 at 2.5×10^{-4} M. Potentiodynamic polarization studies clearly reveal that P1 and P2 act as mixed-type inhibitors without change of the mechanism of hydrogen evolution. The temperature effect on the corrosion behavior of iron in 1 M HCl without and with the inhibitors at 2.5×10^{-4} M has been studied in the temperature range from 298 to 353 K. EIS measurements show that the increase of the transfer resistance with the inhibitor concentration. The inhibitors are adsorbed on the iron surface according to the Langmuir adsorption isotherm model. From the adsorption isotherm some thermodynamic data for the adsorption process (K) are calculated and discussed.

The synergistic effect of halide ions on the inhibition of corrosion of iron in 0.5 M H_2SO_4 solutions by polyaniline has been studied by polarization and impedance methods(101). Addition of 0.5×10^{-3} M I^- ions enhanced the inhibition efficiency of polyaniline at 10 ppm from 53% to 90%. However in the case of bromide and chloride ions, the inhibition efficiency of polyaniline at 50 ppm has been increased from 71% to 90%. The synergism parameter in all cases is found to be greater than 1. The synergistic effect is attributed to enhanced adsorption of polyaniline by the adsorbed halide ions.

The corrosion of iron was studied using gravimetric and potentiodynamic polarization method at different temperatures and at pH 9 level in 0.1 M NaCl solutions containing different concentrations of linear alkyl benzene (LAB) and linear alkyl benzene sulphonate (LABS). Potentiodynamic polarization experiments show that corrosion rate in presence and absence of LAB and LABS increases with increasing temperature from 303 to 338 K. The corresponding activation energies are determined. Moreover, the protective film formation on the metal surface is investigated by means of FTIR. It has been concluded from the results that LABS is more effective in preventing iron corrosion than LAB(102).

The inhibitor performance of chemically synthesized water soluble poly aminoquinone (PAQ) on the corrosion of iron in 0.5 M sulphuric acid was studied in relation to inhibitor concentration using potentiodynamic polarization and electrochemical impedance spectroscopy measurements(103). On comparing the inhibition performance of PAQ with that of the monomer *o*-phenylenediamine (OPD), the OPD gave an efficiency of 80% for 1000 ppm while it was 90% for 100 ppm of PAQ. PAQ was found to be a mixed inhibitor. Besides, PAQ was able to improve the passivation tendency of iron in 0.5 M H_2SO_4 markedly.