

CHAPTER - 1

INTRODUCTION

1.1 Introduction to corrosion

1.1.1 Civilization and corrosion

In the early stages of human civilization, man preserved himself in a hostile environment by functioning as a bio electrochemical machine, converting the solar energy stored in food *via.*, electrochemical reactions into muscle power. But recently man has become increasingly a 'cyberg', he has linked himself more and more with machines that harness nuclear energy and the solar energy stored in coal and oil and has thereby satisfied his needs with increasing efficiency. Thus the machines do man's bidding and become the basis of the material aspects of civilization. Materials mainly metals, used must be stable. If the metals become unstable, then the machines fabricated partly from these metals undergo an undesired obsolescence¹.

An industrial civilization depends in a crucial way upon the stability of metals in moist (and often the impurity-containing) atmosphere. But metals become unstable (corrode) in normal terrestrial environment. Thus, corrosion is a major problem in industries and efforts should be taken to minimize or prevent as far as possible.

1.1.2 Definition of corrosion

Corrosion is a costly and severe material science problem². Corrosion of metals is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical and biochemical interactions with the environment³⁻⁴. Thus, it is exactly the reverse of extraction of metals from ores. In most environments the metals are not inherently stable, but tend to revert to compounds which are more stable, a process which is called corrosion.

Corrosion is also defined as degradation or deterioration of materials due to chemical or electrochemical reaction with the environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion. Fluxing of the lining of a steel furnace,

formation of attractive green patina on copper roofs, formation of mill scale on iron and steel in rolling mills, dulling of brass and fogging of nickel are typical examples of corrosion phenomenon.

1.1.3 Historical background

Bacquerel⁵ proposed that corrosion takes place when there is a difference in metal ion concentration. **Dela Rive**⁶ indicated that the impure zinc dissolved faster in acid solution and therefore trends in corrosion research changed rapidly over the years. **Faraday's** researchers⁷ especially between 1834 and 1840 afforded evidence of the essential connection between a chemical action and the generation of electric currents. As early as 1824, **Sir Humphrey Davy**⁸ proposed a connection with iron or zinc as a means of protecting copper against sea-water. In 1847, **Richard Adie**⁹ demonstrated that difference in oxygen concentration in a flowing stream could give rise to a flow of current between two pieces of iron or zinc. Trends in corrosion research changed rapidly over the years. In 1950 polarization and their applications had been the topic of interest¹⁰⁻¹¹.

In 1970 corrosion research was concentrated on the mechanistic studies of metal dissolution, localized corrosion and high temperature corrosion¹²⁻¹⁸. In recent years corrosion research has been diversified into several newer fields. The optical techniques have revolutionized the field. Surface analytical techniques, such as XRD¹⁹⁻²², SEM²³⁻²⁷, FTIR²⁸⁻³¹ and AFM³²⁻³³ gave more information on the nature, thickness, structure, composition of films and influence of surface oxides on the corroded metals and alloys. Computers³⁴⁻³⁵ and microprocessors³⁶ find application in analyzing corrosion data. The main objectives of all these investigations are to minimize corrosion failures.

1.1.4 Importance of corrosion studies

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

- Increasing use of metals in all fields of technology.
- Use of rare and expensive metals whose protection requires special precautions.
- Increasing pollution of air and water resulting in a more corrosive environment.

- Strict safety standards of operating equipment which may fail in a catastrophic manner due to corrosion.
- Use of new high strength alloys which are usually more susceptible to certain types of corrosive attack

Corrosion studies have also become more important due to increasing awareness of the needs to conserve the world's metal resources. Evidently more concern must be shown for conservation of metals by minimizing losses due to corrosion.

1.1.5 Consequences of corrosion

The consequences of corrosion are many and varied and effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass in metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarized as follows:

- Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown.
- Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leakage domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.
- **Plant shutdowns:** Shutdown of nuclear plants, process plants, power plants and refineries may cause severe problems to industry and consumers.
- Loss of products, leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards. It is well known that at least 25% of water is lost by leakage.
- **Loss of efficiency:** Insulation of heat exchanger tubings and pipelines by corrosion products reduces heat exchange and piping capacity.
- **Contamination:** Corrosion products may contaminate chemicals, pharmaceuticals, dyes, packed goods *etc.*, with dire consequences to the consumers.

- **Nuclear hazards:** The Chernobyl disaster is a continuing example of transport of radioactive corrosion products in water, fatal to human, animal and biological life.

1.1.6 Expense of corrosion

In many countries they spend crores of rupees on research for controlling corrosion. Losses due to corrosion could be direct or indirect.

i. Direct losses

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

ii. Indirect losses

- Contamination of the product.
- Extra working capital because of increased labour requirements and larger stocks of spare parts.
- High maintenance cost
- High fuel and energy loss as a result of steam, fuel, water or compressed air leakage from corroded pipes.
- Safety *e.g.*, sudden failure of equipment may cause explosion or release of toxic product.
- Appearance *e.g.*, corroded materials is usually unpleasant to the eye.

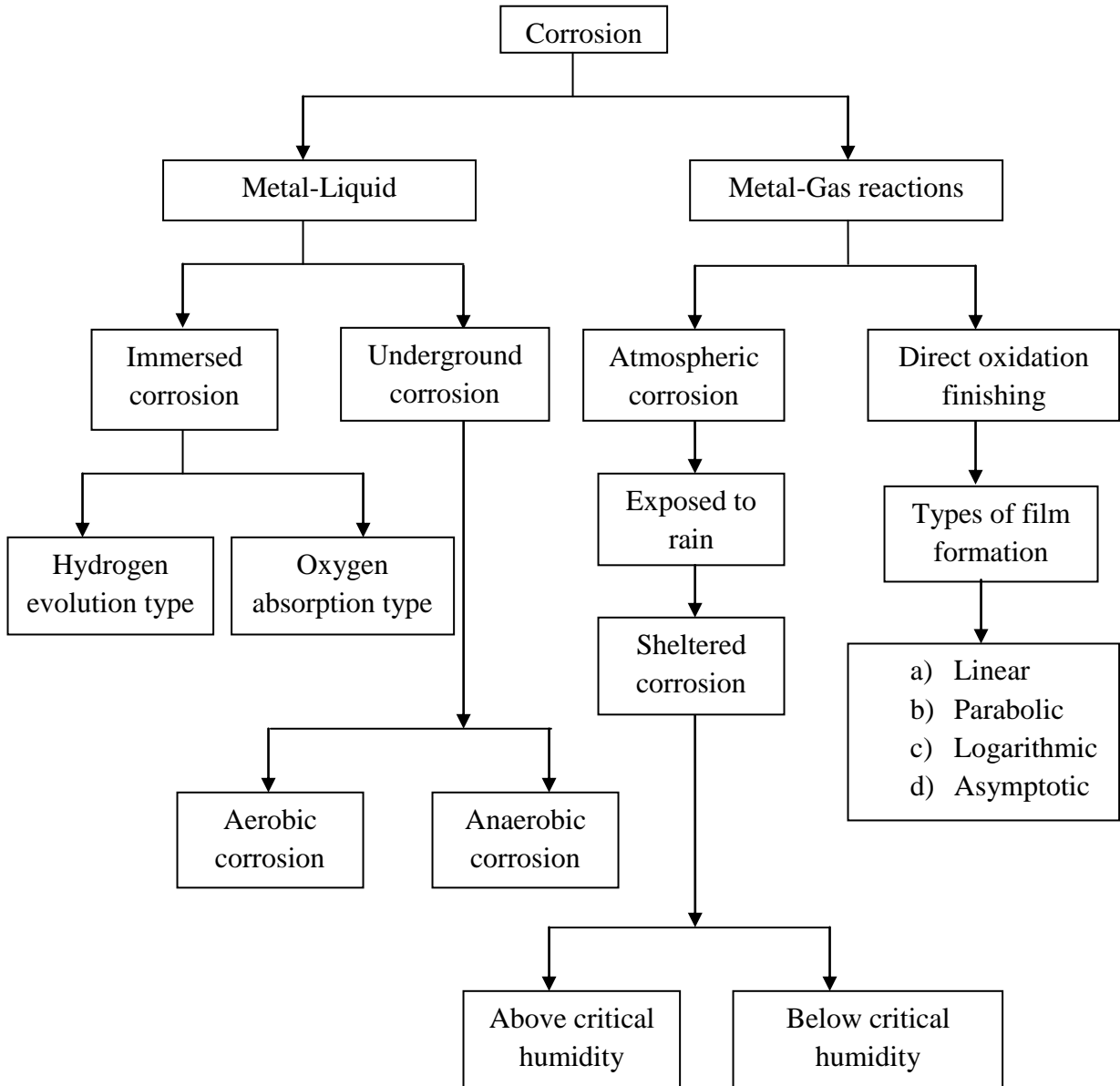
1.1.7 The social implications of corrosion

Virtually all metals suffer corrosion, therefore its effect permeate nearly every aspect of human endeavour and this fact alone makes the study of corrosion and its control more important, not less. Corrosion is therefore the main reason why engineered systems ultimately fail. The following sections provide evidence in support of this,

- The nuclear industry,
- Electrical and electronics industry,
- The automotive industry,
- The marine and offshore industry,
- Fossil fuel energy systems,

- Biomedical engineering,
- Aerospace industry,
- The chemical industry,
- The construction industry and
- Defence industry.

1.1.8 Classification of corrosion process



1.1.9 Classification of corrosion

i. Dry corrosion (or) direct chemical corrosion

This is due to direct chemical action of environment/atmospheric gases such as oxygen, halogens, hydrogen sulphide, nitrogen or anhydrous liquid sulphur dioxide with metal surface in immediate proximity. The extent of corrosion depends upon the

- Chemical affinity between the corrosive environment and solid metals and
- Ability of reaction product to form a protective film on the metal surface.

Three main types of corrosion are

- (a) **Oxidation corrosion:** It is brought about by the direct action of O_2 at low or high temperature on metals usually in the absence of moisture.
- (b) **Corrosion by hydrogen:** Gases like H_2 also attack metals at ordinary temperature. It is known as hydrogen embrittlement.
- (c) **Liquid metal corrosion:** Corrosion is due to chemical action of flowing liquid metal at high temperature on solid metal or alloy.

ii. Wet corrosion (or) electrochemical corrosion

Electrochemical corrosion occurs due to the existence of separate anodic and cathodic areas/peaks between which current flows through the conducting solution. This type of corrosion occurs

- Where a conducting liquid is in contact with metal or
- When two dissimilar metals or alloys are either immersed or dipped partially in a solution.

Electrochemical corrosion, involves an interface. It can be further classified into:

(a) Separable anode/cathode type

In these cases certain areas of the metal can be experimentally identified as predominantly anodic or cathodic. The distance of separation of these areas may be very small, of the order of fractions of a millimeter. There is a macroscopic flow of charge through the metal.

(b) Interfacial anode / cathode type

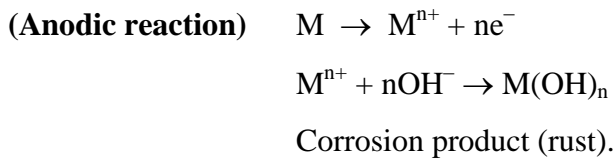
Here one entire interface will be cathode and the other will be anode. In this case charge is transported through a film of reaction product on the metal surface.

(c) Inseparable anode / cathode type

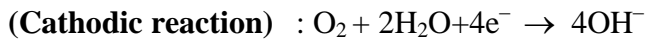
Here the anode and cathode cannot be distinguished by experimental methods, though their presence is postulated by theory, *e.g.*, the uniform dissolution of metal in fused salt, non-aqueous solution, acid, alkaline or neutral solutions.

Different types of electrochemical reactions depending upon the chemical nature of the environment are given below.

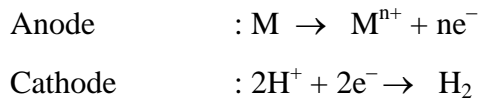
Anode -Neutral media



Cathode

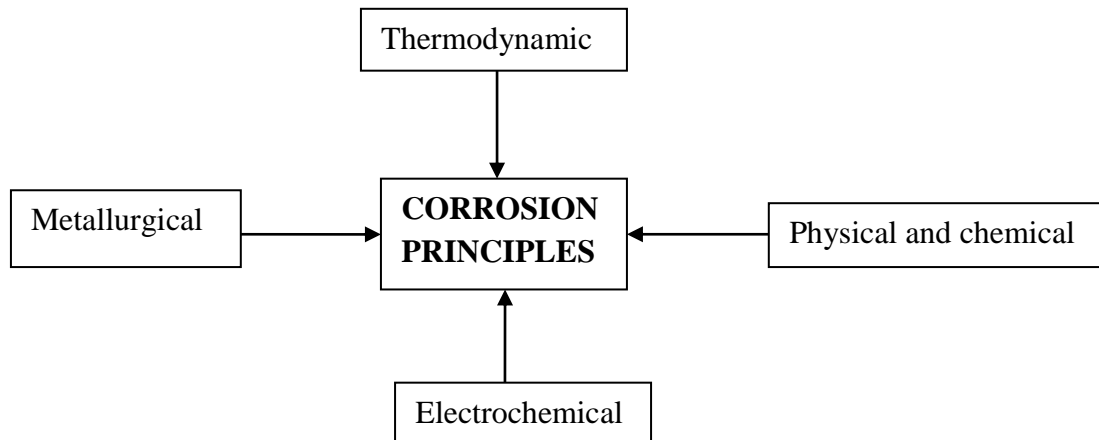


Acid media



1.1.10 Principles of corrosion

Corrosion resistance of a material generally depends upon the following principles.



i. Metallurgical principles

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

ii. Physical and chemical principles

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

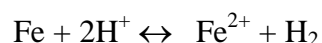
iii. Thermodynamic principles

Thermodynamic principles indicate the spontaneity of a chemical reaction. They can be used to determine whether or not corrosion is theoretically possible. Different metals have different tendencies to corrode in a given corrosive environment. The tendency to corrode depends upon the energy associated with the chemical reaction taking place during corrosion. The scope of thermodynamics is to study the energy changes associated with chemical reactions. By calculating the amount of energy associated in a given chemical reaction it is possible to indicate whether (or) not natural corrosion can take place in a given set of environmental conditions. Thermodynamic principles applicable to corrosion processes do not provide any information on the kinetics of corrosion processes. Thermodynamic principles are applicable to free energy, electrical double layer, Nernst equation for electrode potentials and Pourbaix diagrams.

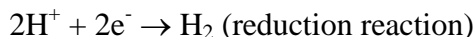
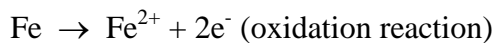
iv. Electrochemical principles

They are extensively used to determine the corrosion behaviour of the material. Here the corrosion reaction can be represented by partial reactions such as metal oxidation and reduction of some reducible species of the environment both occurring simultaneously at equal rates at the mixed potential of the reaction. Corrosion reaction mainly occurs at the metal-environment interface.

This type of corrosion can be illustrated by the attack of iron in HCl. When iron is dipped in acid, a vigorous reaction occurs, as a result hydrogen gas is evolved and iron gets dissolved. The reaction is



There are two partial reactions,



1.1.11 Theories of corrosion

Corrosion theories may be classified into two types

i. Homogeneous theory

A corroding metal irrespective of the presence or absence on its surface of any micro heterogeneity can be regarded as a single electrode on which reactions take place. Metal becomes unstable due to the charge transfer reaction taking place at the interface. Hence it is necessary that the potential difference across the interface be more negative than the equilibrium potential for the metal dissolution (anodic) reaction or more positive than the equilibrium potential for the electronation (cathodic) reaction.

ii. Heterogeneous theory

In this theory, corrosion is caused by the local galvanic elements that arise on the surface of the corroding metal as a result of the chemical structure heterogeneity.

Corroding metal consists of

- An electron sink area where de-electronation reaction occurs.
- Electron source area where electronation reaction occurs.
- An ionic conductor to keep the ion current flowing.

This model is the basis for the local cell theory of corrosion or heterogeneous corrosion.

1.1.12 Factors influencing the rate of corrosion

The rate and extent of corrosion depends on the following factors:

i. Nature of the metal

Position in the galvanic series: When two metals or alloys are in electrical contact in presence of an electrolyte, the more active metal (or higher up in the series) suffers corrosion. Therefore, the rate and severity of corrosion depends on the difference in their positions in the emf series and greater is the difference the faster is the corrosion of the anodic metal /alloy.

Over voltage reduction: Over voltage of the corroding metal/alloy in the corrosive environment is inversely proportional to the corrosion rate.

Relative areas of the anode and cathode: The rate of corrosion will be more, when the cathodic area is larger. When the cathodic area is larger, the demand for electrons will be more and this results in an increased rate of corrosion (dissolution) of metals at anodic area.

Purity of metal: The rate and extent of corrosion increases with increasing exposure and extent of the impurities. Consequently, corrosion resistance of a metal may be improved by increasing its purity.

Physical state of metal: The rate of corrosion is influenced by physical state of the metal such as grain size, orientation of crystals, stress *etc.*, The smaller the grain-size of the metal or alloy, the greater will be its solubility and hence greater will be its corrosion.

Solubility of corrosion products: In electrochemical corrosion, if the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate. If the corrosion product is insoluble in the medium or it interacts with the medium to form another insoluble product, the corrosion product functions as physical barrier thereby suppressing further corrosion.

ii. Nature of the corroding environment

Temperature: The rate of corrosion is directly proportional to temperature. This is because, the rate of the chemical reaction as well as the rate of diffusion of the ions increases with rise in temperature. Hence the corrosion rate is generally enhanced.

Humidity of air: It is the deciding factor in atmospheric corrosion. Critical humidity is defined as the relative humidity above which the atmospheric corrosion rate of the metal increases sharply.

Presence of impurities in the atmosphere: Atmosphere in the vicinity of industrial areas contains corrosive gases like CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 *etc.*, In presence of these gases, the acidity of the liquid, adjacent to the metal surfaces, increases

and its electrical conductivity also increases. This consequently results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surface.

Presence of suspended particles in the atmosphere: In case of atmospheric corrosion if the suspended particles are chemically active in nature they absorb moisture and act as strong electrolytes thereby causing enhanced corrosion. If the suspended particles are chemically inactive in nature they adsorb both sulphur gases and moisture and slowly enhance corrosion rate.

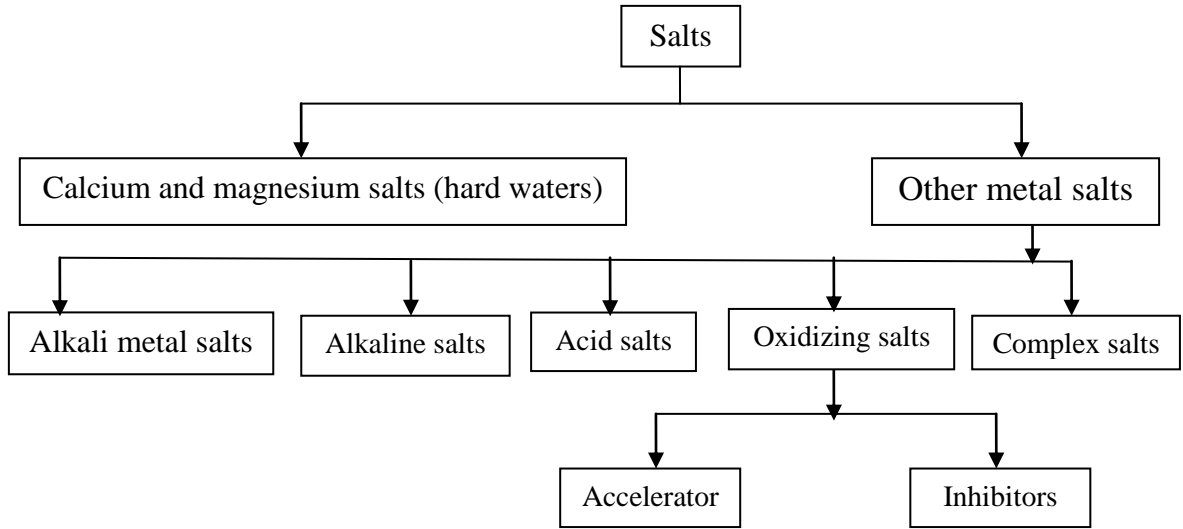
Formation of oxygen concentration cell: With the increase in supply of oxygen/air to the moist-metal surface, corrosion is promoted. Less oxygen concentration parts become anodic while the more oxygenated parts become cathodic thereby leading to the formation of “oxygen-concentration cell” in which the anodic part suffers corrosion. Thus oxidation concentration cell promotes corrosion, but it occurs where the oxygen concentration is lower.

Polarization of electrodes: The potential difference between the anode and cathode is the driving force of electrochemical corrosion process, but the corrosion rate is controlled by the current flowing in the circuit. The extent of corrosion can be reduced by adding certain inorganic and organic substances to the corroding environment. These inhibitors cause certain irreversible changes around the electrodes, which tend to oppose the direction of the corrosion current flow. This is called polarization of electrodes. This alters the potential of the cathode to less cathodic and that of the anode to less anodic. As a result of this, the potential difference and current between the anodic and cathodic areas decreases, thereby the corrosion rate also decreases. When the potential of the polarized electrodes are plotted against current in the corrosion circuit, polarization curves called Evans diagrams are obtained. In these diagrams, the polarization curve possesses a steeper slope for the electrode which is polarized to the greater extent. The point of intersection of the two curves (at which the two electrodes will have identical potential *i.e.*, $I_a=I_c$) is known as the corrosion potential (E_{corr}).

But the factors are generally governed by the nature of dissolved gases, dissolved salts, presence of bacteria, pollutants, temperature *etc.*,

iii. Presence of dissolved salts

The type of salts that affects corrosion can be classified as follows:



(a) Calcium and magnesium salts

Water containing Ca and Mg salts is said to be hard. There is a tendency in these cases to form scale on the metal surface, if the conditions are favourable. So the corrosion rates are generally lower in such water.

(b) Alkali salts

Salts such as NaCl, KCl and Na_2SO_4 accelerate corrosion mainly by making the oxide film less protective and also by activating the dissolution process.

(c) Acid salts

Salts such as AlCl_3 , FeCl_2 , MnCl_2 , NiSO_4 etc., hydrolyze to form acid solution. So corrosion takes place both by hydrogen discharge and oxygen absorption resulting in higher rate of corrosion.

(d) Alkaline salts

Salts such as sodium carbonate, sodium phosphate, sodium silicate which when dissolved in water gives rise to solution of pH greater than 10. The rate of corrosion depends on the nature of the metal and such that they can be either inhibitors or accelerators of corrosion.

(e) Oxidizing salts

These salts can either be accelerators or inhibitors. CuCl_2 , FeCl_3 , HgCl_2 act as accelerators by aiding cathodic depolarization where as sodium chromate, sodium nitrate *etc.*, inhibit corrosion by facilitating the formation of protective oxide film on the surface.

(f) Complexing salts

Cyanide and ammonium ions tend to form soluble complex salts leading to increased corrosion rate. In the case of ammonium salts they form complexes with Cu, Zn and Fe. In the case of iron, ammonium nitrate is about eight times more corrosive than chloride and sulphate.

iv. Presence of dissolved gases

Gases such as CO_2 , O_2 , NH_3 , H_2S and Cl_2 affect the corrosion rate. CO_2 acts by promoting acid-type corrosion and also by increasing the solubility of carbonate responsible for scale formation. Dissolved oxygen is the most significant constituent affecting corrosion. In neutral or near neutral solution, corrosion cannot proceed in the absence of O_2 . Hence the corrosion rate is directly proportional to the oxygen concentration in the solution. Although increase in oxygen concentration accelerates corrosion of iron, it has been observed that beyond a certain concentration, oxygen has a tendency to passivate the metal surface leading to decreased corrosion rate.

1.1.13 Forms of corrosion

Corrosion manifests itself in various forms. Sixteen forms of corrosion that are observed in engineering industries are given below. Each form is classified by external appearance or altered physical properties. Identification of the type of corrosive attack helps to determine the cause and preventive methods of corrosion.

i. Uniform or general corrosion

A uniform regular removal of metal surface is usually the expected mode of corrosion. For uniform corrosion, the corrosive environment must have the same access to all parts of the metal surface and the metal itself must be metallurgically and compositionally uniform. Atmospheric corrosion of ferrous and non-ferrous metals and uniform corrosion of steel in acid solutions are the best examples.

Uniform attack can be prevented or reduced by

- Coatings
- Inhibitors
- Cathodic protection.

ii. Galvanic (or) bimetallic corrosion

This is an aggressive and localized form of corrosion which occurs due to the electrochemical reaction often found between two or more dissimilar metals in an electrically conductive environment. This results from the existence of a potential difference between the metals, which causes a flow of current between them. The emf series and the galvanic series are used to predict the galvanic corrosion tendency of various metals. Galvanic corrosion is often utilized in sacrificial anodes. It is of major interest in the marine industry and also in contact pipes or metal structures.

Factors affecting galvanic corrosion are:

- The corrosion potentials of metals M_1 and M_2 which are forming galvanic couple, in the same environmental conditions where it is used.
- Electrochemical reactions at both the anodic and cathodic surfaces.
- The electrical resistance, concentration, pH and degree of aeration of the electrolyte.
- The relative areas of anode and cathode.

iii. Pitting corrosion

It is often termed as “Under deposit corrosion”. This is a localized, deep penetration of the metal surface with little general corrosion in the surrounding area. In most cases, pitting is extended throughout the entire metal surface, creating an irregular or very rough surface profile. In other instances, pits are concentrated in specific areas, leaving the majority of the metal surface in new condition. Pitting is the most common form of corrosion found where there are incomplete chemical protective films and insulating or barrier deposits of dirt, iron oxide, organic and other foreign substances at the pipe surface. It is prevalent at galvanized steel pipe, where any failure of galvanizing invokes a pitting condition. Pitting corrosion may include: crevice corrosion, water-line attack, under deposit attack, erosion corrosion attack and concentration-cell corrosion.

iv. Crevice corrosion

Another form of localized corrosion which is a major practical problem affecting steel is crevice corrosion. Crevice corrosion occurs in spaces to which the access of the working fluid from the environment is limited. These spaces are generally called crevices. Crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles. They are also created by surface deposits of corrosion products, scratches in paint films *etc.*, This type of attack is called crevice corrosion or sometimes deposit corrosion or gasket corrosion.

Crevice corrosion is usually attributed to one or more of the following inside the crevice:

- Lack of oxygen
- Depletion of an inhibitor
- Changes in acidity
- Built-up of a detrimental species
- Inadequate anodic protection

v. Intergranular corrosion

Grain boundaries are physically and chemically different regions and are usually more reactive than grain matrix. In most applications, this is of little or no consequence, since the grain boundaries are usually only slightly more reactive than the matrix resulting in uniform corrosion of the metal. However, under certain conditions the grain boundaries are very reactive and localized attack occurs adjacent to grain boundaries with relatively little corrosion of the matrix. The attack is usually rapid, penetrating deep into the metal resulting in loss of strength and sometimes catastrophic failures.

vi. Dealloying

Dealloying is a general term used to define corrosion process whereby one constituent of an alloy is removed preferentially from the alloy leaving an altered residual structure. An alloying element that is more active (negative electrochemically) in the major solvent component is likely to be preferentially corroded by dealloying. This process is also known as selective leaching which occurs due to the selective corrosion of a phase or an element. Most common examples of this type of attack are dezincification

(removal of zinc from Cu-Zn alloys) and graphitization (removal of ferrite from gray cast iron).

vii. Erosion corrosion

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

viii. Stress corrosion cracking

The cracking of a metal alloy by conjoint action of a tensile stress and a corrosive environment is known as stress corrosion cracking (SCC). Two classic examples of stress corrosion cracking are caustic embrittlement of riveted steel boilers and the season cracking of brass cartridge cases.

ix. Microbiologically influenced corrosion (MIC)

MIC refers to corrosion that is influenced by the presence and activities of microorganisms (bacteria, fungi *etc.*) and/or their metabolites. An aerobic bacterium produces highly corrosive species as part of their metabolism. Most materials, including metals, polymers, glass and ceramics can be degraded in this manner³⁷. The production of corrosive species such as minerals, organic acids, ammonia, sulphide and the various types of microbes tend to act synergistically in the corrosion of materials with their interactions typically being of a complex nature.

x. Filiform corrosion

It is a special case of crevice corrosion which results in irregularly developed hair-fine lines of filaments of corrosion products below coatings of paint, rubber, lacquer, tin, enamel, paper *etc.*, Filiform corrosion tends to follow grinding and polishing marks and is independent of metallurgical factors.

xi. Exfoliation

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

xii. Corrosion fatigue

Corrosion fatigue is defined as the reduction of fatigue strength due to the presence of a corrosive environment. It can probably be considered as a special case of normal fatigue with certain modifying effects due to the presence of the environment. When metals are subjected to corrosion during repeated cyclic loadings, specimen lifetime and the endurance limit are significantly reduced. If the magnitude of the applied stress is varied during service, the fatigue response of the metal becomes very complex. Cyclic stress in an environment, capable of causing corrosive attack must be avoided³⁸⁻⁴².

xiii. Water line attack

It is a special case of crevice corrosion which occurs just below the liquid level on metals immersed in water. Formation of oxygen concentration cells is largely responsible for this type of attack. Typical example is a steel pipe driven into the soil is particularly attacked just below the ground water level. A steel pipe immersed in sea water is most strongly attacked just below the water line. Protective coatings are used to reduce this type of attack.

xiv. Stray current corrosion

Stray current corrosion is caused by direct current. Great damage may thus be caused by direct current from welding generators used in electric welding.

xv. Cavitation corrosion

Cavitation corrosion is also a result of conjoint action of high liquid flow rate and corrosion. Cavitation denotes the occurrence of gas or vapour bubbles in a liquid. Two types of cavitation should be distinguished namely gas cavitation and vapour cavitation.

xvi. Fretting corrosion

It occurs at the interface between two solid bodies, one or both being metallic, under normal pressure and without lubricant.

1.1.14 Methods of corrosion control

Depending on the metal-environment, suitable effective and economical method has to be adopted. In general, the corrosion is prevented by the following ways.

i. Change of metal

Alloying and surface modifications are common techniques used to prepare metal with improved corrosion resistance properties. Surface modification is mainly employed to improve upon certain properties of metals and alloys like corrosion resistance, wear resistance, fatigue resistance and high temperature resistance.

ii. Change of environment

Corrosion can be minimized by decreasing the corrosivity of the aggressive medium by the addition of organic or inorganic substances which inhibit corrosion. These substances are known as inhibitors, they may be either anodic or cathodic inhibitors.

Anodic inhibitor functions by reacting with the anodic sites of the metal surface to form a compound that is sparingly soluble, even insoluble, thereby preventing or retarding corrosion of the metal. They are of three types.

- (a) **Restrainers:** Organic compounds that interact with the metal and reduce the activity of the anodic sites and so diminish the corrosion. Restrainers are frequently added to pickling acids to reduce the attack of bare metal during the pickling process.
- (b) **Incubators:** Inhibitors that confer temporary protection on metal but eventually corrosion will occur due to break down of inhibitor film. They are usually organic compounds which form organometallic complexes at the metal surface.
- (c) **Passivators:** Substances which function by reaction with the metal to form an insoluble sparingly soluble oxide or salt such that the metal is passivated and made resistant towards corrosion. They are mostly inorganic salts although alkali metal salts of certain organic acids have the same action.

iii. Change of metal/electrode potential

Examination of Pourbaix (potential /pH) diagrams indicates that in most 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 (anodic) direction in the domain of immunity. 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. These two methods are described below.

(a) Cathodic protection⁴³

The cathodic reaction is the evolution of hydrogen in acidic media and the reduction of oxygen in neutral and alkaline media. So, if the entire metal is made to function as cathode without the existence of any anodic sites on the metal surface, it should not undergo any corrosion. This is the basis of cathodic protection. Cathodic protection may be defined as the technique of reducing the corrosion rate of metallic structures, making the steady state or corrosion potential of the metal sufficiently more electronegative.

(b) Anodic protection⁴⁴

In this method the structure to be protected is made anode and potential is set in the passive region. Anodic protection is applied to steel containers for storage of sulphuric acid and phosphoric acid.

iv. Use of coatings for protecting the metal from the environment⁴⁵

Protective coatings are the most common approach to corrosion protection and control. Both metallic and non-metallic coatings are being very widely used in the industrial and domestic fields. Metallic coatings may function as sacrificial coatings and protect the substrate metal by cathodic protection. Alternatively the noble metallic coatings have a greater corrosion resistance than the substrate metal.

Non-metallic coatings include oxides, sparingly soluble films of chromates and phosphates, ceramics and paint films. Protection by paint films are due to barrier effect and offer high electrical resistance in the corrosion cell. The paint-film hinders the diffusion of dissolved oxygen to the metal surface and enhances the cathodic polarization.

1.1.15 Corrosion mechanism in acid solutions

Aqueous acid solutions cause severe corrosion with metals and alloys. Organic compounds such as triple-bonded hydrocarbons, acetylenic alcohols, sulfoxides, sulfides, mercaptans and aliphatic, aromatic or heterocyclic compounds containing

nitrogen and sulfur as well as many other families of simple organic compounds can be added to the metal-electrolyte as inhibitors to reduce corrosive effects. Efficient inorganic compounds include metal salts and oxidizing agents such as SnSO_4 , CuSO_4 , *etc.*, The first step in the mechanism of the inhibitor in an aggressive acid media is the adsorption of the inhibitor by the metal surface. This process depends on several factors:

- The nature and surface charge of the metal.
- The chemical structure of the organic inhibitor.
- The type of aggressive electrolyte.

1.1.16 Corrosion mechanism in neutral solutions

Efficient inhibitors in acid solutions have little or no effect in near-neutral solutions. This is due to differences in the mechanism of the corrosion processes. In acid solutions the inhibitor action is caused by adsorption on oxide free metal surfaces. In these media the main cathodic process is hydrogen evolution. On the other hand, in neutral aqueous solutions the corrosion processes result in the formation of insoluble surface products such as oxides, hydroxides or salts. The cathodic reaction is oxygen reduction. The inhibitors influence the oxide-covered surface by increasing or maintaining the protective characteristics of the oxide or of the surface compounds in the aggressive solutions. If the concentration of inhibitors, the pH value of the inhibitive anion (favored in alkaline solution), the dissolved oxygen concentration and supply in the solution, aggressive anion concentration, the nature of the metal surface and temperature of the solution are well known and controlled, this effect can be accomplished. The basic step of inhibition is the replacement of pre-adsorbed water molecules by adsorbing inhibitor molecules. Chemical or electrochemical reactions of the inhibitor at the surface may also participate in order to explain the inhibitor efficiency and these reactions may consume more inhibitor⁴⁶⁻⁴⁸.

1.1.17 Corrosion mechanism in alkaline solutions

A third group of inhibitors are used in alkaline solutions. If the metal hydroxides are amphoteric or the protective oxides are easily destroyed in the presence of alkalis, the metals are liable to caustic attack. Useful inhibitors consist of organic substances such as tannins, gelatin, saponin, thiourea, substituted phenols and naphthols, beta-diketones

and quinalizarine. They act by expanding the pH stability range of amphoteric oxide and hydroxide layers, protecting pores in oxide and hydroxide films, decreasing the diffusion rate of the reactant to the surface and removing corrosion products from the surface⁴⁹.

1.1.18 Synergistic effect and corrosion inhibition

Synergism can be defined as the marked reinforcement of the inhibiting action of one inhibitor by adding a small amount of another inhibitor, even though the second inhibitor is less effective when used alone. Mixtures of inhibitors often provide better inhibition than either of the individual components or sum effect of the individual components. A mixture of two or more inhibitors is thus synergistic.

The synergistic effect of halides and organic compound inhibitors are often reported in the literature⁵⁰⁻⁵³. The synergism could be interpreted as co-adsorption of both halide anion and organic cation directly on the metal surface⁵⁴. High concentration of these species on the iron surface was found to form a complex film.

1.2 Introduction to corrosion inhibitors

National Association of Corrosion Engineers define inhibitors, as substances which can retard the rate and extent of corrosion, when added to a corroding environment in small concentrations, sometimes as low as 10^{-5} M. Hundreds of chemicals-inorganic and organic have been studied and recommended as inhibitors of corrosion, for various metals in various environments – aqueous, non aqueous, molten salt and dry atmospheres.

Corrosion inhibitors are used to protect metals from corrosion, including temporary protection during storage or transport as well as localized protection, to prevent corrosion that may result from accumulation of small amounts of an aggressive phase. An efficient inhibitor is compatible with the environment, is economical for application and produces the desired effect when present in small concentrations.

The major industries using corrosion inhibitors are oil and gas exploration and production, petroleum refining, chemical manufacturing, heavy manufacturing, water treatment and the product additive industries. The total consumption of corrosion inhibitors in the United States has doubled from approximately \$600 million in 1982 to nearly \$1.1 billion in 1998⁵⁵. US demand for corrosion inhibitors alone is forecast to rise

4.1 percent per year to \$2.5 billion in 2017, with volume demand approaching 1.7 billion pounds. Growth will be driven by higher oil and natural gas output, particularly from shale formations, as well as by increasing chemical production and an expanding economy. Additionally, robust increases in construction spending will support demand for corrosion inhibitors used in cement and concrete, industrial coatings and metal applications. The industry will continue to invest in the development of new, less costly products such as organic corrosion inhibitors with better environmental profiles and improved performance.

The use of organic adsorption type corrosion inhibitors is a wide spread and cost-effective method to control carbon steel corrosion in the oil and gas production. The chemical functionalities employed in inhibitor formulation are very diverse and commercial inhibitors usually contain active components such as amides, amines, imidazolines, quaternary ammonium salts, *etc.*, The inhibitor efficiency depends on a wide range of factors: flow patterns, solution chemistry, temperature, pressure, *etc.*, The mechanism of action of inhibitors is difficult to establish and there is a large amount of research done on the subject.

Inhibitors function by

- Adsorption as a film on to the surface of the corroding medium
- Inducing the formation of thick product
- Changing the characteristics of the environment either by producing protonating precipitates or by inactivating an aggressive constituent, so that it prevents or arrests corrosion process. It can also interfere with the cathodic, anodic or both reactions.

1.2.1 Requirements of corrosion inhibitors

- Effective inhibition of metal dissolution
- Effective at low concentration
- Effective also at higher temperature
- Thermally and chemically stable
- Effective inhibition of hydrogen up-take by the metal
- Good surfactant characteristics
- Good foaming characteristics

1.2.2 Classification of inhibitors

Inhibitors can be roughly classified into three types namely anodic, cathodic and mixed inhibitors based on electrode processes.

i. Anodic inhibitors

An anodic inhibitor increases the anodic polarization and hence displaces the corrosion potential in the positive direction. In this class, we find a number of inorganic inhibitors such as orthophosphates, silicates *etc.*, Even though anodic inhibitors are widely used, a few of them have some undesirable property. If such inhibitors are used in very low concentrations they cause stimulation of corrosion such as pitting and for this reason anodic inhibitors are therefore denoted as dangerous.

ii. Cathodic inhibitors

Cathodic inhibitors shift the corrosion potential in the negative direction. Here the cations migrate towards the cathode surfaces where they are precipitated chemically or electrochemically and thus block these surfaces. Action of As^{3+} and Sb^{3+} on dissolution of Fe in acids is an example.

iii. Mixed inhibitors

Such types of inhibitors retard both the anodic and cathodic processes. The shift in the potential is smaller and the direction is determined by the relative size of the anodic and cathodic sites. Such inhibitors will have the advantage over other inhibitors in that they control both the cathodic and anodic corrosion reactions and hence, they are very safe to apply.

Other tentative classifications of inhibitors have been made by taking into consideration their chemical nature or their technological field of application. Certain classes of inhibitors are given below.

iv. Acid inhibitors

Acid inhibitors may be classified into inorganic and organic inhibitors

(a) Inorganic inhibitors

The compounds such as As_2O_3 , 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 iron and steel by reduction and raising the hydrogen overvoltage and thereby reducing the corrosion. In strong acid solutions, bromide and iodide have been found to be effective inhibitors. Recently, it is shown that the addition of heavy metal ions such as Pb^{2+} , Tl^+ , Mn^+ and Cd^{2+} is found to inhibit corrosion of iron in acids.

(b) Organic inhibitors

These are compounds with atleast one polar function, which facilitates their physical adsorption or chemisorption on metallic surfaces. However the modes of adsorption are dependent upon the chemical structure of the molecule, chemical composition of the solution and the nature of the metal surface. Non-volatile organic inhibitors are used for aqueous and non-aqueous media, acidic, alkaline media and pickling. Usually the corrosion of metals and alloys in acid solution is very severe and this kind of attack can be inhibited by a large number of organic substances.

v. Neutral inhibitors

Inhibitors which are effective in acidic solution do not function effectively in neutral solution. The mechanism of corrosion inhibition is different in the two solutions. In neutral solution, the interaction of inhibitors with oxide covered metal surfaces and prevention of oxygen reduction reactions at the cathodic sites take-place. This type of inhibitors protects the surface layer from aggressiveness. Some surface active chelating inhibitors have been found to be efficient inhibitors in near-neutral solutions.

vi. Alkaline inhibitors

All metals which form amphoteric oxides are prone to corrosion in basic solution. Many naturally occurring organic compounds are often used as inhibitors for metals in basic solution. In basic solution, the compounds such as thiourea, substituted phenols, naphthol, β -diketone *etc.*, have been used as effective inhibitors⁵⁶ *e.g.*, tannin, gelatin, saponin, agar-agar *etc.*,

vii. Pickling inhibitors

Compounds serving as pickling inhibitors require a favourable polar group or groups by which the molecule can attach it to the metal surface. These include the organic N, amine, S and OH groups. The size, orientation, shape and electric charge of

the molecule play a part in the effectiveness of inhibition. Typical effective organic pickling inhibitors for steel are quinolinethiodide, *o* - and *p* - tolylthiourea, propyl sulphide, diamyl amine, formaldehyde and *p*- thiocresol.

Inhibitors are commonly used in the acid pickling of hot - rolled steel products in order to remove mill scale. The advantages of using an inhibitor for this purpose are (1) saving of steel, (2) saving of acid and (3) reduction of acid fumes caused by hydrogen evolution. Inhibited dilute sulfuric or hydrochloric acid is also used to clean out steel water pipes clogged with rust, to clean boiler tubes encrusted with CaCO₃ or iron oxide scales and to activate oil wells underground. For example, boiler scale can be removed by using 0.1% hexamethylene tetramine in 10% HCl at a maximum temperature of 70 °C (160 °F)⁵⁷.

viii. Volatile inhibitors

Vapour phase inhibitors are organic compounds characterized by a slight vapour pressure ranging from 0.0001 to 0.5 mm Hg. The solid amine nitrite differs from alkali metal nitrites in being slightly volatile at atmospheric temperature. This property gives it special industrial importance because it makes possible for the prevention of atmospheric corrosion without the necessity of coating the steel with the inhibitor.

ix. Passivators

Passivators are usually inorganic oxidizing substances *e.g.*, chromates, nitrites or molybdates that passivate the metal and shift the corrosion potential several tenths in the noble direction. Non-passivating inhibitors such as pickling inhibitors shift the corrosion potential by a few milli or centivolts in the noble direction.

x. Slushing compounds

Slushing compounds are used to protect steel surfaces temporarily from rusting during shipment or storage. They consist of oils, greases or waxes containing small amounts of organic additives. Suitable organic additives for use in slushing compounds include organic amines, zinc naphthenate, various oxidation products of petroleum, alkali and alkaline - earth metal salts of sulfonated oils and various other compounds⁵⁸.

A substance that has been used successfully is lanolin, obtained from wool scouring; its active constituents are various high - molecular - weight fatty alcohols and

acids. Sometimes, lead soaps are added to slushing compounds, with these soaps reacting to form relatively insoluble $PbCl_2$ with any $NaCl$ from perspiration transferred to steel surfaces through handling.

xi. Vapour phase inhibitors

Substances of low but significant vapour pressure, the vapour of which has corrosion - inhibiting properties, are called vapour - phase inhibitors. They are used to protect critical machine parts (*e.g.*, ball bearings or other manufactured steel articles) temporarily against rusting by moisture during shipping or storage. Cyclohexylamine carbonate has somewhat higher vapour pressure of 0.4 mm Hg at 25° C and its vapour also effectively inhibits steel⁵⁹. Ethanolamine carbonate and various other compounds have also been described as vapour - phase inhibitors⁶⁰.

Major advantages of vapour phase inhibitors include

- Easy to apply as paper coated VPI for temporary protection.
- Life of inhibitor becomes very long
- These compounds can be immediately used without any removal of residual film on the material.

xii. Film forming inhibitors

Substances that form adsorbed film of the inhibiting species are called film forming inhibitors. They appear to stop corrosion by forming a blocking or a barrier film of material other than the actual inhibiting species itself. Such materials tend to be specific to either the cathode or the anode, but seldom to both. This also forms the basis of classifying film forming inhibitors into (i) anodic filming inhibitors and (ii) cathodic filming inhibitors.

xiii. Green inhibitors

Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the present and in future. Environmental requirements are still being developed, but some elements have been established. One of the methods to protect metals against corrosion is addition of species to the solution in contact with the surface in order to inhibit the corrosion rate. Unfortunately, many of the inhibitors

used are inorganic salts or organic compounds with toxic properties or limited solubility. Increasing awareness of health and ecological risks create more attention to find more suitable inhibitors, which are non toxic. Accordingly research efforts have been directed towards formulating environmentally acceptable inhibitors.

Due to the diversity of their structures, many extracts of common plants have been used as corrosion inhibitors for materials in pickling and cleaning processes. Plant materials contain proteins, polysaccharides, polycarboxylic acids and alkaloids. These compounds are potential acid corrosion inhibitors for many metals. The cost of using green inhibitors is very less when compared to that of organic inhibitors which takes more chemicals and also time for its preparation.

1.2.3 Functioning of organic inhibitors

Organic corrosion inhibitors may function by

- Adsorption/chemisorption of the molecules on a metallic substance,
- Complexing of the molecules with the metal ions which remain in a solid lattice,
- Neutralizing the corrodent and
- Adsorbing the corrodent.

Usually the first contact of a metal with an inhibitor causes its physical adsorption on the metal surface, which may or may not be followed by chemisorption. Whether it is mere adsorption or chemisorption can be determined by characteristics such as adsorption kinetics and heat of adsorption.

1.2.4 Theories of inhibitors

The action of an inhibitor in acidic as well as in alkaline and neutral media has been mainly explained by adsorption and/or film formation. In the case of acid inhibitors, they can also act, in addition, by affecting the kinetics of hydrogen evolution (hydrogen over voltage theory).

i. Adsorption theory

According to adsorption theory, inhibitors are adsorbed on the metal surface forming a protective layer. The mode of adsorption leads to its classification as physical adsorption and chemical adsorption.

(a) Physisorption

It is the result of electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal. The surface charge of the metal is due to the electric field at the outer Helmholtz plane of the electrical double layer existing at the metal-solution interface. The surface coverage can be obtained from the potential of the metal (E_{corr}) vs. its zero charge potential (ZCP) $E_{q=0}$ of the particular metal⁶¹. When the difference $E_{\text{corr}} - E_{q=0} = \phi$ is negative, cation adsorption is favoured. Adsorption of anion is favoured when ϕ becomes positive. This behaviour is related not only to compounds with formal positive or negative charge, but also to dipoles whose orientation is determined by the value of ϕ potential.

Adsorbable anions such as halide ions which may be present in the solution are adsorbed on the metal surface by creating oriented dipole. In aqueous solution the potential difference is large due to adsorption of water molecules, although adsorption of other molecules in solution can also have an effect. Although the water molecule is electrically neutral as a whole, the fact that the two binding electrons are closer to the oxygen atom than to the hydrogen atoms, results in an electric dipole with a positively charged (hydrogen) end and a negatively charged (oxygen) end and consequently a potential difference exists across the molecule Fig. 1.1(a).

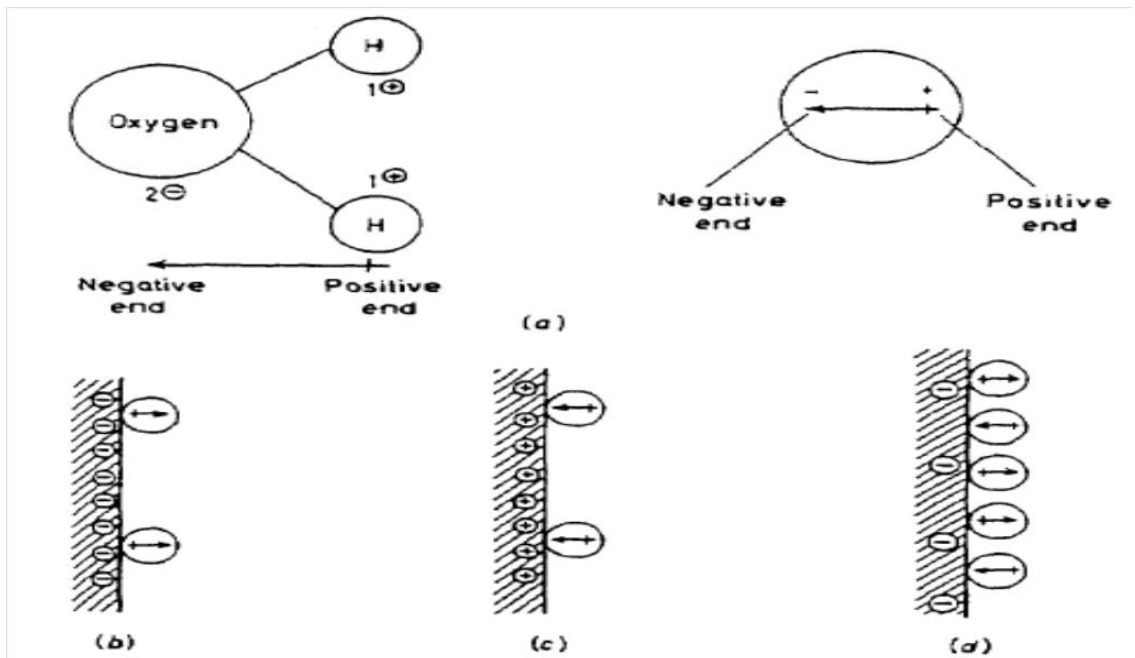


Fig. 1.1: Adsorption of water dipoles

If the metal has a large negative excess charge, the adsorbed water molecules will be oriented with their positive ends towards the metal and their negative ends towards the solution. This layer of oriented dipoles will contribute an additional potential difference to the layer Fig. 1.1(b). The converse situation will arise when the metal has a large positive charge and again the dipoles will contribute to the potential difference Fig. 1.1(c). In the case of a metal with only a small excess charge, dipoles of both orientations will adsorb and the potential difference will be proportional to the excess number of one or the other Fig. 1.1(d)⁶².

The above behavior increases the adsorption of the organic cations on the dipole and creates a positive synergistic effect (when two or more inhibiting compounds are added to a corrosive system, the inhibiting effect is sometimes greater than that which would be obtained. by either of the two or more substances alone.), so that the degree of inhibition when adsorbable anions and inhibitor cations are present, is higher than the sum of the individual effects.

In some chemicals, electrostatic adsorption is responsible for their inhibiting properties. Structural parameters such as hydrocarbon chain length, nature and position of substituents in the organic rings also influence the degree of inhibition. Electrostatic adsorption process has low activation energy and it proves to be relatively independent of temperature. However, it depends on other factors such as

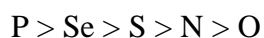
- The electrical characteristics of the organic inhibitors.
- The position of the corrosion potential with respect to the zero-charge potential.
- The type of adsorbable anions present in the aggressive solution.

(b) Chemisorption

The process involves charge sharing or charge transfer from the inhibitor molecule to the metal surface in order to form a coordinate type of bond. The chemisorption process takes place more slowly than electrostatic adsorption and with higher activation energy. It depends on the temperature and higher degree of inhibition is expected at higher temperature. Chemisorption is specific for certain metals and it is not completely reversible⁶³. The bonding occurring with electron transfer clearly depends on the nature of the metal and the nature of the organic inhibitor. Infact, electron transfer is typical for metals having vacant, low energy electron orbitals. Considering the inhibitors

as electron donors, electron transfer can be expected with compounds having more loosely bound electrons. This situation may arise because of the presence of adsorbed inhibitor of multiple bonds or aromatic rings in the inhibitor whose electrons have π -character.

Most of the organic compounds are substances with at least one functional group regarded as the reaction site for chemisorption process. In this case, the strength of the adsorption bond is related to the heteroatom electron density and to the functional group polarizability. For *e.g.*, the inhibition efficiency of homologous series of organic compounds differing only in the heteroatom is usually in the following order.



It has been postulated that the surface bond is of Lewis acid-base type with normally inhibitor as electron donor and the metal as electron acceptor. The principle of soft and hard acids and bases (SHAB) has also been applied to explain adsorption and inhibition effect. The SHAB principle states that the hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases. Metal atoms on the oxide free surface are considered as soft acids which in acid solution bond with soft bases such as sulphur containing inhibitors. By comparison, nitrogen containing or oxygen containing organic compounds are considered as hard bases with metal surface in acid solutions.

ii. Film theory

In order to explain the action of inhibitors in neutral and alkaline media, **Evans**⁶⁴ proposed the film formation theory. **Evans** attributed the inhibition, to the formation of an insoluble film. According to **Putilova et al.**,⁶⁵ in acid solution, inhibition is due to the formation of a layer of insoluble or slightly soluble corrosion products on the metal surface.

iii. Hydrogen over voltage theory

The action of acid inhibitors was explained by hydrogen over voltage theory. This theory postulates that inhibitors which are absorbed on the metal, retard either anodic or cathodic or in some cases both the reaction. This leads to rapid polarization of anodic or

cathodic sites and thus overall corrosion rate is retarded. This theory does not explain the inhibitive action of all types of systems.

1.2.5 Factors affecting the applicability of inhibitors

i. Nature of the metal surface

Clean, smooth surfaces of metals usually require low concentration of inhibitors. Presence of oil, grease or other corrosion products may lead to adverse effects. So before the use of inhibitors, surface treatment is necessary. One of the well known surface treatments is phosphate delayed chromate technique.

ii. Nature of the environment

In all circumstances, it is important to ensure that the inhibitor is compatible with the environment. For example, chromates cannot be used in glycols antifreeze solutions, since oxidation of glycol by chromate will reduce this to trivalent state which has no inhibitive property.

iii. pH of the system

All inhibitors have a pH range in which they are most effective and even in nominally neutral solutions. pH control is often necessary to ensure continuous efficiency of inhibitive treatments.

iv Temperature of the system

At higher temperatures, the inhibitor is required in larger concentrations or the inhibitor losses its efficiency. For example, polyphosphate can inhibit around 40°C above this its inhibitive property is lost because of the formation of orthophosphate. If Ca^{2+} ion is also present precipitation of calcium phosphate takes place.

v. Inhibitor concentration

To be fully effective, the inhibitor is required above a certain minimum concentration. Insufficient quantities of inhibitor used may result in localized corrosion, if it is a dangerous inhibitor.

vi. Scale formation

Scale formation on metal surface screens the metal surface and hence contact between metal and inhibitor is lost. Inhibitor is also incorporated in the scale resulting in

the reduction of heat transfer in cooling systems. In some cases, scale formation results due to the reaction of the inhibitor with the metal surface.

vii. Toxicity disposal and effluent problems

With increasing awareness of environmental pollution problems, the use and disposal of all the types of inhibitors is receiving greater attention than even before. Taking into consideration the disposal of phosphate-chromate inhibitors, formulations containing bio-degradable chemicals are being introduced.

1.2.6 Adsorption isotherm

Adsorption is a phenomenon where organic compounds get adsorbed on the metal surface and provide a blanketing effect over the entire surface.

An adsorption isotherm is a 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 the adsorbed species (*i.e.*, amount adsorbed) and the concentration of species in solution. Plots of variation in corrosion rate with the change in inhibitor concentration have the appearance of being mirror images of adsorption isotherm for most organic inhibitors. This strongly suggests that adsorption of inhibitors on the metal surface (partly) accounts for the inhibition mechanism.

Various adsorption isotherms have been formulated. A list of various isotherms and the corresponding equation is given in the following table. The isotherms are converted into their linear forms and the experimental data are tested with each isotherm. The free energy of adsorption (ΔG_{ads}^o) can be obtained from the isotherm which gives a good straight line.

S. No.	Isotherms	Equation
1.	Henry	$\beta c = \theta$
2.	Freundlich	$\beta c^n = \theta$
3.	Langmuir	$\beta c = \theta/1-\theta$

4.	Frumkin	$\beta c = \theta \exp(-2a\theta)/(1-\theta)$
5.	Temkin	$\beta c = \exp(a\theta)^{-1}/1-\exp\{-a(1-\theta)\}$
6.	Volmer isotherm	$\beta c = (\theta/1-\theta)\exp(\theta/1-\theta)$

where,

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

a = Interaction parameter, a > 0 indicates attraction and a < 0 indicates repulsion.

Most of the organic inhibitors obey Langmuir or Temkin adsorption isotherm. An inhibitor is found to obey Langmuir, if a plot of $\log \theta / 1-\theta$ vs. $\log C$ is linear. Similarly, for Temkin, a plot of θ vs. $\log C$ and for Frumkin plot $\log \theta / (1-\theta) C$ vs. θ will be linear.

1.2.7 Mechanism of inhibitor action in acid corrosion processes

The effect of adsorbed inhibitor on the acid corrosion of metal is to retard either the anodic dissolution reaction of the metal or the cathodic hydrogen evolution or both. The action may occur by means of different mechanisms. They are in the following ways.

i. Changes in the electrical double layer

An inhibitor changes the structure of the electrical double layer at the metal-solution interface. This effect is produced by electrostatic adsorption of ionized inhibiting species. Adsorption of organic cations or anions results in a positive or negative adsorption potential jump. Adsorption of cations (*i.e.*, quaternary ammonium ions or pyridinium ions)⁶⁶ to the iron surface in acid solution causes a positive shift in the potential known as positive adsorption potential jump. In this case the hydrogen evolution reaction is reduced in deaerated acid solutions. In aerated solutions, the hydrogen evolution is inhibited in the presence of organic cations, and the oxygen reduction reaction may become important. Selective inhibitors can retard the hydrogen evolution better than the oxygen reduction reaction. By contrast the adsorption of anions stimulates the hydrogen evolution reaction. Thus, a negative adsorption potential jump is produced.

ii. Formation of a physical barrier

A different type of inhibitor effect is the formation of a multi molecular layer on the metal surface which interferes with the diffusion of ions to or from the metal surface. The hindering of mass transfer causes inhibition of the corrosion reaction. Inhibitors such as sulfoxides, acetylene derivatives or substances with a high number of carbon atoms in the hydrocarbon chain possess this property. The physical barrier formed is independent of the nature of the adsorption force between the molecules of the inhibitor and the metal surface. Attractive lateral interactions, chemisorption bonds, electron interactions and hydrogen bonds can also be involved in this process.

iii. Reduction of metal reactivity

A third type of inhibition mechanism is a reduction of metal reactivity. This mechanism does not necessarily involve total or partial coverage of the metal surface by the inhibitor. Interacting forces, such as chemisorption, are very important in this process and the stronger the bond, the higher is the efficiency obtained. In this process the inhibitor adsorbs on sites active with respect to the partial electrochemical reactions. When this occurs, active sites are blocked and the reduction of either the anodic or cathodic reaction is increased. Consequently, the reaction rate decreases proportionally to the blockage of the active sites by the inhibitor⁶⁷.

iv. Participation of the inhibitor in partial electrochemical reactions

Anodic and cathodic reactions include steps involving adsorbed intermediates on the metal surface. The adsorbed inhibitor can affect the intermediate formation by increasing or decreasing the rate of electrode reaction. This effect depends on the stability of the adsorbed surface intermediate. When an organic molecule produces a decrease in corrosion rate, the formation of a stable surface complex with the inhibitor can be considered. As an example, we may consider the anodic process of iron dissolution. The formation of intermediates such as adsorbed (FeOH) is generally assumed. In the presence of organic inhibitors (Inh), the formation of a stable chelate [(FeOH) Inh_n] adsorbed to the iron surface is considered. The presence of this surface complex reduces the rate of anodic dissolution of iron. As a result, a variation in the anodic Tafel slope is observed⁶⁸.

1.2.8 Quantum chemical approach

Quantum chemical calculations have become an effective tool in the analysis and elucidation of many experimental observations. Experimental means are useful in explaining the corrosion inhibition mechanism but they are often expensive and time consuming since it is always based on large scale trial and error experiments. However, ongoing computer hardware and software advances have opened the door for powerful use of theoretical chemistry in corrosion inhibition research⁶⁹. Quantum chemical calculations can complement the experimental investigations or even predict with confidence some experimentally unknown properties. Recently, there has been an increase in the use of density functional theory (DFT) method as a theoretical tool in elucidating the mechanism of corrosion inhibition of organic compounds by several researchers⁷⁰⁻⁷². The advancement in methodology and implementations has reached a point where predicted properties of reasonable accuracy can be obtained from DFT calculations⁷³. However, despite enormous literature is available on the use of DFT in understanding the corrosion inhibition mechanism, information on the use of statistical analysis as a tool in correlating the experimentally determined inhibition efficiencies and the calculated quantum chemical parameters in the neutral and protonated forms is scarce.

The calculations of global reactivity indices of the inhibitors such as the localization of frontier molecular orbitals, E_{HOMO} , E_{LUMO} , energy gap (ΔE), dipole moment (μ), hardness (η), softness (S), the fractions of electrons transferred (ΔN), electrophilicity index (ω) and mulliken charge distributions together with local reactivity by means of Fukui indices using DFT at B3LYP/6-31G (d,p) basis set level were used to explain the electron transfer mechanism between the inhibitor molecules and the steel surface. Direct interaction between surface metal atoms and the outermost electrons of the organic molecule sometimes lead to chemisorption phenomenon and thereby cause inhibition.

Chemisorption of organic inhibitors may be taken as a linear combination of the participating wave function of the inhibitor molecule as well as the surface metal atoms. The binding energy of the metal-inhibitor adduct may thus be correlated to the energy difference between the lowest unoccupied molecular orbital (LUMO) of the metal atoms

and the highest occupied molecular orbital (HOMO) of the inhibitor molecule. Moreover, its use in corrosion science as a tool to explain experimental results is growing, as is noted by the increasing number of published articles that are increasingly reporting both experimental and quantum chemical results.

Computational details

Different quantum molecular properties may be described better by different computational methods, depending on the sophistication of the computational approaches. In view of this, three different computational methods, *viz.*, Density Functional Theory (DFT), Hartree Fock (HF) and second order Moller–Plesset perturbation theory method (MP2) are selected for the study of the compounds used as corrosion inhibitors. Although HF does not take into account correlation and dispersion effects, it provides useful results for comparison with other methods, Moreover, for cases where HF provides results that are closer to those of sophisticated methods; further study at HF level is done because it is less computationally expensive. DFT takes into account a part of correlation and it has been reported to provide fairly good results for the description of various molecular properties such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), electronegativity (χ), ionization potential, *etc.*,⁷⁴.

B3LYP, a version of the DFT method that uses Becke's three parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP)⁷⁵, is used to carry out quantum calculations. Then, full geometry optimization together with the vibrational analysis of the optimized structures of the inhibitor is carried out at the B3LYP/6-31G (d,p) level of theory using G03W package. The quantum chemical parameters are calculated for molecules in neutral as well as in the protonated form for comparison. It is well known that the phenomenon of electrochemical corrosion occurs in liquid phase. As a result, it is necessary to include the effect of a solvent in the computational calculations. In the G03W program, SCRF methods (Self-consistent reaction field) are used to perform calculations in aqueous solution. These methods model the solvent as a continuum of uniform dielectric constant and the solute is placed in the cavity within it.

There is no doubt that the recent progress in DFT has provided a very useful tool for understanding the molecular properties and for describing the behaviour of atoms in molecules. DFT methods have become very popular in the last decade due to their accuracy and less computational time. Besides, the geometries of the compounds, an analysis of quantum chemical parameters provide valuable information on the reactivity and selectivity of the compounds. These informations are valuable in selecting a suitable compound or compounds (among compounds of similar structural features) to use as corrosion inhibitor as they inform which molecule has greater tendency to donate electrons, receive electrons or bind more strongly to the metal surface.

1.3 Corrosion monitoring techniques

Corrosion monitoring is the use of any method or methods which can deduce or predict the amount of corrosion actively occurring on any elements of a structure or entire equipment. Recording data and analyzing historical corrosion trends is also a key part of corrosion monitoring and can be effectively used to manage corrosion.

Aqueous corrosion is the most common form of corrosion. As corrosion mainly involves electron transfer, most modern methods of corrosion monitoring are based on analyzing the rate of electron transfer. Such methods employ direct and indirect techniques of measuring the rate of electron transfer.

1.3.1 Definition of corrosion monitoring

Corrosion monitoring may be defined as the systematic measurement of corrosion rate of materials with the objective of diagnosis and controlling corrosion.

Corrosion monitoring has been found to improve output, increase the life of the plant, improve the quality of the product and reduce capital and operating costs. Corrosion monitoring techniques have been divided into

- Physicochemical methods
- Electrochemical methods
- Non-destructive testing (NDT) methods

1.3.2 Physicochemical methods

Physicochemical methods include techniques such as weight loss and gasometric method.

i. Weight loss method (Coupon method)

The simplest and most accurate method of estimating the corrosion rate is weight loss analysis. A weight sample (coupon) of the metal or alloy under consideration is introduced into the corrosive environment, and later removed after a reasonable time interval. The coupon is then cleaned of all the corrosion products and is reweighed. The weight loss can also be determined by the amount of metal dissolved into the solution as corrosion product using instrumental techniques such as atomic absorption spectroscopy (AAS). The weight loss is converted to an average corrosion rate as follows:

$$\text{Corrosion rate (g cm}^{-2} \text{ h}^{-1}\text{)} = \frac{534 \times \text{Weight loss in g}}{\text{Density} \times \text{Area (cm}^2\text{)} \times \text{Time in hrs}} \longrightarrow 1.1$$

The technique requires no complex equipment or procedures, merely an appropriately shaped coupon, a carrier for the coupon and a reliable means of removing corrosion product without disruption of the metal substrate. The weight loss measurement is still the most widely used means of determining corrosion loss, despite being the oldest method currently in use. Weight loss determination has a number of attractive features that account for its sustained popularity.

- Simple – No sophisticated instrument is required to obtain a result.
- Direct – A direct measurement is obtained, with no theoretical assumptions or approximations.
- Versatile – It is applicable to all corrosive environments and gives information on all forms of corrosion.

The method is commonly used as a calibration standard for other means of corrosion monitoring, such as linear polarization and electrical resistance. The percentage inhibition efficiency (IE %) is calculated for the compound under investigation according to the following equation

$$\text{Inhibition efficiency (\%)} = \frac{W_b - W_i}{W_b} \times 100 \longrightarrow 1.2$$

where, W_b = weight loss without inhibitor; W_i = weight loss with inhibitor.

ii. Gasometric method

This method is reliable and accurate. The volume of gas (in acid corrosion) is measured directly at a constant temperature and atmospheric pressure and the metal loss

is calculated. **Nathan**⁷⁶ and **Hackerman**⁷⁷ and **Mathur et al.**,⁷⁸ have used this technique and designed gasometric apparatus operating under controlled conditions of temperature and pressure. The main advantage is that this cannot be applied to strong oxidizing medium.

1.3.3 Electrochemical methods

Electrochemical methods are used widely for testing inhibitors. The electrochemical corrosion is the result of current flow between anodic and cathodic areas on a metal surface. The effect of the inhibitor is to reduce this current.

Corrosion reactions are broadly classified as activation controlled and diffusion controlled reactions. The rates of corrosion process of metals under immersed conditions are obtained from the application of mixed potential theory of **Wagner** and **Traud**⁷⁹. For activation controlled reactions, the current and potential of the metal is related as,

$$i = i_{\text{corr}} \left[\frac{(2.3)(E - E_{\text{corr}})}{b_a} \exp \frac{(2.3)(E - E_{\text{corr}})}{b_c} \right] \longrightarrow 1.3$$

For diffusion controlled reactions, the rate expressions is

$$i = i_{\text{corr}} \left[\exp \frac{(2.3)(E - E_{\text{corr}})}{b_c} \right] - i_d \longrightarrow 1.4$$

Using these relationships, the kinetics of corrosion reactions, are determined by Tafel polarization and linear polarization methods.

i. Tafel polarization method

In this method E vs. log i data is obtained. At high over potentials, the rate expression is

$$i = i_{\text{corr}} \left[\exp \frac{(2.3)(E - E_{\text{corr}})}{b_c} \right] \longrightarrow 1.5$$

Taking log on both sides,

$$\log i = \log i_{\text{corr}} + \left[\frac{(E - E_{\text{corr}})}{b_c} \right] \longrightarrow 1.6$$

The plot of E vs. log i gives a straight line and the slope gives b_c and the intercept gives i_{corr} .

When an electrochemical method is used to measure the corrosion, the fundamental concept is based on the determination of the oxidation current at the

corrosion potential. The Tafel technique is commonly used to determine the corrosion rate of a material. By this method, a controlled-potential scan is typically applied to a metal sample. The range of this potential starts from E_{corr} and extends into either the anodic or the cathodic direction for a few hundred millivolts. When the resultant potential-current relationship is plotted on semi-log paper, it characteristically exhibits a linear region. This is true for both anodic and cathodic plots. The plot itself is known as a Tafel plot and the slope of the linear region in V/decade of current is known as the Tafel Constant (Fig. 1.2a). A projection of the linear region defines I_{corr} at the intersection with E_{corr} and thus the corrosion rate.

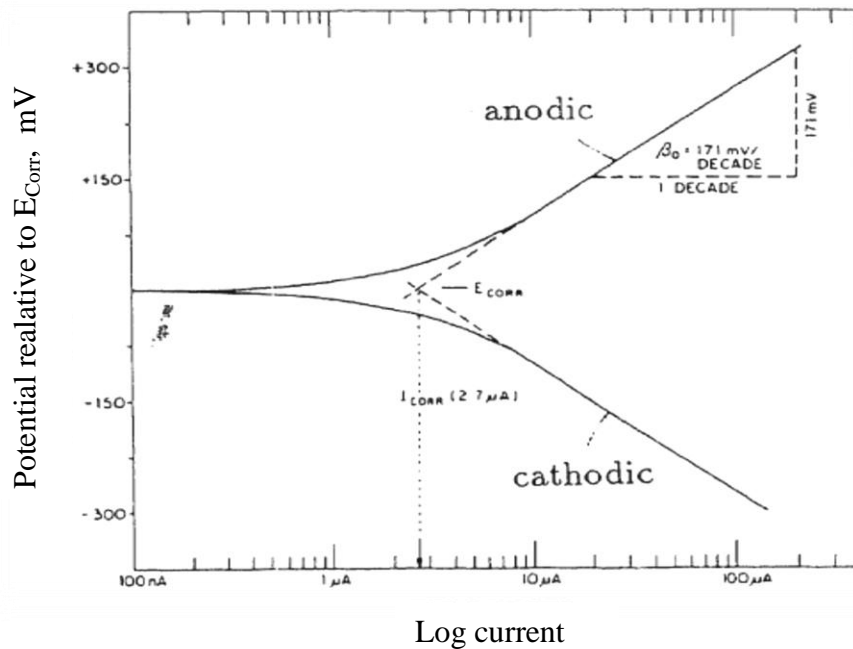


Fig. 1.2a

According to Faraday's Law

$$Q = \frac{nFW}{M} \longrightarrow 1.7$$

where, Q =Coulombs; n =number of electrons involved in the electrochemical reaction;

F =the Faraday, 96487 coulombs; W =weight of electroactive species

M =molecular weight of electroactive species.

By rearrangement and since equivalent weight (Eq.wt) = M/n and $Q = it$,

$$W/t = \frac{i(\text{Eq. wt})}{F} \longrightarrow 1.8$$

W/t is the corrosion rate (C.R.) in grams per second. It is convenient and customary to express corrosion rate as milli-inches per year (mpy). This unit gives an indication of penetration.

Dividing the above equation by the electrode area and the density gives

$$C. R(\text{cm sec}^{-1}) = \frac{i(\text{Eq. wt})}{dFA} \longrightarrow 1.9$$

After converting seconds to years, centimeters to milli-inches, and the Faraday (amp-sec/eq) to microamps, this becomes

$$C. R(\text{mpy}) = \frac{i(\text{Eq. wt}) \times 3.16 \times 10^6 \times 10^3}{dFA \times 2.5 \times 10^6} \longrightarrow 1.10$$

Expressing the term i/A as current density and combining all the constants gives

$$C. R(\text{mpy}) = \frac{0.13 I_{\text{corr}}(\text{Eq. wt})}{d} \longrightarrow 1.11$$

where, I_{corr} = Corrosion current density; Eq. wt. = Equivalent weight of the corroding species

d = Density of the corroding species, g/cm^3 . This equation is used to calculate the corrosion rate directly from I_{corr} .

The current is a measure of electron flow when a reduction or oxidation reaction occurs. The corrosion potential or open-circuit potential is the potential a metal will assume when placed in contact with a conductive medium. It is due to a chemical equilibrium established at the metal-solution interface.

The Tafel plot technique provides an extremely rapid means of determining the corrosion rate when compared with weight-loss measurements. The technique can be very advantageous for such studies as inhibitor evaluations, oxidizing effects and alloy comparisons. Experimentally, it can happen that the extrapolations of the anodic and cathodic linear Tafel regions do not intersect at E_{corr} . The true value of the corrosion current will then be subject to interpretation. If this occurs, the inference must be drawn that there is an error in the measurement, since the rate of oxidation must equal the rate of reduction at E_{corr} . In most cases, the error is probably in the anodic measurement. Since the metal specimen is corroding, the surface is changing and the mechanism of corrosion may be extremely complex. As a result, the measured Tafel plot could then reflect the

combination of several different Tafel slopes. If this behaviour is observed, it is probably safest to measure I_{corr} at the point where the cathodic Tafel extrapolation intersects E_{corr} .

ii. Linear polarization method

The electrochemical technique of polarization resistance is used to measure absolute corrosion rates, usually expressed in milli-inches per year (mpy). Polarization resistance measurements can be made very rapidly, usually in less than ten minutes. Excellent correlation can often be made between corrosion rates obtained by polarization resistance and conventional weight loss determination. Polarization resistance is also referred to as linear polarization.

Stern and Geary⁸⁰ have shown that there is a linear relationship between current and potential. On measuring the slope of E vs. i plot, the corrosion current for activation controlled anodic and cathodic reaction is obtained from the following relationship.

$$\frac{\Delta E}{\Delta i} = \frac{b_a b_c}{(2.3)(b_a + b_c)(I_{\text{corr}})} \longrightarrow 1.12$$

$\Delta E/\Delta i$ = slope of the polarization resistance plot, where ΔE is expressed in volts and Δi is expressed in μA . The slope has units of resistance, hence, polarization resistance. Even low corrosion rates can be followed with high accuracy. But this method requires conducting liquid as a medium.

b_a and b_c = anodic and cathodic Tafel constants. These constants have units of volts/decade of current. I_{corr} = corrosion current in μA . Rearranging equation 1.12

$$I_{\text{corr}} = \frac{b_a b_c}{(2.3)(b_a + b_c)} \frac{\Delta i}{\Delta E} \longrightarrow 1.13$$

The corrosion current can be related directly to the corrosion rate through the following equation.

$$\text{C. R (mpy)} = \frac{0.13 I_{\text{corr}}(\text{Eq. wt})}{d} \longrightarrow 1.14$$

where, Eq. wt = equivalent weight of the corroding species (g); d = density of the corroding species (g/cm^3); I_{corr} = corrosion current density ($\mu\text{A}/\text{cm}^2$)

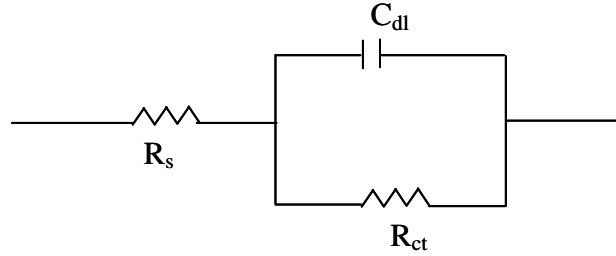
iii. A.C-Impedance method

Among the various AC techniques, the method based on faradic impedance is widely used due to the main advantage that the double layer capacitance and charge

transfer resistance can be determined. The term resistance and impedance both imply a restriction to the current flow. When dealing with DC, only resistors produce this effect. But in the case of AC both inductors and capacitors influence electron flow. The equivalent circuit of a corroding metal⁸¹ is represented as

$$I_{\text{corr}} = \frac{b_a b_c}{(2.3)(b_a + b_c)R_{\text{ct}}} \longrightarrow 1.15$$

where, b_a and b_c are Tafel slopes, R_{ct} is obtained from the impedance plots.



where, R_s = solution resistance, C_{dl} = double layer capacitance and R_{ct} = charge transfer resistance.

The cell impedance is resolved into two parts *i.e.*, real part $z' = |z| \cos$ and imaginary part $z'' = |z| \sin$.

The impedance z can be shown to be,

$$z = z' - jz'' \longrightarrow 1.16$$

where,

$$Z' = R_s + \frac{R_{\text{ct}}}{1 + \omega^2 C_{dl}^2 R_{\text{ct}}^2} \longrightarrow 1.17$$

$$Z'' = \frac{\omega C_{dl} R_{\text{ct}}^2}{1 + \omega^2 C_{dl}^2 R_{\text{ct}}^2} \longrightarrow 1.18$$

From equation 1.16 the plot of z' vs. z'' for various frequencies results in a semicircle which cuts the real axis at higher and lower frequencies (Fig. 1.2b). At higher frequency end, the intercept corresponds to R_s and at lower frequency end, the intercept correspondsto $R_s + R_{\text{ct}}$. The difference between these two values gives R_{ct} and from the values corrosion rate can be calculated. The double layer capacitance is obtained from the frequency at which z'' is maximum.

$$\omega(z'' \text{max}) = \frac{1}{C_{dl} \times R_{ct}} \longrightarrow 1.19$$

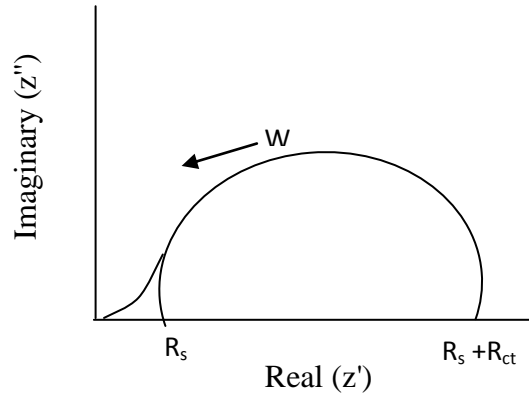


Fig. 1.2b

Inhibition efficiency is calculated using the formula

$$I.E (\%) = \frac{R_{ct}^* - R_{ct}}{R_{ct}^*} \times 100 \longrightarrow 1.20$$

where,

R_{ct}^* - charge transfer resistance with inhibitor and R_{ct} - charge transfer resistance without inhibitor.

Other methods such as coulostatic, Faradaic distortion and Faradaic rectification methods have been developed for the measurement of corrosion rates.

Advantages

- AC impedance involves measurement of both capacitance and charge transfer resistance, hence this technique is more valuable.
- This technique uses amplitude in the range of 5 - 10 mV peak to peak. Hence the perturbation is minimum and reduces the errors caused by the measurement.
- This method does not involve potential scan and therefore can be applied to low conductivity media. The impedance of the corroding system at various frequencies can be measured using lock in amplifiers for high frequencies and fast Fourier transform⁸² technique for low frequencies.

1.3.4 Non-destructive testing (NDT) methods

NDT methods are widely used for detecting the defects and damages taking place on the components during the service as well as after or before the service. Some important methods are described below:

i. Visual examination method

Examination of the internal or external surface of a component with naked eye or magnifying glass gives an indication of corrosion damage (general or localized) and extent of surface damage could be assessed. In addition to magnifying glass, an instrument called endoscope or boroscope can be used in the visual examination. These instruments are used to allow visual examination of the interior of hollow components which are otherwise inaccessible to the eye. The image of the investigating spot is transferred from objective to eye piece by a lens system in the endoscope and a source of light is also provided along with, for illuminating the spot. For the inspection of curved hollow components a flexible endoscope is used. The flexible endoscope employs glass fiber optics for transmitting the light and image. A measuring system can also be attached to the endoscope to assess the depth of the corroded region.

ii. Dye penetrant method

Dye-penetrant tests are used to detect cracks and pores which originate in the surface or, are closely associated with it. In these tests, liquids of low surface tension are used to penetrate the defects and later they are sucked out with an absorbent developer applied to the surface resulting in the colouring of the area. Very fine cracks and pores can be detected by this technique. Components made from materials which are not attacked or coloured by the testing chemicals can be examined by this method. The surface of the components which have a porous structure such as sintered metal or sprayed metal coatings cannot be examined by this method.

iii. Magnetic stray flux method

This technique is particularly suited for the detection of defects in or immediately below the surface of ferromagnetic materials. Due to different magnetic permeability of ferromagnetic materials compared with air or non magnetic inclusions at boundaries in

the materials magnetic stray, flux is produced on magnetization. If the cross section through which the magnetic lines of force are flowing changes, suddenly, then a part of the magnetic lines of force comes out of the material, including stray fluxes. If the cracks lie below the surface, the action of the stray flux is smaller. If the cracks lie parallel to the lines of force, no stray flux arises. The method consists of first magnetization of the material and then detection of the stray flux by applying magnetic powder above the surface. Magnetic probes are also used to detect the stray fluxes above the crack.

iv. Potential drop method

This method is utilized for the measurement of depth of the crack which has been detected by visual methods. If an electric current is passed through a work piece, a constant potential (voltage) drop is measurable between two probes on the surface at a constant distance apart, provided the electrical resistance of the work piece remains constant and there is no crack in the region between the two probes. If however, there is a crack between the two probes, the current has to travel a longer path, depending on the crack, which leads to a greater voltage drop compared with the crack-free case. The potential difference compared with the crack-free state is a direct measure of the crack depth. Alternating current (ac) or direct current (dc) can be used for detection and measurement of defects.

v. Eddy current method

When an alternating magnetic field produced by a test coil acts on a work piece with a certain electrical conductivity and magnetic permeability, eddy currents are induced in the work piece. Those eddy currents cause an alternating magnetic field, which by Lenz's law, is in the opposite direction to the original field. Local changes in the material influence the secondary magnetic field induced by the eddy currents. This effect is used in eddy current method to discover defects in the material resulting from cracks or by localized corrosion attack. Eddy current testing is particularly suitable for indicating inhomogeneities or corrosion damage in heat exchanger tubes. Examination using eddy current is carried out by using a suitable travelling probe. In regular monitoring and maintenance procedures, the results of such testing are stored in a data

file so that, on subsequent testing, critical changes in the components can be quickly recognized.

vi. Ultrasonic method

In the ultrasonic method mechanical vibrations having frequency of above 20 kHz (which is the upper limit for detection by human ear) are used for detecting the defects in the material. The usual working frequency for material testing lies in the region of 100 kHz to 20 MHz. Piezoelectric effect is used in the test heads of the probe to produce and receive ultrasonic waves. A coupling medium (which is usually oil) has to be used to transmit the ultrasonic waves to the test piece. The velocity of propagation of the waves is a material constant. When the waves encounter a boundary between two materials or different transmission velocities they are reflected and refracted. Flaws such as cracks, shrinkage cavities, or other inhomogeneities are detected since the ultrasonic waves are reflected at these flaws as well as at boundaries of the work piece. For optimal application of ultrasonic testing, perpendicular sounding technique is used in which the defect is at right angle to the incident waves. For most applications, the oblique method in which incident waves, waves at 35° to 80° are generally used. Ultrasonic testing can also be used for measurements of wall thickness of components. Structural components which are subjected to corrosion or wear can be regularly examined for changes in wall thickness with ultrasonics. Portable instruments for measuring wall thickness are commercially available.

vii. Radiographic methods

In these methods, x-rays or gamma -rays are used to view the interior of the material and to detect the hidden defects. The method can be used to detect corrosion cracks/ defects in components while in service. This is also used for the detection of blockages and deposits and monitoring components exposed to corrosion or abrasive wear for reduction in wall thickness. Due to the very short wave length of 10^7 and 10^{10} cm, x-rays, gamma-rays can penetrate the solid materials. The radiation is attenuated in passing through the material. This is a function of the density and thickness of the irradiated object. Less radiation absorption occurs at areas of defects or regions of smaller wall thickness. The photographic film placed behind the irradiated object receives

different amounts of radiation owing to the different radiation absorption at in homogeneities or varying wall thicknesses. Depending upon the nature of the problem and also on the accessibility of the components, either x-rays or gamma-rays can be selected.

A specific type of a particulate radiation called neutrons can also be used to form a radiographic image of a test piece. This form of NDT method is known as neutron radiography. In neutron radiography, interaction of neutron with the nuclei of the atoms in specimens is used rather than interaction with orbital electrons as in the case of conventional radiography. Neutron radiography is advantageous in imaging low atomic number materials present in high atomic number matrices. For example, it is possible to detect certain isotopes of hydrogen radiographically. The high attenuation of hydrogen offers many possibilities of application including inspection of component assemblies for detection of adhesion, explosives, lubricants, water, hydrides, corrosion plastics or numbers. Corrosion of zirconium alloy components in water in nuclear reactor core can be easily detected by this technique as the corrosion is associated with hydride formation.

viii. Acoustic emission detection method

Acoustic emission is a high frequency stress wave generated by rapid release of strain energy that occurs within a material during crack growth, oxide scale cracking, plastic deformation, phase transformation, *etc.*, This energy may originate from a stored elastic energy as in crack propagation or from stored chemical free energy as in the case of phase transformation. Acoustic emission inspection detects and analyzes minute acoustic emission signal generated by discontinuities material under stress. Proper analysis of these signals can provide information concerning initiation and location of defects and cracks. Basically there are two types of acoustic emissions: continuous and burst. The wave form of continuous type emission is similar to Gaussian random noise, but the amplitude varies with acoustic emission activity. In metals, the form of emission is associated with the dislocation movement in the grains. Burst type emissions is of short duration pulse (10 μ s to a few ms in length) and are associated with discrete release of strain twinning, micro yielding and development of micro and macro cracks. Burst type emission has greater amplitude than the continuous type. Detection of acoustic emission from components can be used for: continuous surveillance of pressure vessels for location

and detection of active flaws; detection of incipient fatigue fracture; determination of onset of localized corrosion (particularly stress corrosion cracking and hydrogen embrittlement).

ix. Photo electrochemical laser imaging method

This is a recent technique in which the principles of photo-electrochemistry have been utilized for characterization of surface films. The technique is sensitive to change in thickness, composition and structure of passive film. In this technique, a laser beam of size about 10 μm is scanned over the surface and response of photo current is measured at each point. Since the photo current is highly dependent on surface properties, a 3-dimensional image (photo electrochemical) can be constructed. This technique is considered to be useful in the insitu studies of corroding and non-corroding surfaces.

x. Infrared imaging method (thermography)

This is also a new technique and is based on the measurement of heat distribution across the surface of the object. This is essentially mapping of ac temperature distribution on the surface of the object in a non-contact manner. Thermography makes use of infrared (IR) spectral band. The system basically consists of an IR scanner, monitor and control unit. This technique can be used for detection of corrosion on the inner surface of tubes. By suitably monitoring the thermal distribution, it is possible to identify the corroded areas. This detection depends on parameters like emissivity variation on the surface of the tube, presence of adjacent heat sources, temperature differential inside and outside the tube and material wall thickness and curvatures.

1.4 Introduction to chalcones

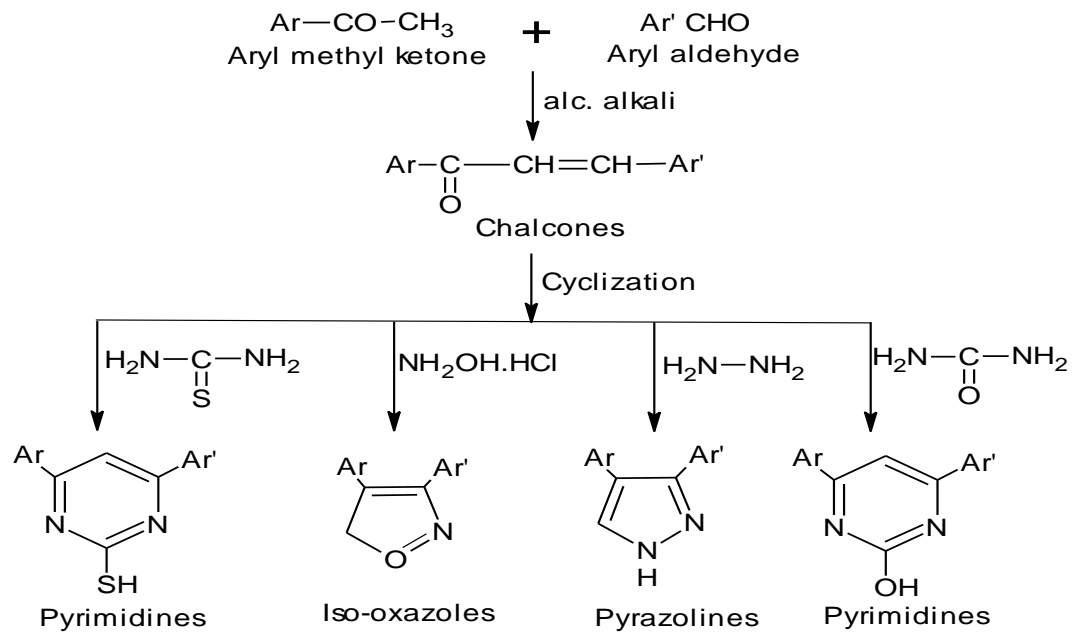
The chemistry of chalcones has generated intensive scientific studies throughout the world. Especially interest has been focused on the synthesis and biodynamic activities of chalcones. The name chalcones was given by **Kostanecki** and **Tambor**⁸³. These compounds are also known as benzalacetophenone or benzylidene acetophenone. In chalcones, two aromatic rings are linked by an aliphatic three carbon chain. Chalcone bears a very good synthon so that variety of novel heterocycles with good pharmaceutical profile can be designed.

Chalcones belong to a class of α , β -unsaturated ketone containing the reactive keto-ethylenic group $-\text{CO}-\text{CH}=\text{CH}-$. These are coloured compounds because of the presence of the chromophore $-\text{CO}-\text{CH}=\text{CH}-$, which depends in the presence of other auxochromes and find vast applications in pharmaceuticals, agriculture and industry. Moreover, a large number of chalcones have been reported and found to possess significant activity against inhibitors. In agriculture certain chalcones are used to destroy phytopathogenic organisms, whereas in industry they are used in controlling corrosion of steel⁸⁴.

Recent reports show increased attention to chalcone compounds as corrosion inhibitors in especially acidic environments for various metals like steel and aluminium⁸⁵⁻⁸⁹. The greatest advantage of many chalcone compounds is that, they can be conveniently synthesized from relatively cheap raw material, readily soluble in acid solution and low toxicity. These compounds, in general, are adsorbed on the metal surface blocking the active corrosion sites. A few research reports reveal that the inhibition efficiency of chalcones is much higher than that of corresponding arylmethylketone and aryl aldehyde. This may be due to the presence of conjugated double bonds and a completely delocalized π -electron system on both aromatic rings in the molecule.

Different methods are available for the preparation of chalcones⁹⁰⁻⁹². The most convenient method is the Claisen-Schmidt condensation of equimolar quantities of arylmethylketone with aryl aldehyde in the presence of alcoholic alkali⁹³. Chalcones are used to synthesize several derivatives like isoxazoles, pyrazolines and pyrimidines having different heterocyclic ring systems as shown in **Scheme 1.1**.

The various applications of chalcone and its derivatives in various fields motivated us to synthesize some chalcone derivatives and evaluate their corrosion inhibition property against mild steel in acid medium.



Scheme 1.1

1.5 REFERENCES

1. J.O.M. Bockris, A.K.N. Reddy, Modern electrochemistry, Plenum press, New York, **2** (1977) 1267.
2. O. Riggs Jr., Theoretical aspects of corrosion inhibitors and inhibition, NACE, Houston, Texas (1974).
3. M.G. Fontana, N.D. Greene, Corrosion Engineering, McGraw Hill, New York (1978).
4. G. Wranglen, An introduction to corrosion and protection of metals, Chapman and Hall, New York (1985).
5. A.C. Bacquerel, Annales, des chimie et des Physique., **35** (1827) 113.
6. A. Dela Rive, Annales, des chimie et des Physique., **43** (1830) 425.
7. Faraday's Diary, Vol. I -VII, 1820-1822, London-G. Bell and sons, 1932-1936.
8. H. Davy, Journal of Nicholson's., **4** (1800) 337 and Philos. Trans. R. Soc., London **116** (1826) 333.
9. Richard Adie, Philos. Mag., **31** (1847) 351.
10. M. Stern, A.L. Geary, J. Electrochem. Soc., **104** (1957) 56.
11. M. Stern, Corros., **14** (1958) 440.
12. L. Gaiser, K.E. Heusler, Electrochim. Acta., **15** (1970) 161.
13. K.E. Heusler, L. Gaiser, J. Electrochem. Soc., **117** (1970) 762.
14. P. Robert, Frankenthal, Japan Seminar, March 10-12, (1975) 10.
15. W.J. Lorenz, F. Hilbert, Y. Miyoshi, G. Eichkon, Proceedings, 5th ICMC, Tokyo, Japan, May (1972) 74.
16. J.A. Thuiller, Mater. Performance., **15** (1976) 9.
17. Blackburn, Mater. Performance., **16** (1977) 24.
18. R.W. Revie, B.G. Baker, J.O.M. Bockris, 6th ICMC, Sydney, Australia, Dec 3-9, (1975) 1.
19. S. Rajendran, B.V. Apparao, N. Palaniswamy, Bull. Electrochem., **17** (2001) 171.
20. T. Kowalik, H.J.P. Adler, A. Plaggead, M. Stratmann, Macromol. Chem. Phys., **201** (2000) 2064.
21. M. Nicola, I. Maior, Revista De Chimie., **53** (2002) 575.

22. J.M. Yeh, C.L. Chen, Y.C. Chen, C.Y. Ma, K.M. Lee, Y. Wei, S.X. Li, *Polym. J.*, **43** (2002) 2729.
23. S. Sharma, R.S. Chaudhary, *Bull. Electrochem.*, **16** (2000) 267.
24. S.A.M. Razaey, *Appl. Surf. Sci.*, **157** (2000) 199.
25. R. Vera, H. Romera, Y.E. Ahumada, *J. Chin. Chem. Soc.*, **48** (2003) 350.
26. V.B. Singh, A. Gupta, *Indian J. Chem. Technol.*, **12** (2005) 347.
27. M.A. Nigahed, M. Abd-El-Raouf, A.M. Al-Sabagh, H.M. Abd-El-bary, *Electrochim. Acta.*, **50** (2005) 4683.
28. A.J. Amalraj, M. Sundaravadivelu, A.P.P. Regis, S. Rajendran, *Bull. Electrochem.*, **17** (2001) 179.
29. S.T. Selvi, V. Raman, N. Rajendran, *J. Appl. Electrochem.*, **33** (2003) 1175.
30. R. Ravichandran, S. Nanjundan, N. Rajendran, *Appl. Surf. Sci.*, **236** (2004) 241.
31. K.D. Demadis, S.D. Katarachia, M. Koutmos, *Inorg. Chem. Commun.*, **8** (2005) 254.
32. A.A. Valeria, A.M. Chiorcea Paquim, A. Cacaleiro, M.A. ChristopherBrett, *Corros. Sci.*, **47** (2005) 2871.
33. R.J. Holness, G. Williams, D.A. Worsley, H.N. Ac Murray, *J. Electrochem. Soc.*, **152** (2005) 373.
34. M.W. Kendig, E.M. Meyer, G. Lindberg, F. Mansfeld, *Corros. Sci.*, **23** (1983) 1007.
35. R.A. Adey, S.M. Niku, C.A. Brebbia, *Ocean Res.*, **8** (1986) 209.
36. G. Rose, *Anti-Corros Method M.*, **28** (1981) 4.
37. www.corrosion-doctors.org/atmcorrosion/mechanil.htm.
38. www.corrosion_doctors.org/corrosion-history/types.htm, by: McKa & Worthington, (1936).
39. www.corrosion_doctors.org/atm_corros/mechanil.htm
40. http://www.counteractrust.com/type_of_corrosion.htm
41. <http://www.corrosioncost.com/>
42. www.corrosion-doctors.org/microbial/frames.htm
43. L.L. Shrier, *Corros.*, Vol.11, George Newness Ltd., London (1984).
44. H.H. Uhlig, *Corrosion and corrosion control*, John Wiley and Sons, Inc., (1971).
45. J.A. Von Fraunhofer, J. Boxal., *Protective paint coatings for metals*, Partcull publishers survey, Redhill, U.K. (1976).

46. G. TrabANELLI, V. Carassiti, *Advances in Corrosion Science and Technology* (M. G. Fontana, R.W. Staehle, eds.), Vol. 1, Plenum, New York, (1970) 147.
47. L.L. Shreir, *Corrosion*, Vol. 2, Newnes-Butterworths, London, (1976) 183.
48. I. L. Rosenfeld, *Corrosion Inhibitors*, McGraw-Hill, New York, (1981) 110.
49. C.C. Nathan, *Corrosion Inhibitors*, NACE, Houston, Texas, (1973).
50. R.M. Hudson, Q.L. Loony, G.J. Warning, *Br. Corros. J.*, **2** (1967) 81.
51. R.M. Hudson, G.J. Warning, *Corros. Sci.*, **10** (1970) 121.
52. R.L. Yuechhenko, S.V. Ivashchenko, T.N. Pilipenko, I.S. Pogrebova, *Russ. J. Appl. Chem.*, **78** (2005) 511.
53. C.M.V.B. Almedia, B.F. Giannetti, *Mater. Chem. Phys.*, **69** (2001) 261.
54. E.E.F. Elsherbini, S.M.A. Wahaab, M. Deyab, *Mater. Chem.*, **8** (2005).
55. S. Muller, S. Ritzvi, K. Yokose, W. Yang, M. Jackel, *Corrosion Inhibitors*, SCUP Home, October (2009).
56. R.I. Lerry, *Corros.*, **34** (1978) 98.
57. W. Cerna, *Proceedings of the Seventh Annual Water Conference*, Pittsburgh, PA (1947).
58. H. Baker, W. Zisman, *Ind. Eng. Chem.* **40** (1948) 2338.
59. E. Stroud, W. Vernon, *J. Appl. Chem.*, **2** (1952) 178.
60. I. Putilova, S. Balezin, V. Barannik, *Metallic corrosion inhibitors*, G. Ryback, translator, Pergamon Press, New York, (1960) 63 .
61. L.I. Antropov, *First international congress of metallic corrosion*, Butter worths, London (1962) 147.
62. T.P. Hoar, R.P. Khera, *Proceedings of the 1st European symposium on corrosion inhibitors*, Ann. Univ. Ferrara., N. S., Sez.V., Suppl.3 (1961) 73.
63. L.L. Shreir, *Corrosion*, Vol 1 & 2, Newnes-Butterworths, Boston (1976).
64. U.R. Evans, *Zeitschrift fier Elektrochemie.*, **62** (1958) 619.
65. J.N. Putilova, S.A. Belezin, V.P. Barannik, “*Metallic Corrosion Inhibitors*”, Pergamon Press, London (1960).
66. C. Lee, W. Yang, R. G. Parr, *Phys. Rev.*, **B37** (1988) 785.
67. T.P. Hoar, R.D. Holiday, *J. Appl. Chem.*, **3** (1951) 502.
68. F. Mansfeld, *Corrosion Mechanisms*, Marcel Dekker, Inc. New York, 1987.

69. L.I. Antropov, I.S. Pogrebova, G.I. Dremova, *Prot. Met.*, **7** (1971) 1.
70. G. Gece, *Corros. Sci.*, **50** (2008) 298.
71. G. Bereket, C. Ogretir, A.Yurt, *J. Mol. Struct. (THEOCHEM)* **571**, (2001), 13.
72. M.K. Awad, *J. Electroanal. Chem.*, **567** (2004) 219.
73. M.K. Awad, F.M. Mahgoub, M.M. El-iskandrani, *J. Mol. Struct.*, (THEOCHEM) **531** (2000) 105.
74. I.B. Obot, N.O. Obi-Egbedi, *Corros. Sci.*, **52** (2010) 657.
75. A.K. Chandra, M.T. Nguyen, *Int. J. Mol. Sci.*, **3** (2002) 310.
76. C.C. Nathan, *Corros.*, **9** (1959) 199.
77. N. Hackerman, K. Amarakki, *J. Electrochem. Soc.*, **15** (1982) 1007.
78. R.B. Mathur, T. Vasudevan, *Corros.*, **38** (1982) 171.
79. C. Wagner, W. Traud, *Zeitschriftfur, Electrochemie., ZEELA*, **44** (1938) 391.
80. M. Stern, A.L. Geary, *J. Electrochem. Soc.*, **104** (1957) 56.
81. J. Epel Boin, H. Takenouti, *J. Electrochem. Soc.*, **118** (1971) 1282.
82. K. Kanno, M. Suzuki, Y. Sato, *J. Electrochem. Soc.*, **125** (1978) 1389.
83. S.V. Kostanecki, Tambor, *J. Chem Ber.*, **32** (1899) 1921.
84. E.T. Oganesyans, A.S. Saraf, *Khim. Far. Zh.*, **18** (1991) 22.
85. A.S. Fouda, K. shalabi, N.H. Mohamed, *Int. J. Inn. Res. Sci. Eng. Tech.*, **3** (2014) 9861.
86. A.S. Fouda, K. Shalabi, G.Y. Elewady, H.F. Merayyed, *Int.J. Electrochem.*, **9** (2014) 7038.
87. Pooja Singh, M.A. Quarishi, E.E. Ebenso, Chandra Bhan Verma, *Int. J. Electrochem.*, **9** (2014) 7446.
88. B.A. Bhat, K.L. Dhar, A.K. Saxena, M. Shanmugavel, *Bioorg. Med. Chem.*, **15** (2005) 177.
89. L.E. Michael, M.S. David, S.S. Prasad, *J. Med. Chem.*, **33** (1990) 1948.
90. H. Rupe, D. Wassserzug, *J. Chem. Ber.*, **34** (1901) 3527.
91. S.A. Hermes, *Chem. Ber.*, **70** (1969) 96422h.
92. D.S. Breslow, C.R. Houser, *Chem. Ber.*, **62** (1940) 2385.
93. K. Kazauki, K. Hitayama, S. Yokomor, T. Soki, *Chem Abstr.*, **85** (1976) 591.