CHAPTER - 1

INTRODUCTION

1.1 DEFINITION AND IMPORTANCE OF CORROSION

Corrosion is known commonly as rust, an undesirable phenomenon which destroys the luster and beauty of objects and shortens their life. The corrosion since ancient times has affected not only the quality of daily lives of people, but also their technical progress. Corrosion is the disintegration of metal through an unintentional chemical or electrochemical action, starting at its surface. All metals exhibit a tendency to get oxidized, some more easily than others. The driving force that causes metals to corrode is a natural consequence of their temporary existence in metallic form. To reach this metallic state from their occurrence in nature in the form of various chemical compounds (ores), it is necessary for them to absorb and store up for later return by corrosion, the energy required to release the metals from their original compounds [1-3].

The importance of corrosion was recognized in the sixties when it was realized that damage was being caused to the economics of the industrialized nation, resources are being wasted by anti-metallurgical process and useful life of manufactured goods were being reduced [4]. The corrosion, an inherently difficult phenomenon to understand, is a widely researched subject as it involved issues pertaining to the human life and safety, huge environmental and economic impact, and conservation of materials. The effects of corrosion in our daily lives are both direct, in that corrosion affects the useful service lives of our possessions, and indirect, in that producers and
suppliers of goods and services incur corrosion costs, which they pass on to consumers. The environmental impact and economic losses are the prime motive for much of the current researches in the field of corrosion. The economic losses due to corrosion are divided into direct losses and indirect losses [5]. Direct losses are those losses associated with the direct replacement of corroded industrial equipment, machinery or their components such as pipelines, condenser tubes, and replacement of various parts of equipments and plants. Perhaps most dangerous of all is corrosion that occurs in major industrial plants, such as electrical power plants or chemical processing plants. Plant shutdowns can and do occur as a result of corrosion. Indirect losses are more difficult to assess and contains plant shutdown, loss of efficiency, loss of products as well as contamination of products and over design.

1.2 COST OF CORROSION

Corrosion has a huge economic and environmental impact on virtually all facets of the world’s infrastructure, from highways, bridges and buildings, to oil and gas, chemical processing, and water and wastewater systems. Enormous losses occur due to corrosion every year in all countries. The losses due to corrosion vary from country to country, depending upon the climatic conditions prevailing in the country. Losses sustained by industry, by the military and are municipalities’ amount to many billions of dollars annually.

Corrosion is recognized as one of the most serious problem in our modern societies and the resulting losses each year are in the billions of dollars. The cost of corrosion studies have been undertaken by several countries including, the United States, the United Kingdom, Japan, Australia, Kuwait, Germany, Finland, Sweden,
India and China. The studies have ranged from formal and extensive efforts to informal and modest efforts. The common finding of these studies was that the annual corrosion costs ranged from approximately 3 to 5 percent of the Gross National product (GNP) of each nation [6]

A recent report describes the annual direct and indirect costs of metallic corrosion in the United States [7, 8]. The total direct cost of corrosion is estimated around $276 billion per year, which is 3.1 percent of the 1998 U.S. gross domestic product (GDP). This cost was determined by analysing 26 industrial sectors, in which corrosion is known to exist, and extrapolating the results for a nationwide estimate.

The indirect cost of corrosion was conservatively estimated to be equal to the direct cost (i.e., total direct cost plus indirect cost is six percent of the GDP). Evidence of the large indirect corrosion costs are lost time, and thus lost productivity because of outages, delays, failures and litigation.

Some details of corrosion losses are mentioned below.

- The corrosion cost of gas and liquid transmission pipe lines in USA exceeds seven billion US dollars. The figure for the major oil producing countries in the gulf region are not known, however the costs are expected to be very high because of highly corrosive environment in this region.

- The corrosion free life of automobiles in the coastal region of Arabian Gulf is about six months only.
• Nearly 95% of concrete damages in the Arabian gulf coastal region is caused by reinforcement corrosion and consequent spelling of concrete.

• It is estimated that 10% of all aircraft maintenance in USA is spent on corrosion remediation.

• Major annual corrosion losses to the tune of £350 million in transport €280 million in marine £250 million in building and construction and €180 million in oil and chemical industries, have been reported in UK.

• About $120 billion is spent on maintenance of ageing and deteriorating infrastructure in USA.

• Automotive corrosion costs about 23.4 billion US dollars annually in USA.

• Every new born baby in the world now has an annual corrosion debt of $40.

• There is a huge loss has observed in heating and cooling water system pipelines, Thermal and nuclear power plants, heat transfer equipment.

It is observed that the corrosion exists where and there is no industry or house it does not penetrate and it demands a state of readiness for engineers and scientists to combat this problem.

**Cost of Corrosion in India**

Corrosion is inevitable in any large industrialized society and India is not an exception. The cost of corrosion in India is estimated to be around $364 billion as of
2004 [9]. This does not include the indirect cost and other consequential damages. If this is taken into account, it would go up several times from the present level of 3.1% of GNP [10].

1.3 CONSEQUENCES OF CORROSION

The corrosion are often more serious than the simple loss of a metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. The harmful effects of corrosion can be summarized as follows:

- Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown.
- Loss of time in availability of profile-making industrial equipment.
- Reduced value of goods due to deterioration of appearance.
- Contamination of fluids in vessels and pipes.
- Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings.
- Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
- Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products
- Added complexity in the designing of equipment to withstand certain amount of corrosion and to allow corroded components to be conveniently replaced.
Metal, energy, water and human efforts are large investments and they are lost due to corrosion effects and also in rebuilding the corroded equipments.

1.4 CLASSIFICATION OF CORROSION

Corrosion has been classified in many different ways. In one way it is classified into low-temperature and high-temperature corrosion. In another way it is classified into wet corrosion and dry corrosion. The convenient way of classification is in which it manifests itself. In this way, it is classified into eight different forms. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is required. The identification of the different forms of corrosion is very much helpful in understanding the intensity of problem and finding the solutions.

(i) Uniform or General attack

Uniform or General attack is the most common form of corrosion. It is characterized by a chemical or electrochemical reaction in which corrosion takes place uniformly over the entire exposed surface area of the material. This type of corrosion is not too great concern from the technical standpoint because life of equipment can be accurately estimated using simple tests like immersion of specimen in the fluid of our interest. This form of corrosion can be prevented or reduced by proper selection of materials, protective coatings, use of inhibitors and applying cathodic protection to the affected equipment.
(ii) **Galvanic or Two-metal corrosion**

Two dissimilar metals or alloys are exposed to an electrolyte (corrosive or conductive) a potential difference is developed between these two. If these two are electrically coupled or placed in contact, this potential difference causes an electron flow from the more active metal to less active metal. The more active metal undergoes corrosion (anodic) and the less active metal is protected from the corrosion (cathodic). Because of the electric current and two dissimilar metals are involved, this corrosion is called as Galvanic or Two-metal corrosion. Galvanic corrosion has several applications e.g.: Dry cells, cathodic protection etc., [11]. Galvanic corrosion can be minimized by 1. Coupling of dissimilar metals which are close together in galvanic series. 2. Use anode area as large as possible. 3. Electrically insulate dissimilar metals from each other. 4. Apply protective coatings on the metal surface. 5. Add inhibitors to reduce the aggressiveness of the environment. 6. Proper designing of metal article. 7. Electrically connect a third metal that is anodic to both metals in the galvanic contact.

(iii) **Crevice corrosion**

Crevice corrosion is an intensive localized corrosion occurs within crevices and other shielded area on metal surfaces exposed to a corrosive environment. Crevice corrosion is more likely to occur in holes, gasket surfaces, lap joints, surface deposits and crevices under bolt and rivet heads that retain solutions and take longer time to dry out. This form of corrosion is sometimes called as deposit or gasket corrosion. The rate of crevice corrosion is based on some important factors such as lack of oxygen, changes in acidity, inadequate anodic treatment and decrease or
depletion of an inhibitor. Crevice corrosion can be prevented by the use of high resistance alloy, use of welded joints instead of riveted or bolted joints, maintaining clean surfaces, use of solid non-absorbent gaskets and frequent removal of accumulated deposits and designing containment vessels to avoid stagnant areas and ensure complete drainage.

(iv) **Pitting corrosion**

Pitting corrosion is extremely localized attack that results from inhomogeneities in metal due to inclusions, coring and distorted zones which set up difference of potential at localized spots to cause deep isolated hole or pits. These holes may be smaller or larger in diameter, but in most cases they are relatively small and because of their smaller size and are often covered by corrosion products, they are not easily identified. It is very much difficult to measure quantitatively and compare the extent of pitting because of the varying depths and number of pits that may occur on identical conditions. Pitting is an autocatalytic process. This process is self-stimulating and self-propagating. This corrosion processes usually requires an initiation period. The period ranges from months to years depending on both the specific metal and the corrosive. Depth of pitting is some time expressed as pitting factor, which is the ratio of the depth of deepest pit to the average penetration as calculated from weight loss. This form of corrosion can be prevented by removing deposits of solids from exposed metal surface, by selection of material, by using corrosion inhibitors suitable for the environment and by preventing formation of oxygen concentration cell [12].
(v)  **Intergranular corrosion**

Intergranular corrosion is a localized attack at and adjacent to the grain boundaries with relatively little corrosion of the grains. In this corrosion alloy disintegrates and loss its strength. Intergranular corrosion is a non-uniform corrosion. It can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements or depletion of one of these elements in the grain boundaries. The well-known example is the failure of 18-8 stainless steel due to IGC [13]. When 18-8 stainless steel is heated to 950 - 1450°F, depletion of chromium takes place by metallurgical reaction with carbon, this chromium carbide being insoluble and precipitates out of the solid solution along the grain boundaries. When carbon content is higher than 0.02% then the resultant structure is susceptible to intergranular attack. Stainless steel may be protected from intergranular corrosion by the following measures: (1) subjecting the sensitized material to a high-temperature heat treatment in which all chromium carbide particles are re-dissolved,(2) lowering the carbon content below 0.02 % so that carbide formation is inimal, and (3) alloying the stainless steel with another metal such as niobium or titanium, which has a greater tendency to form carbides than does chromium so that the chromium remains in solid solution.

(vi)  **Selective leaching or Parting**

Selective leaching is generally found in solid solution alloys. It occurs when one element or constituent is completely removed by corrosion processes. Selective leaching is also called as de-alloying and parting. The most common examples are dezincification of brass and graphitization. Dezincification of brass is the selective
leaching of zinc from yellow brass leaving porous mass of copper which may be red colour or copper colour. Graphtitization is the selective leaching of iron from grey cast iron leaving weak, porous and inert graphite. It is a slow process and occurs in relatively mixed corrosive environments such as soil or water. Selective leaching also occur with other alloy systems in which aluminium, cobalt, chromium and other elements are vulnerable to preferential removal. Selective leaching reduces the mechanical properties of the alloy. The colour and appearance of the material is also changed. Selective leaching can be minimized by reducing the aggressiveness of environment, cathodic protection and using less susceptible alloys.

(vii) Erosion corrosion

Erosion corrosion usually occurs due to the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion. This type of corrosion is associated with systems where the corrosive fluid having high velocities. Rate of erosion corrosion depends upon the nature of surface film, corrosion environment, velocity, presence and size of air bubbles, chemical compositions, suspended solid, corrosion resistance and metallurgical properties of metals and alloys. This type of attack can be observed in piping system such as bends, elbows, and tees, valves, pumps, blowers, centrifugals, impellers, heaters and condensers etc. All types of equipments exposed to moving fluids are susceptible to erosion corrosion. Among the available alloys, Ti has been found to possess the greatest resistance to erosion corrosion and 70: 30brass is known to have poor resistance to erosion. Erosion corrosion can be prevented by selection of materials with better
resistance, proper design, change of aggressive environment, use of surface coating and cathodic protection.

(viii) Stress corrosion

Stress corrosion sometimes termed as stress corrosion cracking, results from the combined action of an applied tensile strength and a corrosive environment. In this corrosion small cracks are formed first and then propagate in a direction perpendicular to the stress. The main cause of stress corrosion cracking depends upon metallurgical factors such as chemical composition of alloys, preferential orientation of grains, composition and distribution of precipitates. The source of stress can be applied, residual, thermal, welding or corrosion products in constructed regions. As stress corrosion crack penetrates the metal, the cross sectional area decreases and the cracking failure occurs due to mechanical action. Long-term stress corrosion cracking tests are necessary to assess the cracking tendencies of alloys. The mechanisms of stress corrosion can be broadly classified as dissolution based and cleavage based. Corrosion plays an important role in the initiation of cracks. Stress corrosion can be minimized by lowering the magnitude of stress, eliminating the critical environment species, changing of alloy composition, applying cathodic protection, adding inhibitors and coatings [14].

1.5 CORROSION PREVENTION AND CONTROL METHODS

Corrosion control is the application of engineering principles and procedures to minimize corrosion to an acceptable level by the most economical method. The various methods of corrosion control are as follows:
1.5.1 Materials selection

The selection of the proper metal or alloy for a particular corrosive service is a common method of preventing corrosion. It is of major importance in the chemical process industries. A criterion for selection of ferrous and non-ferrous materials in equipment of construction is largely dependent on stability for the intended service, availability, ease of fabrication and cost-economics. Carbon and low alloy steels are the most widely used materials of construction as they satisfy all the above criteria, i.e., they are easy to fabricate, easily available and are inexpensive [15]. The physical and chemical properties of the oxide film formed on an alloy and the service environment determine the corrosion resistance of the alloy. Stainless Steels are extensively used in petrochemical plants because of the highly corrosive nature of the catalysts and solvents that are often used [16]. The corrosion resistance of stainless steels is due to the protective nature of the surface oxide film that forms a barrier between the environment and the alloy. High silicon cast irons (with 14% Si) are extremely corrosion resistant because of a passive surface layer of silicon oxide that forms during exposure to many chemical environments [17]. Tantalum is resistant to most acids at all concentrations and temperatures and is generally used under conditions where minimal corrosion is required, such as implants in the human body.

High-nickel cast iron (with 13 to 36% Ni and up to 6% Cr) has excellent corrosion, wear and high temperature résistance because of the relatively high alloy content [18]. Copper and copper-nickel alloys are widely used in marine application. Titanium is also susceptible to crevice corrosion in hot seawater and other hot aqueous chloride environments. The choice of a corrosion resistant material is quite
complicated and is accomplished in several stages. There are also metallurgical factors, such as crystallography, grain size and shape, grain heterogeneity, second phases, impurity inclusions, and residual stress that can influence corrosion. Thus, alloying, metallurgical treatments, and mechanical treatments can greatly affect the corrosion resistance of the resulting alloy.

### 1.5.2 Proper design

Corrosion control makes the greatest economic sense at the design phase. The proper choice of materials and pro-active detailing can provide handsome savings of maintenance dollars, at very little cost expense. The mistakes in plant design are the most frequently cited cause (58%) of corrosion failure in chemical process industries. Proper design for corrosion control must include consideration of proper material selection, finish selection, drainage, sealants, galvanic coupling of materials, application of corrosion-inhibiting compounds, access for maintenance, the use of effective corrosion control programs in service, and consideration of environmental issues. Designs that introduce local stress concentrations directly or as a consequence of fabrication should be carefully considered.

### 1.5.3 Protective coatings

The application of protective coating is one of the popular options of corrosion control [19]. Essentially, protective coatings are a means for separating the surfaces that are susceptible to corrosion from the factors in the environment which cause corrosion to occur. They give long terms protection under a broad range of corrosive conditions, extending from atmospheric exposure to full immersion in strongly
corrosive solution. The application of a surface coating is common with a number of different products, ranging from electrical wiring to printed labels. The coatings are also helpful in preventing rust or enhancing the function of the product, as in the case of coated cookware. One of the most common examples of protective coatings is electrical wiring. The wires that actually carry the flow of current are covered with polymer coatings designed to contain power generated by the wires. At the same time, the coating protects the wires from exposure to any outside element that could cause a short or corrode the wires. The protective coatings in themselves provide little or no structural strength, yet they protect the materials so that the strength and integrity of a structure can be maintained. The protective coatings are further classified into following types:

(i) **Organic coatings**

These coatings afford protection by providing a physical barrier between the metal and the environment. It is most widely used protective coating and is being used for protecting aluminium, zinc and carbon steel against corrosion. According to the Department of Commerce Census Bureau, the total amount of organic coating material sold in the United States in 1997 was 5.56 billion L, at a value of $16.56 billion. The total sales can be broken down into architectural coatings, original equipment manufacturers (OEM) coatings, special-purpose coatings, and miscellaneous paint products. These coatings can also contain corrosion inhibitors. Organic coatings include paints, resins, lacquers, and varnishes. Heavy organic coatings, such as mastics and coal tars, are sometimes used to protect aluminum surfaces that are embedded in soils and concrete.
(ii) Inorganic coatings

These coatings are also used to provide a barrier between the environment and the metal. Inorganic coatings also include enamels, glass linings, and conversion coatings. The treatments change the immediate surface layer of metal into a film of metallic oxide or compound which has better corrosion resistance than the natural oxide film and provides an effective base or key for supplementary protection such as paints.

(iii) Metallic coatings

Metallic coatings are another type of coating which provide a barrier between the metal substrate and the environment. In addition, metallic coatings can sometimes provide cathodic protection when the coating is compromised. Metallic coatings and other inorganic coatings are produced using a variety of techniques, including hot dipping, electroplating, cladding, thermal spraying, and chemical vapor deposition.

1.5.4 Changing the environment

Environment also provides a versatile means for reducing corrosion. For aqueous corrosion, the environment can be made less aggressive by removing constituents or modifying conditions that facilitate corrosion. This can be achieved by decreasing temperature, decreasing velocity, preventing access of water and moisture, removing dissolve oxygen, and increasing pH for steel. However, this method is limited to closed system in which changes in the corrosion medium can be tolerated.
1.5.5 Cathodic protection

Cathodic protection can be applied in practice to protect metals, such as steel, copper, lead, and brass, against corrosion in soils and in almost all aqueous media. When an external electric current is applied to a metallic structure to be protected, the corrosion rate can be reduced to practically zero. Under cathodic protection, the metal can remain indefinitely in a corrosive environment without deterioration. Cathodic protection was first suggested by Sir Humphrey Davy in 1824 that copper could be successfully protected against corrosion by coupling it to iron or zinc [20]. The most rapid development of cathodic protection was made in the United States of America and by 1945, the method was well established to meet the requirements of the rapidly expanding oil and natural gas industry, which wanted to benefit from the advantages of using thin-walled steel pipes for underground transmission. It is often most cost effective course of action for the corrosion protection. The method is now well established and is used on a wide variety of immersed and buried facilities and infrastructure, as well as reinforced concrete structures, to provide corrosion control.

Cathodic protection can be used effectively to minimize corrosion fatigue, intergranular corrosion, stress corrosion cracking, dezincification of brass, or pitting of stainless steels in seawater, or steel in soil. It can however be fairly expensive in the consumption of electric power or the extra metals involved in controlling the potential within this region. Cathodic protection is also applied to canal gates, condensers, submarines, water tanks, marine piling, offshore oil-drilling structures, chemical equipments, bridge decks, parking garages, and other reinforced concrete structures. Cathodic protection is fundamental to preserving a pipeline's integrity.
Cathodic protection is a method of corrosion control that is achieved by supplying an external direct current that neutralizes the natural corrosion current arising on the pipeline at coating defects. Current required to protect a pipeline is dependent on the environment and the number and size of the coating defects. For a particular environment, greater the number and size of coating defects, the greater the amount of current required for protection. Coating plays an integral part in the functioning of a pipeline's cathodic protection system. The principle involved in cathodic protection is to change the electrode potential of the metallic structure so that it lies in the immunity region. Within this region the metal is in the stable form of the element and therefore corrosion reactions are impossible. In electrochemical terms, there are two types of cathodic protection applying to a metal structure:

(i) Impressed current method

Impressed current cathodic protection (ICCP) technique is widely used for the protection of buried pipelines and the hulls of ships immersed in seawater. A d.c. electrical circuit is used to apply an electric current to the metallic structure. The negative terminal of the current source is connected to the metal requiring protection. The positive terminal is connected to an auxiliary anode immersed in the same medium to complete the circuit. The electric current charges the structure with excess electrons and hence changes the electrode potential in the negative direction until the immunity region is reached. The layout for a typical impressed current cathodic protection system is shown in Figure 1.2. ICCP is most specialized technology and can be very effective if correctly designed and operated. Typical materials used for anodes are graphite, silicon, titanium, and niobium plated with platinum. Coatings are
often used in conjunction with ICCP systems to minimize the effect of corrosion on marine structures. One of the difficulties in designing a combined coating and ICCP system is that coatings deteriorate with time. Precious metals are used for impressed current anodes because they are highly efficient electrodes and can handle much higher currents. Precious metal anodes are platinized titanium or tantalum anodes; the platinum is either clad to or electroplated on the substrate. Impressed current systems are more complex than sacrificial anode systems and mostly used to protect pipelines.

(ii) Sacrificial anode method

The principle of this technique is to use a more reactive metal in contact with steel structure to drive the potential in the negative direction until it reaches the immunity region. Sacrificial metals used for cathodic protection consist of magnesium-base and aluminum-base alloys and, to a lesser extent, zinc. No external power source is needed with this type of protection system and much less maintenance is required. These metals are alloyed to improve the long-term performance and dissolution characteristics. Sacrificial anodes serve essentially as sources of portable electrical energy. For cathodic protection of offshore platforms, aluminum anodes, made from aluminum-zinc alloys, are the preferred material [21]. Most offshore petroleum-production platforms use sacrificial anodes because of their simplicity and reliability, even though the capital costs would be lower with impressed-current systems. Magnesium anodes have been used offshore in recent years to polarize the structures to a protected potential faster than zinc or aluminum alloy anodes. Magnesium tends to corrode quite readily in salt water, and most designers avoid the use of magnesium for permanent long-term marine cathodic
Zinc anodes are also used to protect ballast tanks, heat exchangers, and many mechanical components on ships, coastal power plants, and similar structures. In seawater, passivity can be avoided by alloying additions, such as tin, indium, antimony, or mercury. The three most common types of sacrificial anodes are: activated aluminum, zinc and magnesium. Aluminum is the most widely-used material for anodes, as it has a higher current capacity in comparison to the other metals. Magnesium should be considered when the chloride content is less than 10,000 ppm.

1.5.6 Anodic protection

Anodic protection is an electrochemical method of controlling corrosion and is based on the phenomenon of passivity. Passivity refers to the loss of chemical reactivity experienced by certain metals and alloys under particular environmental conditions. This method is most often used in highly corrosive environment to protect metal immersed in solution with uncommonly acidic or basic qualities. Anodic protection can be used to control the corrosion of metals in chemical environments that exhibit very interesting behavior when subjected to anodic polarization. To anodically protect a structure a device called potentiostat is required. When the potential of the working electrode relative to the reference electrode is controlled and shifted in the more positive direction, the current required to cause that shift varies. If the current required for the shift has the general behavior with respect to potential, the metal is termed active passive and can be anodically protected. If the metal was in passive state its corrosion rate could be reduced. Anodic protection is applicable only to metals and alloys which are readily passivated when anodically polarized. Anodic
protection has been used for storage vessels, process reactors, heat exchangers, and transportation vessels. The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements. It is not applicable, for example, to zinc, magnesium, cadmium, silver, copper, or copper-base alloys.

1.5.7 Use of corrosion inhibitors

The application of corrosion inhibitors is another prevalent method used for corrosion control in closed systems. Corrosion inhibitor may be defined as a chemical substances which, when added in small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment [22]. Corrosion processes, being surface reactions, can be controlled by inhibitors which adsorb on the reacting metal surface. The term adsorption refers to molecules attached directly to the surface, normally only one molecular layer thick, and not penetrating into the bulk of the metal itself. In general, an inhibitor forms a protective film in situ by reaction with the corroding surface and as a result, the rate of the anodic and/cathodic reactions are retarded. Corrosion inhibition is reversible and a minimum concentration of the inhibiting compound is required to maintain the inhibiting surface film. The effectiveness of corrosion inhibitors is dependent on the metal to be protected as well as on the operating environment. They reduce the corrosion rate by: (i) Increasing or decreasing the anodic and/or cathodic reaction (ii) Decreasing the diffusion rate for reactants to the surface of the metal (iii) Decreasing the electrical resistance of the metal surface Inhibitors are mostly used in three types of environments: (iv) Re-circulating cooling water systems (e.g., of internal combustion engines, rectifiers, and
cooling towers) in the range of pH 5 to 9. (v) Primary and secondary production of crude oil and subsequent process and (vi) Pickling acid solution for the removal of dust and mill scale during the production and fabrication of metals parts or post service cleaning. The inhibitors can be classified into the following types:

(i) **Passivating (anodic) inhibitors**

This type of inhibitors (e.g., chromates and phosphates) acts by preventing the anodic reaction. The inhibitors are incorporated into the oxide film on the metal, thereby stabilizing it and preventing further dissolution. They cause the anodic curve of polarization to shift such that less current flows. They have the ability to passivate the metal surface. The passivating-type inhibitors are very efficient and reduce corrosion rates to very low values. Some alkaline compounds such as NaOH, Na₃PO₄, and Na₂B₄O are known to facilitate passivation of iron by favoring adsorption of dissolved oxygen. There are two categories of passivating inhibitors namely, oxidizing anions and non-oxidizing anions. Oxidizing anions have the ability to passivate metal in the absence of oxygen. Typical oxidizing anions are chromate, nitrite and nitrate. Non-oxidizing ones such as phosphate, tungstate and molybdate require oxygen to perform passivation. However, one major drawback of such inhibitors is that in order to maintain sufficient passivation of the metal and thus providing sufficient inhibition, the concentration of the inhibitor must be kept well above a critical or minimum concentration. If the concentration is below the minimum value, it is likely that the metal, which is to be protected in to the first place, will suffer from localized corrosion such as pitting. Phosphate is widely used as an additive in boiler water or cooling circuits and in pickling baths for metals. These
inhibitors slow down anodic reaction by forming passive film on the metal surface in presence of oxygen.

(ii) **Precipitation inhibitors**

This class of inhibitor (e.g., zinc salts) block the cathodic reaction by precipitating at the cathode due to elevated pH values locally. They precipitate on the metal surface, forming a protective barrier. Hard water is rich in magnesium and calcium. When these salts precipitate on the metal surface, for example at the cathode where the pH is higher, they establish a protection layer on the metal.

(iii) **Cathodic inhibitors**

Those substances, which reduce the cathodic area by acting on the cathodic sites and polarize the cathodic reactions, are called cathodic inhibitors [23]. Cathodic inhibitors reduce the rate of cathodic reaction namely, oxygen reduction in near neutral environments and hydrogen evolution in acid solutions, respectively.

(iv) **Organic inhibitors**

The inhibitors used for protection of steel in acidic solution are generally organic inhibitor. These types of inhibitors are film-forming in nature. They form a hydrophobic layer on the surface of the metal to prevent dissolution of metal. Most organic inhibitors are substance, which possess at least one functional group considered as the reaction center for the adsorption process. The adsorption of the inhibitor is related to the presence of heteroatom such as nitrogen, oxygen, phosphorus and sulfur as well as triple bond or an aromatic ring in their molecular
structure through which they can adsorb on the metal surface [24-27]. The efficiency of this type of inhibitors depends upon the chemical composition and molecular structure of the compounds as well as their affinity with the metal. They are further classified into organic anodic and cathodic or both depending on the reaction mechanism and the potential of the metal at the interface [28].

(v) **Inorganic inhibitors**

The common inorganic inhibitors used are crystalline salts, for instance, sodium chromate and molybdate. The addition of heavy metal ions like Pb\(^{2+}\), Mn\(^{2+}\), Cd\(^{2+}\) is found to inhibit corrosion on iron in acidic medium. This may be due to the deposition of these metal ions over the iron surface [29].

(vi) **Mixed inhibitors**

Corrosion inhibitors are rarely used as a single compound. The formulation can be composed of two or more inhibitors which will carry different characters. The use of mixed inhibitors is due to following three main factors: A single inhibitor can only inhibit a few numbers of metals. When the environments involve multi-metal system, the inhibitive action may sometimes cause jeopardizing effects to other metals. Advantages from anodic and cathodic inhibitors can be combined and optimized for best performance. Addition of halide ions improves the action of organic inhibitor in acid solutions.
Neutral inhibitors

These inhibitors include cathodic inhibitors, anodic inhibitors and mixed or general inhibitors [30]. The compounds used in neutral media are borates, molybdates and salts of organic acids like benzoates and salicylates.

Vapor-phase corrosion inhibitors

Vapor-phase corrosion inhibitors or volatile corrosion inhibitors (VCIs) are similar to organic adsorption-type inhibitors. These inhibitors possess moderately high vapor pressure and consequently can be used to inhibit atmospheric corrosion of metals without applying VCIs directly on the metal surface. Volatile corrosion inhibitors are secondary-electrolyte layer inhibitors that possess appreciable saturated vapor pressure under atmospheric conditions, thus allowing vapor-phase transport of the inhibitive substance” [31]. They are usually effective if used in enclosed spaces such as closed packages or the interior of machinery during shipment [32]. Vapor phase inhibitor function by forming a bond on the metal surface or by forming a barrier layer to aggressive ions.

1.6 REVIEW OF LITERATURE

Organic inhibitors

Inhibition of corrosion using organic substance has been the subject of several publications [33-40]. The compounds containing nitrogen, oxygen and sulphur atoms, which can donate lone pair of electrons, have proved to be very effective in inhibiting the rate of corrosion of metals [41]. Nitrogen containing organic compounds has been
found to serve as good inhibitors of corrosion [42-48] and their inhibiting action has been explained in terms of the number of mobile electron pairs [49], the $\pi$-orbital character of free electrons [50] and the electron density around the nitrogen atom [51]. It has also been reported that sulphur containing compounds are more effective because of the high density of electrons around the sulphur atom and that the combined effect of nitrogen and sulphur both being present in a compound will be more than their individual effects [52, 53].

**Azoles as corrosion inhibitors**

Azoles have been widely used as corrosion inhibitors in several environments (54-58). Among the azole compounds, the remarkable efficiency of benzotriazole (BTA) as a corrosion inhibitor for copper alloys in aqueous environment has been well established for several decades. Investigations have been carried out on the chemical nature, composition, thickness and structure of the protective layer formed on copper by BTA. The techniques used were electrochemical polarization [59], electrochemical impedance spectroscopy [60]. Infrared reflectance spectroscopy [61] and X-ray photoelectron spectroscopy [62], but the real nature of this film is still the subject of controversy. In fact, it is generally accepted that its action resulted from its chemical adsorption on copper or on its surface oxides. The layer being described as thin by some authors [63], thick by others and composed of a surface complex with only $\text{Cu}^+$ ions or with both $\text{Cu}^+$ and $\text{Cu}^{2+}$ ions [64].

Corrosion inhibition of copper in aerated 0.5M $\text{H}_2\text{SO}_4$ solution in the presence of two classes of heterocyclic compounds, namely phenylazopyrazolones (PAP) or hydroxy quinoline and bromobenzyl-carboxy-1,2,3 triazole (BCT) derivatives was
studied [65]. The corrosion parameters were obtained for different inhibitors and the concentration, temperature effect was also investigated. The corrosion rate of copper was determined using Tafel method and the polarisation resistance (Rp) technique. The electrolyte was analysed using cyclic voltammetry and UV-visible spectroscopy. The results were compared with that of some prepared Cu-complexes in order to explain the inhibition mechanism.

The corrosion inhibition of copper in 0.1M HCl in the presence of pyrazole was studied by Geler and Azambuja [66] using potentiodynamic techniques with rotating disc and rotating ring disc electrodes (RRDE). Pyrazole behaved like a cathodic inhibitor and the inhibition efficiency was influenced by mass transport.

Zhang et al., [67] investigated the effect of bis-(1- benzotriazolymethylene)-(2,5-thiadiazoly)-disulfide (BBTD), on the corrosion of copper in 3%NaCl and 0.5MHCl. Potentiodynamic polarisation studies clearly showed that the BBTD was mixed-type inhibitor for copper in chloride solutions. The anodic reaction rate decreased compared to the cathodic reaction rate and it renders the open–circuit potential of copper more positive in either HCl or NaCl solutions. The FT-IR spectra indicated that BBTD prevented copper from corrosion by adsorption on the copper surface to form a protective complex with the Cu (I) ion.

Sherif et al., [68] investigated the corrosion inhibition of copper by 3- amino-1,2,4-triazole-5-thiol (ATT) in aerated 0.5M HCl using electrochemical techniques and weight-loss measurements, along with Raman spectroscopy.
Corrosion inhibition of copper in 0.5M HCl by 5-(3-Aminophenyl)-tetrazole (APT) was studied by Sherif et al., [69] using potentiodynamic polarisation, Chronoamperometry (CA), EIS, Raman spectroscopy and Weight-loss measurements. The results showed that the presence of APT and the increase of its concentration significantly decreased the corrosion rates.

Modestov et al., [70] studied the effect of benzotriazole (BTA) on the corrosion of brass in 0.1 N HCl, 0.1 N HSO$_4$ and 0.1 N NH$_4$Cl by galvanostatic measurements. BTA showed a good inhibition effect in some corrosive media. The percentage inhibition in 0.1N HCl was found to increase with increasing BTA concentration. In contrast, the percentage inhibition in 0.1N H$_2$SO$_4$ was inversely proportional to the BTA concentration. The highest inhibition efficiency was obtained in 0.1N NH$_4$Cl. The role of BTA as an inhibitor for brass was explained in terms of the chemisorption of BTA molecules at some active sites on brass surfaces.

The effect of addition of some tetrazolic type organic compounds, 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT), 1,2,3,4-tetrazole (TTZ), 5- amino-1,2,3,4-tetrazole (AT) and 1-phenyl-1,2,3,4-tetrazole (PT) on the corrosion of brass in nitric acid was studied by Mihit et al., (2006) [71] using weight loss, polarisation and EIS measurements. The explored methods gave almost similar results. Results obtained revealed that the PMT was the best inhibitor and the inhibition efficiency IE% follows the sequence: PMT > PT > AT > TTZ. Polarisation measurements also indicated that tetrazoles acted as mixed type inhibitors.
Correlation between the highest occupied molecular orbital energy (E\text{HOMO}) and inhibition efficiencies was sought. The comparative study of corrosion behaviour of brasses 70Cu-30Zn and 60Cu-40Zn in HNO$_3$ in absence and in presence of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) was studied by Mihit et al (2007) [72] using gravimetric and electrochemical methods. Results obtained were in good agreement and revealed that the corrosion rate depends on immersion time and zinc content in the alloy. Cu and Zn losses from each specimen studied, at various immersion times, were estimated by atomic absorption spectroscopic analysis. The results showed that the inhibition efficiency of the inhibitor towards Cu is more significant than Zn. PMT was adsorbed preferentially on the Cu surface and inhibited the process of corrosion of brasses in the nitric acid medium.

Ravichandran et al., [73] investigated the effect of N-[1- (benzotriazol-1-yl) methyl] aniline (BTMA) and 1-hydroxy methyl benzotriazole (HBTA) on corrosion of brass in neutral aqueous NaCl solution. Polarisation studies showed that these inhibitors were found to act as mixed type for brass in chloride solution. Solution analysis was used to calculate the dezincification factor. The FT-IR was used to characterize the surface film.

Abd El Meguid and Awad [74] studied the effect of benzotriazole (BTAH) on the dissolution of $\alpha$-brass (70% Cu–30% Zn) in 1.0 M LiBr. Polarisation curves showed that an initial active region of the alloy dissolution followed by two well defined anodic current peaks then a narrow passivation region before the pitting potential ($E_{pit}$) was reached. The initial active anodic region exhibited Tafel slope with
90 mV dec\(^{-1}\) attributed to the formation of complexes. The anodic current peaks were attributed to the formation of CuBr and Cu\(^{2+}\) ions, respectively.

Kosec et al., [75] investigated the inhibitive effect of benzotriazole (BTAH) on the corrosion of copper, zinc and copper-zinc (Cu–10Zn and Cu–40Zn) alloys in chloride solution using electrochemical techniques, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Electrochemical reactions and surface products formed at the open-circuit potential and as a function of the potential range were discussed. The addition of benzotriazole to aerated, near neutral 0.5 M NaCl solution affected the dissolution of Cu, Zn, Cu–10Zn and Cu–40Zn alloys.

El Warraky [76] studied the effect of 2-methyl benzimidazole (MBIA) and Armohib 28 inhibitors on corrosion behaviour of brass 70Cu/30Zn in deaerated solutions of dilute HCl and acidified 4% NaCl of pH 1.8 - 2 at different temperatures between 25 and 60°C by the weight loss method. The effect of the addition of different concentrations of 2-methyl benzimidazole (MBIA) and Armohib 28 inhibitors on the dissolution of the alloy in both media was tested at 60°C. MBIA has no effect in the case of acidified 4% NaCl, but with pure dilute HCl the inhibition efficiency in the presence of 300 ppm of MBIA amounted to 84.6%. On the other hand, the inhibition efficiency reached 93.4% and 94.6% in the presence of 10 ppm Armohib inhibitor in dilute HCl and acidified 4% NaCl, respectively.

The effect of 1,2,4-triazole (TA) and its amino derivatives: 3- amino-1,2,4-triazole-5-thiol, 3-amino 1,2,4- triazoleand, 3,5-diamino- 1,2,4-triazole, 3-amino 5- mercapto 1,2,4-triazole, 3-amino 5-methylthio 1,2,4-triazole on copper corrosion in chloride media was studied[77-83]. The results showed that the molecules strongly
adsorbed on the Cu surface in chloride solution, formed a complex with Cu$^+$ and inhibited copper corrosion by preventing the formation of CuCl$_2$ through which Cu dissolution occurs.

Hope et al., [84] observed that the adsorption of BTA onto the copper surface was reversible at pH levels below 3, and depended upon both solution pH and the applied electrode potential. At lower pH the coordination between Cu and BTA as well as the chemisorption of BTAH$^{2+}$ onto the electrode surface observed, whereas at higher pH levels the surface layer [Cu(I)–BTA] was observed on the electrode.

Tromans and Sun [85] concluded that BTA can react with the clean copper surface to form the protective film. The study of Xu et al., [86] conducted on the clean copper surface proved that adsorbed BTA anchored directly to the metal. The metallic copper reacted with BTA at a faster rate providing much better anticorrosion effect than the oxidized surface. It was proposed that the surface moiety was [Cu(I)–BTA] and the isolated product was [Cu(II)–(BTA)$_2$]. In neutral solutions, BTA functions as a ligand by means of the unshared pair of electrons on the “pyridine”-type nitrogen.

Xu et al., [86] studied the initial steps in the reaction of BTA with copper surfaces of varying oxidation states. The results indicated that dissociation of BTA into BTA- and H$^+$ upon adsorption was likely and under low solution concentration conditions the initial step of the reaction of BTA in solution with both copper oxide surfaces (Cu$_2$O and CuO) was to form not more than a single layer of chemisorbed BTA- species, and not a much thicker mixed complex layer. The de-protonation of BTA molecule by adsorption onto the metal was also observed by Cao et al., [87]. According to them, the film structure depended on the potential. The initially formed
complex \([\text{Cu(I)}–\text{BTA}]_n\) changed to \([\text{Cu(I)}–\text{BTA}]_4\) at more negative potentials. That is, the coordinated BTA-anion may rebind with \(\text{H}^+\), and as a result, the surface polymer film decomposed and the inhibition efficiency was diminished.

The formation of cuprous oxide underlayer was also observed by Finšgar et al., [88]. Bratescu et al., [89] suggested that incomplete surface coverage of BTA was sufficient to induce significant changes in the corrosion process of \(\text{Cu}_2\text{O}\) in deionized water, due to the fact that corrosion of the surface would occur on the highest surface energy sites first which were also most likely to participate in adsorption events.

Al Kharafi et al., [90] and Bayoumi et al., [91] analyzed the kinetics of interaction of BTA with the surface of copper in 3.5\% NaCl. In the beginning, it was found that the linear growth of the \([\text{Cu(I)}–\text{BTA}]\) complex formed with time. The thickness of the multilayer film formed was independent of the concentration of BTA in the electrolyte.

Finšgar et al., [91] compared the effectiveness of the benzotriazole and 1-hydroxybenzotriazole (BTAOH) inhibitors on the copper specimen in 3\% NaCl and then the correlated the effectiveness of the inhibitor to their molecular structure and electronic properties. The results showed that BTA behaved as an inhibitor for general copper corrosion over a wide range of potential and superior to BTAOH. The formed Cu–BTAOH film was poorly protective against the attack of chloride ions, however, the adsorption of BTA was fast and that it formed a strongly protective film. The only difference in structure was that in BTAOH a hydroxyl group was bonded to the \(\text{N}_4\)-nitrogen instead of hydrogen in BTA.
Loo et al., [92] and Tromans and Silva [93] observed that the introduction of methyl group to BTA molecule, by which tolytriazole (TTA) was produced, increased the film hydrophobicity hence improved the copper corrosion prevention. The studies conducted on 5-alkyl-derivatives of benzotriazole [94] and on the series of alkyl esters synthesized from the mixture of 4- and 5-carboxybenzotriazole (4-CBTA and 5-CBTA) lead to the conclusion that the inhibition efficiency increased with hydrocarbon chain length [95]. This was attributed to increase in physisorption of the alkyl chain as more methyl groups were introduced and chemisorptions through azole ring N.

Arancibia et al., [96] conducted a research of the effect of BTA and its derivatives 5-methyl-BTA and 5-chloro-BTA on the copper corrosion inhibition in aerated 0.1 M HCl. BTA and 5-methyl-BTA action were associated with adsorption of BTAH$^{2+}$ on Cu. 5-chloro-BTA action mechanism was associated with passivation and Cu-BTA formation. Chloride group in 5-position enabled the formation of the partially protonated species BTAH while nitrogen was responsible for bonding with copper. It was noticed that the interaction between inhibitor and metal surface enhanced with substituent in 5-position of inhibitor molecule, while electron acceptor groups had better effect than electron-donor.

Zhou et al., [97] investigated the effect of 1-(2,3-dicarboxypropyl) benzotriazole (BT-250) which was a derivative of BTA but was less efficient as copper corrosion inhibitor in NaCl solution. Bis-(1-benzotriazoly methylene)-(2,5-thiadiazoly)-disulphide (BBTD), that contains two BTA moieties and one thia diazole moiety, was more efficient inhibitor of copper corrosion in comparison with BTA.
The effect was more pronounced in 3% NaCl than in 0.5 M HCl which was attributed to the stability of cuprous oxide in neutral solution [98]. The mechanism of action was the adsorption of BBTD on the Cu surface and formation of protective [Cu(I)–BBTD] complex.

Ye et al., [99] studied the structure of the protective film of 1-phenyl-5-mercaptotetrazole (PMTA) formed by pre-filming the electrode by immersion in the PMTA solution. The film contained a layer of inert, insoluble and long-lasting polymeric Cu (I) complex. These films were probably built over Cu$_2$O layer through surface reaction of PMTA and Cu (I) ions.

Zucchi et al.,[100] studied the inhibiting action of tetrazole derivatives: tetrazole (T), 5-mercapto-1-methyl-tetrazole (5Mc-1Me-T), 5- mercapto (Na salt)-1-methyl-tetrazole (5NaMc-1Me-T), 5-mercapto-1-acetic acid (Na salt)-tetrazole (5Mc-1Ac-T), (PMTA), 5-phenyl-tetrazole (5Ph-T) and 5-amino-tetrazole (5NH$_2$-T) in 0.1 M NaCl solution in the range of pH from 4 to 8. The superior protective characteristics were shown by derivatives containing phenyl group.

The focus of Blajiev and Hubin [101] was on the interaction between the copper atom of Cu$_2$O surface and AMTD or MMTD. The chloride ions adsorbed on different positions and altered the oxide geometry and charged density periodicity. The addition of inhibiting molecules to the solution led to their competitive adsorption on the surface of the copper oxide and to the modification of the hydrolysis and chloride surface complexation processes. The adsorption can be achieved via two sulphur atoms, or via one sulphur and one nitrogen atom. The influence of the potential and polarisation conditions on the adsorption kinetics and structure of
MMTD on copper in 0.1M NaF was studied [102]. The results showed that MMTD reacts strongly with copper, whereas a dense organic layer was formed by the adsorption of MMTD via a thiol–sulphur bonding to the copper surface.

Vera et al., [103] also investigated the ability of the tetradeutate 1,5-bis(4-dithiocarboxylate-1-dodecyl-5-hydroxy-3-methylpyrazolyl)-pentane, (BDTCPP) on the inhibition of copper corrosion in 3.5% NaCl. The high inhibition efficiency can be attributed to the good adherence of the complex on the copper surface.

Tommesani et al., [104] studied the protective action of 1,2,3- benzotriazole derivative films against copper corrosion. dilute solution of BTA alkyl derivatives induce formation protective surface films on OHFC copper specimens improving copper resistance to corrosion in 3.5% NaCl solutions at the pH of 7. The efficiency of corrosion inhibition is strongly reduced, although to different extents depending on the inhibitor used, at lower pH values. As a general result, the film effectiveness increases with alkyl chain length and coating treatment time.

Mernari et al., [105] investigated the inhibitive effects of 3, 5-bis(N-pyridyl)4-amino-1,2,4-triazoles on the corrosion of mild steel in 1M hydrochloric acid. The electrochemical study reveals that this compound is anodic inhibitor.

Gasparac et al.,[106] studied the nature of chemical interaction between imidazole derivatives and copper surface using X-ray photoelectron spectroscopy and secondary ion mass spectrometry. They also studied the activation energies and thermodynamic adsorption and concluded that the adsorption behaviour of the
imidazole derivatives on the copper electrode surface follows a Freundlich-type isotherm.

Subramanian and Lakshminarayanan [107] studied the adsorption properties and the effect of some azoles such as benzotriazole, mercaptobenzothiazole, benzimidazole, imidazole and tetrazole on the growth of oxide film on copper in 0.1M NaOH. Mercaptobenzothiazole is found better to control oxide film formation. All these azole contain nitrogen and/or sulphur atoms, which can co-ordinate with copper through the lone pair of electrons to form complexes. These complexes are generally believed to be polymeric in nature and form a protective film on the copper surface, which acts as a barrier to oxide film formation. The inhibitor action of these azoles may also be due to physisorption or chemisorption onto the copper surface.

Trachli et al., [108] studied the protective effect of electropolymerised aminotriazole towards corrosion of copper in 0.5M NaCl solution. They found that the protection of aminotriazole reaches 99% after one month immersion test.

Nagiub and Mansfeld [109] studied the corrosion behaviour of 26000 brasses in artificial sea water using EIS and ENA techniques. BTA, gluconic acid sodium salt and polyphosphoric acid sodium salt were evaluated as corrosion inhibitors.

Qafsaoui et al., [110] studied the quantitative characterization of protective film developed on copper by anodic polarization in a borate buffered solution containing benzotriazole and aminotriazole.
Al-Kharafi and Ateya [111] investigated the effect of sulfides on the electrochemical impedance of copper in benzotriazole-inhibited media.

Shukla and Pitre [112] studied the electrochemical behaviour of brass and the inhibitive effect of imidazole in acid solution.

Huynh et al., [113] studied alkyl esters of carboxy benzotriazole on copper in sulphate environments. They proposed that the protonated species is chemisorbed on the copper through azole nitrogen and at low pH. IE is determined by vanderwaal’s forces of attraction between adjacent alkyl chains oriented away from the copper surface, which are increased with the length of the alkyl chain. On the contrary it is proposed that at high pH a polymeric complex is formed and steric hinderance acts to make the film less protective. Polarization, EIS and SERS studies confirm the hypothesis.

Otmacic and Stupnisek-Lisac [114] studied the corrosion inhibition of various imidazole derivatives on copper in neutral media.

Lagrenee et al.,[115] investigated the mechanism and inhibiting efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,3-triazole on mild steel corrosion in acidic media. This inhibitor behaved better in 1M HCl than in 0.5 M H₂SO₄.

Wang [116] studied the evaluation of 2-mercaptobenzimidazole as corrosion inhibitor for mild steel in phosphoric acid. The studies reveal that the inhibitor is effective for the inhibition mild steel over a wide concentration range of H₃PO₄ solutions and retards the anodic and cathodic corrosion reactions.
El-Azhar et al.,[117] investigated the corrosion inhibition of mild steel by the new class of inhibitors [2,5-bis(n-pyridyl)-1,2,4-thiadiazoles] in acid media using weight loss and electrochemical impedance spectroscopy. Results obtained reveal that these compounds are mixed type inhibitors and behave better in 1M HCl than 0.5M H₂SO₄.

Wu et al.,[118] studied the effect of KI on improving copper corrosion inhibition efficiency of benzotriazole in sulphuric acid. The nature of this effect has been studied systematically by using electrochemical techniques and X-ray photoelectron spectroscopy. The synergistic effect is due largely to the formation of a film of Cu(I)-BTA complex and is probably polymeric in nature.

Laachach et al.,[119] studied the electrochemical behaviour of Cu-Ni alloy in NaCl medium polluted by sulphides and inhibiting effect of aminotriazole. The potentiodynamic and electrochemical impedance measurements showed that sulphides accelerate the corrosion of the alloy in NaCl solution. The aminotriazole inhibited both anodic and cathodic corrosion processes. The inhibiting effect was higher when the solution contained the S²⁻ ion.

Quraishi et al.,[120] studied the inhibition of dezincification of 70-30 brass by aminoalkyl mercaptotriazoles in NaCl medium. Solution analysis showed selective dissolution of zinc compared with copper. The lowest concentration of zinc, achieved in the tests with the optimum inhibitor addition.

Bentiss et al.,[121] studied the inhibitor effect of triazole derivatives on corrosion of mild steel in acidic media, showed that these organic compounds are very good inhibitors. Triazoles are able to reduce the corrosion of steel more
effectively in 1M HCl than in 0.5M H$_2$SO$_4$. Ammeloot[122] studied the characterization of the oxide layers on a Cu-13Sn alloy in a NaCl solution with and without 0.1M benzotriazole. Hollander and May[123] studied the chemistry of azole copper corrosion inhibitors in cooling water. Under these conditions, benzotriazole and tolyl triazole exhibits significantly different inhibition behaviour. The differences can be explained on the basis of TTA forming a much thinner but more hydrophobic film than does BTA.

Ashour and Sayed [124] studied the effect of benzotriazole on the corrosion of $\alpha$-Al-bronze in saline water. BTA was found to have a stronger inhibiting effect on the anodic dissolution of copper than on the cathodic reduction of oxygen.

Yan et al., [125] investigated the inhibition of 2-mercaptobenzoxazole for copper corrosion in NaCl solution. It is concluded that MBO reacted with the cuprous species from the corrosion process, and produced a water-insoluble cuprous complex to form the inhibition film and to retard the corrosion of copper.

Rodrigues [126] studied the effect of benzotriazole for type 304 stainless steel in water-ethanol media containing 2M H$_2$SO$_4$. BTA acts as a cathodic and anodic inhibitor over the entire range of potentials studied.

Although there is an extensive literature on the corrosion properties of triazole such as aminotriazole and benzotriazole on steel and copper, there are very few reports devoted to the various functional groups in BTA derivatives on the dezincification of brass. In the cases where these benzotriazole derivatives have been considered, they have first been introduced as effective corrosion inhibitors in marine environment.
1.7 OBJECTIVES OF THE WORK

Corrosion inhibitors have been widely used in industry to reduce the corrosion rate of different metals and alloys which are in contact with aggressive environments. Many studies have been carried out to find out the suitable compounds as corrosion inhibitors. Most of these compounds are synthetic chemicals which may be very expensive and hazardous to living creatures and environments. It is very important to choose low cost and safely handled compounds to be used as corrosion inhibitors.

The main objectives are:

- To evaluate the inhibition efficiency of some benzotriazole derivatives for brass corrosion in seawater by electrochemical measurements at different temperatures
- To establish the effect on the kinetics of the corrosion reactions of each compound by potentiodynamic polarization
- To evaluate the interaction of each compound with the brass alloy.
- To investigate the effect of temperature on the rate of dissolution of brass in seawater
- To examine the nature of the species adsorbed on the brass
- To verify the adsorption of organic inhibitors on brass surface.
- To determine the elemental composition on the surface of brass before and after exposure to the inhibitor solution
- To analyze the leaching characteristics of copper-nickel alloy in the optimum concentration of inhibitors in seawater.
In order to achieve the above-mentioned objectives, the following techniques were used to analyse the corrosion inhibition efficiency of some of the benzotriazole derivatives on brass in seawater.

1. **Weight-loss Method**

   - to verify the inhibition efficiency of the inhibitors.

2. **Polarisation Measurements**

   - to study the corrosion behavior of brass in marine environment.

   - to evaluate the corrosion inhibition efficiency of some benzotriazole derivatives.

   - to study the effect of temperature on the rate of dissolution of brass in seawater containing optimum concentration of the investigated inhibitors.

3. **Electrochemical Impedance Spectroscopy (EIS)**

   - to identify the formation of compact surface layer in the presence of inhibitors.

4. **Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)**

   - to determine the alloying elements leached out from the test material.
5. **Thermodynamic Parameters and Adsorption Isotherm**

   - To explain corrosion inhibition mechanism using the thermodynamic parameters including heat of adsorption, free energy of adsorption and the entropy of adsorption.

6. **Energy Dispersive X-ray Analysis (EDAX)**

   - To identify the elemental composition of surface of the alloy.

7. **Scanning Electron Microscopy (SEM)**

   - To understand the surface morphological change.