

# INTRODUCTION

## 1.1- The Electrochemical Nature of Corrosion

Corrosion is the natural process of deterioration of metals and alloys in a corrosive environment. This is a very broad definition, but corrosion occurs in a wide variety of forms, both in pure metals and in alloys. Resulting in an actual decrease in the thickness or size of the original metallic structure. This wasting away occurs relatively uniformly over the surface exposed to the corrosive environment. Metals such as steel and copper and alloys such as brass and stainless steel appear to be fairly rugged and able to withstand a great deal of physical abuse. This is not true when these metals are surrounded by a corrosive environment. They can be quickly reduced to thin, rusty or oxide-encrusted specimens. To put it another way, these metals always have a tendency to return to their naturally occurring forms. Metallic elements such as iron, copper, zinc and nickel occur naturally in the form of oxides, sulfides and carbonates. In metal making, this natural process is reversed and the metallic element is separated from its oxide. This requires a great deal of energy, as anyone who has seen a blast furnace can tell you. The resulting metal or alloy is in a high-energy state and, under the right conditions; it will attempt to return to its more natural, lower-energy, reacted state. A detailed corrosion study

of a piece of metal is the study of how this happens, the rate at which it happens and what causes it to happen. There are several conditions that must be met before these reactions can occur.

1. The metal, in this case, iron, must be reactive. It must be inherently unstable in the metallic form, thereby tending to corrode.
2. The metal must be in contact with an electrolyte. An electrolyte is a solution, usually aqueous, which can conduct electric current and support ionized species.
3. The electrolyte must contain dissolved species. This can be either dissolved gases, such as oxygen or chlorine, or dissolved ions, such as the hydrogen ion, which acts as an oxidizing agent.
4. The kinetics of the situation (the rate at which the corrosion reactions can occur) must be rapid enough to be of practical significance.

The first requirement, that the metal must have sufficient reactivity, is exhibited by metals such as iron, copper and steel. They readily corrode under the proper conditions. On the other hand, gold and platinum are more noble metals and do not react readily with their environment. Without the presence of dissolved gases or minerals in an electrolyte, such as water, even highly reactive metals do not corrode. Water contains many types of minerals.

## **1.2-Classification of corrosion**

The preferred classification of corrosion is:

### ***(i)Dry or chemical corrosion:***

Dry corrosion occurs in the absence of a liquid phase or above the dew point of the environment. Vapors and gases are usually coordinates; it is often associated with high temperature. An example is the attack of steel by furnace gases.

### ***(ii)Wet or electrochemical:***

Corrosion occurs when a liquid is present in contact with the metal. This occurs in aqueous solutions or electrolytes. A common example is corrosion of steel by water.

## **1.3-Factors influencing corrosion**

The nature and extent of corrosion depend on the metal and the environment. The important factors which may influence the corrosion process are:

- |                                  |                                    |
|----------------------------------|------------------------------------|
| a) Nature of the metal.          | f) Electrode potential.            |
| b) Environment.                  | g) Aeration.                       |
| c) Temperature.                  | h) Agitation                       |
| d) Concentration of electrolyte. | k) Hydrogen over voltage.          |
| e) pH of the electrolyte.        | i) Nature of the corrosion product |

#### **1.4-Various forms of corrosion<sup>(1)</sup>**

Corrosion can manifest itself in the following main forms:

##### **1.4.1-General and local electrochemical corrosion<sup>(2)</sup>**

When separate corrosion cells can be distinguished by variation of the electrode potential over the metal surface, by the appearance of corrosion currents or of separate anodic and cathodic corrosion products, local electrochemical corrosion is said to occur.

General electrochemical corrosion occurs when separate anodic surfaces do not appear or they are of small dimensions (sub micro cells ) or fluctuate over the surfaces, the attack will be more uniform. Hence there are possibilities for corrosion products to form a continuous film and retard continuous attack. Therefore general electrochemical corrosion leads to uniform attack whereas local electrochemical corrosion results in localized attacks.

##### **1.4.2-Galvanic corrosion or dissimilar metal corrosion**

Galvanic corrosion occurs when two or more dissimilar metals in electrical contact are placed in an electrolyte. This causes a potential difference between the metals which results in the flow of current between them. Several investigators <sup>(3,4)</sup> have shown that galvanic corrosion is directly proportional to the area ratio of the cathodic metal to the anodic

metal, galvanic corrosion is maximum at the junction of the two metals. The attack decreases with increasing distance from the junction.

#### **1.4.3-Crevice corrosion** <sup>(5,6)</sup>

This occurs in certain metal-environment combinations. Only metals and alloys which depend upon the oxide film for corrosion resistance are susceptible to crevice corrosion. It is an intense localized corrosive attack which occurs within the confined space or crevices created by certain mechanical configurations. They are created by surface deposits of corrosion products, scratches in paint films etc.

#### **1.4.4-Filiform corrosion** <sup>(1)</sup>

This is special type of crevice corrosion which results irregularly developed hair- fine lines or filaments of corrosion products below coatings of paints, tin, silver, etc. It does not destroy the component but affects the surface appearance.

#### **1.4.5-Intergranular corrosion** <sup>(7)</sup>

Grain boundaries are usually more reactive than the grain matrix. Hence localized attack occurs at adjacent to grain boundaries with relatively little corrosion of the matrix. This attack is usually rapid and penetrates deep into the metal resulting in loss of strength and causes catastrophic failures.

Most metal alloys are susceptible to intergranular corrosion, when exposed to specific corrodents. Mostly corrosion of iron-nickel-chromium alloy is considered because of its commercial importance. Many reviews <sup>(8,9)</sup> have appeared on this subject.

#### **1.4.6-Pitting corrosion**

This is also a form of intensive localized attack, the rate of attack being nonuniform. It is most destructive form of corrosion and results in sudden failure of the equipment due to the formation of pits or holes. It is reported to occur in the presence of chloride ions depending upon the concentration of chloride ions <sup>(9, 10, 11, and 12)</sup>.

#### **1.4.7-Exfoliation <sup>(13)</sup>**

The loss of metals as layers or leaves from a solid metal or alloy is called exfoliation. This type is observed mostly in wrought products. Further Al- Mg, Al- Cu, Al- Zn and Al- Mg- Si alloys undergo exfoliation.

#### **1.4.8-Stress corrosion cracking <sup>(14)</sup>**

The cracking of metal or alloy due to the simultaneous presence of tensile stress and a specific corrosive environment is known as stress corrosion cracking.

#### **1.4.9-Corrosion fatigue cracking <sup>(15,16)</sup>**

Reduction in the fatigue strength due to the presence of a corrosive environment is known as corrosion fatigue cracking. It occurs due to the combined action of cyclic stress and corrosive environment.

#### **1.4.10-Fretting corrosion <sup>(17)</sup>**

This type of corrosion occurs between two surfaces in contact with each other in dry or humid air when subjected to slight relative motion of small amplitude. Various alternate terms such as friction oxidation, wear oxidation, chafing. False brinelling are used to describe this phenomenon.

#### **1.4.11-Erosion corrosion**

Erosion corrosion is defined as increased corrosion rate to relative motion between metal surface and the environments usually liquid or gas. This type of corrosion is also known as impingement corrosion <sup>(15)</sup>. Such corrosion occurs in agitators, copper pipes, centrifuge etc. Localized attack due to erosion corrosion usually has bright surface from corrosion products. Eg. Pits, rounded holes and valleys.

#### **1.4.12-Cavitation corrosion <sup>(18)</sup>**

This is a special type of erosion corrosion caused due to the formation of vapor bubbles in a corrosive environment near a metal surface

and when the bubbles collapse attack arises. Eg. Hydraulic turbulence, ship propellers etc.

### **1.5- Electrochemical theory of corrosion**

The corrosion of metals in aqueous solutions is an electrochemical process as established in the first half of the 19<sup>th</sup> century. Whitney <sup>(19)</sup> gave the most acceptable electrochemical theory.

### **1.6- Corrosion inhibitors**

Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors can be classified into liquid- and vapor phase inhibitors.

#### **1.6.1-Classification of inhibitors**

Inhibitor selection is based on the metal and the environment.

##### ***(i)Vapor phase inhibitor***

Vapor phase inhibitors are compounds which don't have low, but also significant vapor pressure (about 0.1 – 1.0 mm Hg) and produce vapor that has corrosion inhibiting properties. The inhibitors can therefore be used for the temporary protection of metals in corrosive atmospheres. They are essentially soluble filming inhibitors and include nitrite, benzoate and /or carbonate anions attached to a suitable heavy organic cation, e.g.



dicyclohexylammonium nitrite, which is one of the most effective of this type of inhibitors.

***(ii) Liquid-Phase Inhibitors***

Liquid-phase inhibitors are classified as anodic, cathodic or mixed inhibitors, depending on whether they inhibit the anodic, cathodic or both electrochemical reactions.

**a- Anodic inhibitors.**

Anodic inhibitors are usually used in near-neutral solutions where sparingly soluble corrosion products, such as oxides, hydroxides, or salts are formed. They form or facilitate the formation of passivating films that inhibit the anodic metal dissolution reaction. Anodic inhibitors are often called passivating inhibitors. When the concentration of an anodic inhibitor is not sufficient, corrosion may be accelerated, rather than inhibited. The critical concentration above which inhibitors are effective depends on the nature and concentration of the aggressive ions.

**b- Cathodic inhibitors.**

Cathodic inhibitors control corrosion by either decreasing the reduction rate (cathodic poisons) or by precipitating selectively on the cathodic areas (cathodic precipitators).

**c- Mixed inhibitors.**

About 80% of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors. The effectiveness of organic inhibitors is related to the extent to which they adsorb and cover the metal surface. Adsorption depends on the structure of the inhibitor, on the surface charge of the metal, and on the type of electrolyte. Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorptions and film formation.

**1.7-Literature survey on corrosion inhibition of copper in aqueous solutions.**

Copper is a metal widely used with a cause of a good corrosion resistance combined with mechanical workability, excellent electrical and thermal conductivity. It is noble to hydrogen in the e.m.f. series, and thermodynamically inert with no tendency to corrode in water and in non oxidizing acids free of dissolved oxygen. In oxidizing acids or in aerated solutions of ions that form copper complexes (e.g.  $\text{CN}^-$ ,  $\text{NH}_4^+$ ), corrosion can be server. Copper dissolves anodically in most aqueous environment forming the divalent ion  $\text{Cu}^{2+}$  (i.e.  $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$   $E^\circ = -0.337\text{V}$ ). Equilibrium relation at the metal surface indicates that the reaction ( $\text{Cu} + \text{Cu}^{2+} \longrightarrow 2\text{Cu}^{2+}$ ) is displaced far to the left. On the other hand if complexes are formed, as for example between  $\text{Cu}^+$  and  $\text{Cl}^-$  in chloride solution, the continuous depletion of  $\text{Cu}^+$  by conversion to  $\text{CuCl}_2^-$  favours

the univalent ion as the major dissolution product. Comparatively, when the anhydrous ion forms, as in the oxidation of copper in air at elevated temperatures only  $\text{Cu}^+$  exists because  $\text{Cu}_2\text{O}$  has a lower oxygen dissociation pressure than  $\text{CuO}$ .

Fiala et al.<sup>(20)</sup> synthesized ketene dithioacetal derivatives, namely 3-[bis(methylthio)methylene] pentane-2,4-dione (1), 3-(1,3-dithian-2-ylidene) pentane-2,4-dione (2) and 3-(1,3-dithiolan-2-ylidene) pentane-2,4-dione (3) and investigated their respective capacity to inhibit copper corrosion in 3M  $\text{HNO}_3$  by means of weight loss, potentiodynamic polarization, scanning electron microscopy (SEM) and energy dispersive X-ray fluorescence (XRF). The obtained results indicate that the addition of these compounds significantly decreases the corrosion rate. Potentiodynamic polarization studies clearly showed that the inhibition efficiency increases with increasing concentration of the investigated compounds at a fixed temperature, but decreases with increasing temperature. These results on the whole showed that the studied substances are good cathodic inhibitors for copper corrosion in nitric acid medium. SEM and energy dispersive X-ray analysis (EDXA) examination of the copper surface revealed that these compounds prevented copper from corrosion by adsorption on its surface to form a protective film, which acts as a barrier to aggressive agents. The presence of these organic compounds adsorbed on the electrode surface was confirmed by XRF investigations.

Fouda et al.<sup>(21)</sup> investigated the inhibition effect of some phthalimide derivatives on the corrosion of copper in acidic media by weight loss and polarization techniques. Results obtained revealed that these organic compounds are good inhibitors. Galvanostatic polarization studies showed that these compounds are mixed type inhibitors. The adsorption of these inhibitors on the copper surface obeys Temkin's adsorption isotherm. The effect of temperature on the corrosion behavior of copper in nitric acid in presence of definite concentration of the inhibitors was studied in the temperature range 30–45°C. The associated activation corrosion and free adsorption energies have been determined.

Tan et al.<sup>(22)</sup> prepared the self-assembled monolayers (SAMs) of a series of substituted benzenethiol (BT) molecules, X–C<sub>6</sub>H<sub>4</sub>–SH (where X = meta-NH<sub>2</sub>, ortho-NH<sub>2</sub>, para-NH<sub>2</sub>, para-NHCOCH<sub>3</sub>, para-F, para-CH<sub>3</sub> and para-CH(CH<sub>3</sub>)<sub>2</sub>), by adsorption from a solution onto a fresh copper (Cu) surface pretreated by a nitric acid etch. The corrosion inhibition efficiency of the modified Cu surfaces in a sulfuric acid solution was investigated by electrochemical characterization. The protection afforded by the substituted functional groups on BT is strongly influenced by the type and the position of the substituent on the benzene ring. BT molecules without any substituent group on the ring are ineffective corrosion inhibitors, indicating that the chemical configuration is the key factor in determining the efficacy of the SAMs as barriers to electrochemically corrosive ions. It is further

proposed that the steric hindrance offered by the substituted group in the SAMs plays a very important role in determining its barrier properties.

Assaf et al.<sup>(23)</sup> used stripping voltammetry and conductance measurements for the first time to study the corrosion and inhibition of copper. The effect of nitric acid concentration, temperature and some organic compounds on the corrosion rate was studied. Regression analysis using four modes (linear, logarithmic, power and exponential) was used to correlate the results. Data obtained showed that the linear regression is the best to fit the relationship between  $\text{Cu}^{2+}$  concentration–time (stripping voltammetry) and conductance–time (conductance measurements). The inhibition efficiencies of the organic substances during the active stage of copper dissolution are generally lower than in the incubation period. The increase in temperature and nitric acid concentration brought about a parallel increase in the corrosion rate. Galvanostatic polarization measurements, using simple circuit, were used to study the corrosion process of copper in nitric acid.

Khodari et al.<sup>(24)</sup> investigated the kinetics of copper dissolution in nitric acid solution. The anodic stripping voltammetry and the conductance measurements, were used also, galvanostatic polarization measurements using very simple circuit used to study the corrosion process of copper in nitric acid. The effect of several factors was studied, namely nitric acid concentration, the copper surface area and stirring. The effect of inorganic substances and their role as inhibitors or promoters was also investigated.

By applying the anodic stripping voltammetric technique it was found that the rate of copper dissolution during the incubation period is constant and time independent. Also, stirring prevents the corrosion of copper almost completely.

Henríquez-Román et al. <sup>(25)</sup> investigated a theoretical study of some aniline derivatives toward the corrosion of copper in hydrochloric acid by applying cluster models for aniline–copper surface systems and ab initio Hartree Fock calculations. This study showed that the interaction of aniline molecules is highly favored in surface defects like the corner. The adsorption energy increases in several orders of magnitude rising from 30 to 67 Kcal/mol. The interaction occurs between the surface defect and the amino group of the aniline molecule. The adsorption energy increases with anilines possessing electron donor substituent's and decreases with anilines possessing electron acceptor substituents. These results showed that the corrosion inhibition by aniline molecules can be associated mainly to local properties acting on highly active sites, like defects, present in the copper surface. In addition, the possibility of ion pair formation between protonated aniline and chloride ion, and its influence on the general adsorption of aniline on copper is also analyzed.

The inhibition of corrosion of copper in hydrochloric acid by 2-mercapto-1-methylimidazole was investigated using dc polarization, ac impedance and weight loss techniques <sup>(26)</sup>. A significant decrease in the corrosion rate of copper was observed in the presence of the investigated

compound. The corrosion rate was found to depend on the concentration of the inhibitor. The degree of surface coverage of the adsorbed inhibitor is determined by ac impedance technique, and it was found that the results obey the Langmuir adsorption isotherm. The potentiodynamic polarization data indicated that the inhibitor was of mixed type, but the anodic effect is more pronounced. The slopes of the cathodic and anodic Tafel lines are approximately constant and independent on the inhibitor concentration. This inhibitor lowered the corrosion reaction by blocking the copper surface through physical and chemical adsorption. The mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitor. Also, some thermodynamic data for the adsorption and dissolution processes are calculated and discussed. The reactivity of the compound under investigation was analyzed through Fukui indices, which are reactivity descriptors derived from density functional theory (DFT), to explain the great efficiency of this compound as corrosion inhibitor comparatively to other imidazole derivatives.

The influence of derivatives of 1,2,4 triazole, 3-amino 1,2,4-triazole (ATA), 3-amino 5-mercapto 1,2,4 triazole (AMT) and 3-amino 5-methylthio 1,2,4 triazole (AMTT) and ionic surfactants cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) on the corrosion control of copper in acidic solution was investigated by Lalitha et al. <sup>(27)</sup> using gravimetric and electrochemical methods. The combined effect of triazoles and surfactants was also evaluated. Electrochemical parameters

like corrosion potential corrosion current density, corrosion rates and inhibition efficiencies were determined. The results reveal the fact that of the AMTT shows best inhibition and anionic surfactant SDS protects the surface better than the cationic surfactant CTAB. The polarization data reveals that all inhibitors behave as a mixed type inhibitor. Adsorption of these inhibitors on the surface of copper is found to obey the Langmuir adsorption isotherm. A marked inhibition synergism effect is shown by all the combinations of triazole and surfactant.

Phthalazin derivatives were used as corrosion inhibitors for dissolution copper in 1M H<sub>2</sub>SO<sub>4</sub> using electrochemical polarization and weight loss techniques <sup>(28)</sup>. This study monitored the evolution of the inhibitory effect of the phthalazin derivatives, according to their substituents. A significant decrease in the corrosion rate of copper was observed in the presence of the investigated inhibitors. The inhibition efficiency increases with increasing inhibitor concentration. The potentiodynamic polarization data indicated that, the inhibitors were of mixed type, but the cathodic effect is more pronounced. The slopes of the cathodic and anodic Tafel lines are approximately constant and independent on the inhibitor concentration. The mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitors. The adsorption on the copper surface follows the Langmuir isotherm model.



The efficiency of two organic compounds of the triazoles type namely: bis [4-amino-5-hydroxy-1,2,4-triazol-3-yl] methane and bis [4-amino-5-hydroxy-1,2,4-triazol-3-yl] butane as corrosion inhibitors for copper in 4.0M HNO<sub>3</sub> solutions at 25°C was investigated using both weight loss and galvanostatic polarization techniques <sup>(29)</sup>. The results showed that the predominant action of the inhibitors was cathodic. The two inhibitors proved to be effective (>99%) with long term effectiveness. Galvanostatic polarization measurements confirm weight loss measurements

The homologous series of aromatic secondary amines with various substituents have been investigated as corrosion inhibitors for copper dissolution in hydrochloric and sulfuric acids using electrochemical and gravimetric measurements <sup>(30)</sup>. The nonsubstituted secondary amine [N-(2-furfuryl)-p-toluidine] has the least-effective inhibiting properties. The introduction of substituents (-Cl, -Br, -NO<sub>2</sub>, -CH<sub>3</sub>) in the 5-position of N-(2-furfuryl-p-toluidine) increased the degree of copper protection in acidic media. The comparison of results obtained in hydrochloric acid with those related to sulfuric acid point to the activity of electrolyte anions.

The inhibitive efficiency of imidazole and its derivatives, 4-methylimidazole, 4-methyl-5-hydroxymethylimidazole, 1-phenyl-4-methylimidazole, and 1-(p-tolyl)-4-methylimidazole of copper in 0.5M hydrochloric acid was studied using potentiodynamic methods <sup>(31)</sup>. 1-(p-tolyl)-4-methylimidazole has the best inhibition efficiency. Activation energies were obtained by measuring the temperature dependence of the

corrosion current. The activation energies in the presence of the various inhibitors are low (3-5 KJ/mol), with the best inhibitor showing the highest value. The adsorptive behavior of the imidazole derivatives on the copper electrode surface follows a Freundlich-type isotherm. The standard free energies of the adsorption are also low (14-16 KJ/mol), indicating that imidazole and its derivatives physisorb on the copper surface.

Falewicz and Kuczkowska <sup>(32)</sup> have studied the utility of nitrilo-trimethylene phosphoric acid as inhibitors for the protection of copper and brass in neutral aqueous media. They found that this compound in combination with phthalic acid anhydride and zinc ions can serve as an excellent inhibitor for the corrosion protection of industrial cooling and heating water installations. Zucchi et al. <sup>(33)</sup> have investigated the usefulness of pyrimidine and thiadiazole derivatives as inhibitors for the corrosion of copper in NaCl solutions. The inhibition of commercial 67/33 brass in HCl (0.1M) acid solutions by some amino pyrazole derivatives 3(5)-amino, 5(3)-phenyl pyrazole; 3(5)-amino, 5(3)[4-chlorophenyl] pyrazole; 3(5)-amino, 5(3)[4-methoxy phenyl] pyrazole; 3(5)-amino, 5(3)[4-methyl phenyl] pyrazole; 3(5)-amino, 5(3)-cyano pyrazole; and 3(5)-amino, 4-phenyl-5(3)-methyl pyrazole was tested using polarization, capacitance and weight-loss measurements <sup>(34)</sup>. These compounds predominate as cathodic inhibitors and inhibition efficiencies up to 91% were obtained. Some triaryl and trialkyl phosphates have been investigated as corrosion inhibitors for copper in HNO<sub>3</sub> solutions <sup>(35)</sup>. The inhibition efficiency from weight loss

measurements was in good agreement with those obtained from polarization studies.

Ethoxylated fatty acids from soybean oils having the general formula  $R\text{-COO}(\text{CH}_2\text{-CH}_2\text{O})_n\text{-H}$ , where R is mainly a mixture of  $\text{C}_{17}\text{H}_{29}$ ,  $\text{C}_{17}\text{H}_3$  and  $\text{C}_{17}\text{H}_{33}$  and (n) is the number of ethylene oxide per mol ( $n = 10, 16, \text{ and } 30$ ) have been used as corrosion inhibitors for copper in 2M  $\text{HNO}_3$  <sup>(36)</sup>. The inhibition efficiency of the tested compounds was determined from weight loss and polarization measurements. At higher additives concentrations the inhibition efficiency starts to decrease. In presence of one and the same inhibitor concentration, the surface coverage increases with increasing the number of ethylene oxide. Inhibition of copper corrosion by these compounds is assumed to take place *via* a blocking adsorption mechanism, i.e. they inhibit both the cathodic and anodic reactions. This is the case actually supported from comparison of both the protection efficiency of the corrosion reaction,  $P_{\text{icorr}}$ , and the protection efficiency of the cathodic reaction,  $[P_{\text{io}}/P_{\text{icorr}} \sim 1]$ .

The effect of the some azoheterocyclic dyes of the type 3-arylazo 1,2,4-triazole (AT) on the corrosion of copper in nitric acid solution at different temperatures and at different AT concentrations has been investigated <sup>(37,38)</sup>. Potentiodynamic polarization and Tafel electrochemical methods have showed that, AT compounds are good inhibitors of copper corrosion in  $\text{HNO}_3$  solution. The effect of 1-[N,N-bis-(hydroxyethyl)aminomethyl]-benzotriazole (BTLY) on the corrosion and

dezincification of a 60/40 brass in aqueous  $\text{H}_2\text{SO}_4$  at  $30^\circ\text{C}$  has been investigated by means of solution analysis, potentiodynamic and surface enhanced Raman scattering (SERS) techniques <sup>(39)</sup>. Overall, the inhibition (for copper and zinc dissolution) increased on increasing the inhibitor concentration to a maximum (63.1%) at the  $5 \times 10^{-4}$  M this was comparable to that observed for benzotriazole (BTAH) under the same conditions. Solution analysis indicates that the compound BTLY is in effective in preventing dezincification. Polarization studies show that the compound BTLY acts initially to suppress the cathodic and anodic corrosion reactions.

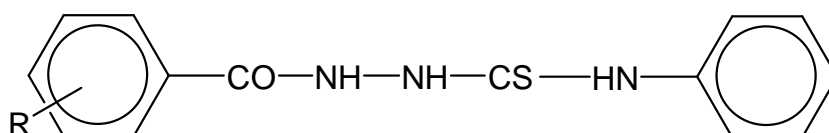
Fouda et al.<sup>(40)</sup> studied the effect of some substituted phenols as corrosion inhibitors for copper dissolution in 2N  $\text{HNO}_3$  by weight loss and galvanostatic polarization techniques. Polarization data suggested that in case of inhibitors, the cathode is preferentially polarized under the influence of the external current. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm. The inhibiting effect of tested compounds is due to the destruction of the  $\text{HNO}_2$  formed and its interference with cathodic reaction.

Baccaria et al.<sup>(41)</sup> examined the inhibitive efficiency of glucose, fructose, mannose and galactose on copper corrosion 0.1-1M nitric acid at  $15-30^\circ\text{C}$ . The structures of the various saccharides (pyranosic for furanosic) affect neither the efficiency nor the mechanism of inhibition. Inhibition was practically zero at the monosaccharides concentration of  $10^{-3}$ - $10^{-1}$  M. At 1.0M, 65-70% inhibition was reached in 0.01 and 0.1M nitric

acid and 50-60% in 1.0M acid. In 1.0M nitric acid, the saccharides acted as cathodic inhibitors, whereas in 0.1 and 0.01M nitric acid they also acted as anodic inhibitors by forming an organometallic compound containing  $\text{Cu}^{2+}$ .

Mor <sup>(42)</sup> studied the behaviour of copper in 1M solutions of HCl,  $\text{HNO}_3$  and HCl- $\text{HNO}_3$  mixture, containing various amount of tannic acid. As tannic acid is a mixture of galloylglucose, the same mineral acids containing gallic acid or glucose have also been studied. Glucose inhibits the corrosion of copper in  $\text{HNO}_3$  solution to a very slight extent and has no effect in other solutions. Gallic and tannic acids have no effect in HCl but, at the highest concentrations tested, show an inhibitive efficiency of 80% and 70% respectively, in  $\text{HNO}_3$  and in 65-70% HCl- $\text{HNO}_3$  mixtures. Gallic acid may be considered to be a cathodic inhibitor that does not interfere directly with the cathodic process but modifies the corrosive environment. Tannic acid behaves both as cathodic and anodic inhibitor due to the formation of oxidizing compound that is adsorbed on the copper surface.

The effect of 1-benzoyl-4-phenyl-3-thiosemicarbazide derivatives as corrosion inhibitors for copper in 3M nitric acid solution <sup>(43)</sup> by galvanostatic polarization and weight loss methods was studied. The chemical structure of these derivatives are :



- |                   |                  |
|-------------------|------------------|
| (a) R = p-Methoxy | (b) R = p-Methyl |
| (c) = o-Methyl    | (d) = o-Hydroxy  |
| (e) = o-Chloro    | (f) = Hydrogen   |
| (g) = p-Nitro     |                  |

The used additives act as mixed type inhibitors. The results of polarization measurement carried out for the inhibition efficiency of the additives agreed with those obtained from weight loss. The order of decreasing inhibition efficiency is :  $a > b > c > d > e > f > g$ .

The adsorption of these compounds on the surface of copper metal obeys Langmuir adsorption isotherm, but the gradient is not equal to unity as expected for the ideal behaviour. This deviation from unity can be explained on the interaction between the adsorbed species on the metal surface. The inhibition efficiency of copper in nitric acid solution depends on the polar character of substituents, their molecular structure and concentration.

Gomah <sup>(44)</sup> studied the behaviour of copper in 3M nitric acid containing various concentrations of 2-(acetoacetamido)pyridinearyl-hydrazone derivatives as corrosion inhibitors. Galvanostatic polarization and weight loss techniques are used to determine the inhibition efficiency of these compounds over the concentration range  $5 \times 10^{-6}$  -  $1 \times 10^{-3}$  mol/l. it is evident that nearly complete inhibition is attained at a concentration of

$10^{-3}$  -  $4 \times 10^{-2}$  mol/l for all compounds. The order of decreasing inhibition efficiency over the concentration range  $5 \times 10^{-6}$  -  $1 \times 10^{-3}$  mol/l is: VII > VI > III > II > I.

The efficiency of poly(4-vinylpyridine) (I) as an inhibitor for acid corrosion of Cu was investigated <sup>(45)</sup>. The effect of (I) on the corrosion rate was measured in 3M HNO<sub>3</sub> at various temperature and concentrations. (I) had a significant inhibiting effect on the corrosion of the metal; protection efficiencies approaching 80% were measured. The results of the apparent activation energies in absence and presence of the inhibitor suggest that (I) do not change the mechanism of the rate-determining step of the corrosion process. The mechanism of inhibition was proposed on the basis of the formation of a protective film by (I) molecules on the metal surface.

Zhou et al. <sup>(46)</sup> used 2-mercapto benzimidazole (MBI) as a copper corrosion inhibitor in aerated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solutions. A synergistic effect existed when MBI and iodide ions were used together to prevent copper corrosion in sulfuric acid. It was found that IE reached 95.3% in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solutions containing 0.75 mmol L<sup>-1</sup> MBI and 0.25 mmol L<sup>-1</sup> KI. X-ray photoelectron spectroscopy (XPS) analysis of the copper samples showed that a (Cu<sup>+</sup> MBI) complex<sup>-</sup> film formed on the surface to inhibit the copper corrosion and the iodide ions did not participate in the formation of the inhibitor film. The synergistic effect was attributed to the adsorption of

iodide anions on the copper surface, which then facilitated the adsorption of protonated MBI and the formation of an inhibitive film.

The electrochemical behavior of copper (Cu), iron (Fe) and Cu–20%Fe alloy was investigated by El-Egamy <sup>(47)</sup> in 1.0 M sodium chloride solution of pH 2. The effect of thiourea (TU) addition on the corrosion rate of the Cu–20%Fe electrode was also studied. Open-circuit potential measurements (OCP), polarization and electrochemical impedance spectroscopy (EIS) were used. The results showed that the corrosion rates of the three electrodes follow the sequence: Cu < Cu–20%Fe < Fe. Potentiostatic polarization of the Cu–20%Fe electrode in the range -0.70 V to -0.45 V (SCE), showed that iron dissolves selectively from the Cu–20%Fe electrode surface and the rate of the selective dissolution reaction depends on the applied potential. At anodic potential of -0.45 V, thiourea molecules adsorb at the alloy surface according to the Langmuir adsorption isotherm. Increasing thiourea concentration (up to 5 mM), decreases the selective dissolution reaction and the inhibition efficiency reach 91% at [TU] > 5 mM, the dissolution rate of the Cu–20%Fe electrode increases due to formation of soluble thiourea complexes. At cathodic (-0.6 V), the inhibition efficiency of thiourea decreases markedly owing to a decrease of the rate of the selective dissolution reaction and/or desorption of thiourea molecules. The results indicated that thiourea acts mainly as inhibitor of the selective dissolution reaction of the Cu–20%Fe electrode in chloride solution.



Self-assembled monolayers (SAMs) derived from adsorption of allyl thiourea onto the surface of copper in ethanol solution were evaluated in neutral aqueous sodium chloride solutions<sup>(48)</sup>. The electrochemical behaviors and anticorrosion features of copper in the presence of allyl thiourea in neutral aqueous sodium chloride solutions were investigated using electrochemical techniques. SAMs of allyl thiourea against copper corrosion hinder the copper oxide formation. Protective properties of allyl thiourea layers on copper surfaces depend on the applied potential, the concentration of allyl thiourea and the chloride ions in the environment.

Vera et al.,<sup>(49)</sup> studied the efficiency of 1,5-bis(4-dithiocarboxylate-1-dodecyl-5-hydroxy-3-methyl-pyrazolyl)pentane (BDTCPP) as copper corrosion inhibitor in 3.5% NaCl solutions by electrochemical polarization methods (Tafel extrapolation and polarization resistance method), electrochemical impedance spectroscopy and immersion assays. Results obtained in this study reveal that BDTCPP is a good inhibitor and the potentiodynamic polarization studies clearly show that BDTCPP is a mixed-type inhibitor for copper in chloride solutions. It decreases the anodic reaction rate more strongly than the cathodic reaction rate and it renders the open circuit potential of copper more positive in 3.5% NaCl solutions. The UV analysis of the protective layer of BDTCPP after corrosion experiments shows that the inhibitor prevents copper corrosion by physisorption on the metal surface, followed by chemisorption of a protective Cu(II)-complex. This Cu (II) is generated by oxidation of the Cu

(I) ion formed at the beginning of the corrosion process in the aerated solution of NaCl.

The effects of benzimidazole (BIM) and 2-methylbenzimidazole (MBIM) on the electroreduction of Cu(II) on a rotating Pt disk electrode in chloride media were investigated by Scendo, Hepel<sup>(50)</sup>. These studies undertake in conjunction with earlier observation that these imidazole derivatives act as inhibitors of copper corrosion processes and are non-toxic. BIM and MBIM also form adsorption films on Pt which are able to inhibit one-electron reduction of Cu(II) to Cu(I) and prevent the development of convective diffusion limiting current wave. The inhibition found to be controlled by electric field-assisted mass transfer through the film. The ingress of Cu(II) species into the film detected using the EQCN technique. The EQCN measurements indicate that small fraction of Cu(I) formed in the film by reduction of Cu(II) is retained in the film, most likely in the form of CuCl. The amount of CuCl retained in strongly inhibiting films (e.g., at lower pH) is diminished. The inhibition effectiveness of Cu(II) reduction process by Pt–BIM and Pt–MBIM films increases strongly with increasing acidity of the medium in the pH range from 3 to 1. The mechanism of this remarkable pH effect has proposed. The orientation of inhibitor molecules on an electrode surface evaluated using quantum mechanical calculations for a BIM molecule physisorbed on a model Pt<sub>18</sub> atom cluster.

The inhibiting action of two new Schiff bases namely SB<sub>1</sub>: 2-(4-methyl-3-[(2-sulfanyphenyl)imino]butylidene/amino)-1-benzenethiol and SB<sub>2</sub>: 2-(4-(1,2-diphenyl-2-[(2-sulfanyphenyl)imino]ethylidene/amino)-1-benzenethiol on the corrosion of copper in hydrochloric acid was studied<sup>(51)</sup>. The Schiff bases synthesized and studied as inhibitors for corrosion of copper. Results of electrochemical impedance and Tafel polarization measurements consistently identify both compounds as good inhibitors. Impedance spectroscopy revealed that the corrosion of copper in hydrochloric solution influenced to some extent by mass transport since the Warburg impedance observed in some cases. Polarization curves indicate that both studied Schiff bases act as mixed type (cathodic/anodic) inhibitors. Differences in inhibition efficiency between SB<sub>1</sub> and SB<sub>2</sub> are correlated with their chemical structures. Langmuir isotherm is found to provide an adsorption description of Schiff bases.