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Effect of the alloying elements on behavior of corrosion resistance and mechanical properties of alpha brass alloys

Graduation research
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بسم الله الرحمن الرحيم

يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ (١١)

صدق الله العلي العظيم

{سورة المجادلة}

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Baneen Shakir Jawad
2023

Dedication

To my role model, and my ideal in life .... My father

To those who can't find words that can give her right.
.... My mom

To my support, my muscles .... My brothers

To the highest symbols of sincerity, loyalty and the
companions of the path .... My friends

To the honorable ones who did not hesitate to extend
a helping hand to me ..... My teachers?

I dedicate my humble research to you

Supervisor Certificate

I certify that this Graduation research entitled (Effect of the alloying elements on behavior of corrosion resistance and mechanical properties of alpha brass alloys) is prepared by Banen Shaker Jawad under my supervision in the Department of Metallurgical Engineering/ College of Materials engineering / University of Babylon in partial fulfillment of the requirement for the Bachelor's degree in Materials Engineering/ Metallurgical Engineering.

Signature

Dr. Ali Hubi Haleem

Date : / 6 / 2023

Abstract

Corrosion is a natural process which converts the refined metals to a more stable form, such as its oxides, hydroxides or sulfides. It is a metal gradual destruction by chemicals and /or electrochemical reactions with its environments. The corrosion engineering is the field devoted to monitor and stop corrosion. Brasses used in heat-exchangers tubes and condensers areextensively subjected not to corrosion only, but to corrosion/erosion phenomenon, these tubes are widely used in power plants, ships, desalination plants, oil, petrochemical plants, refineries, and other industries.

Samples were prepared by die-casting. Aluminum as alloying element was individually added for the cast, such. Many relevant tests were conducted which include, simple immersion, Potentiostatic polarization, with and without inhibitor) and metallographic tests.

The present work represents an attempt to use an effective, available, not toxic, and almost cost free, organic material Palm frond extract to protect brass tubes used in heat exchangers.

The alloying elements aluminum added to the melt were produced significant improvements, in corrosion resistance, but they are costly.

The corrosion currents observed by the addition of Al for instance, in the samples {69. 65 Cu / 28.41 Zn / 1.53Al), were reduced to 0.13%. Compared to that observed with bar brass (reference sample) {A (69.53%Cu / 29.96% Zn)}.

The great improvement was introduced by the use of the cost free organic inhibitor. The corrosion current obtained by Potentiostatic polarization was only (≈0.05) of the corresponding value of the reference sample.

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CHAPTER ONE

Introduction

Chapter One

1 Introduction

Till now, Metallic materials are considered the most used materials around the world especially in the transportation industry and mechanical engineering. Metals are commonly used in electronics industries and it is also used in the industry of construction. However, one common problem that constrains the metals alloys usefulness is known as corrosion [1].

1.1 Definition Corrosion and Importance of Corrosion Problems

Corrosion is a material destruction that results from interaction with the environment. It is considered as major problem that should be dealt for economic reasons and safe environment [2]. Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment.

The three main reasons for the importance of corrosion are: economics, safety, and conservation. To reduce the economic impact of corrosion, corrosion engineers, with the support of corrosion scientists, aim to reduce material losses, as well as the accompanying economic losses, that result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, and so on. Corrosion can compromise the safety of operating equipment by causing failure of, for example, pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms. Safety is a critical consideration in the design of equipment for nuclear power plants and for disposal of nuclear wastes. Loss of metal by corrosion is a waste not only of the metal, but also of the energy, the water, and the human effort that was used to produce and fabricate the metal structures in the first place [3].

1.2 Corrosion inhibition

Adding of an inhibitor to the electrolyte is known as one method of inhibiting corrosion. Many studies on the addition of inhibitors have been done in the field of copper and brass corrosion inhibition in the different environments. The use of inhibitors is one method to reduce corrosion and to protect metals and alloys in the aggressive medium [4]. The role of inhibitors is to form a barrier of one or several molecular layers against acid attack. This protective action is often associated with chemical and/or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other [5].

In water –cooling systems, metals corrosion has great importance in the applications of industry. For lower pipes corrosion, inhibitors of heat exchangers corrosion have been applied widely. In cooling water systems, it is a known scientific fact that at the water/ metal contact of interface notice processes of frequent corrosion which gives an evidence about the corrosion products deposition, such as scales. Because of the formation of the scales exchanging heat turns to be even more difficult, which disturbs industrial installation of the normal function? So, using inhibitors is one way to decrease corrosion and for the protection of metals and alloys in such aggressive mediums [4].

1.3 Brasses

Copper and its alloys such as brasses. Fig (1-1), have been widely used because of their excellent thermal and electrical conductivities for several applications [6]. The corrosion resistance of copper and copper alloys has been attributed to a protective cuprous oxide layer, Cu2O, formed upon exposure [7]. Adding zinc to copper raises ductility, strength, erosion, corrosion resistance, and cavitation in waters. Alloys have also shown resistance to the corrosion of chloride-induced stress cracking. From these alloys, brasses are most commonly

Used in pipes and hoses for the transport of feed water, condensers systems and heat exchangers in various cooling water systems [8].

Brasses: blain brass, copper and zinc binary alloys, comes into two types of crystal structure.

a / Alpha Brass: it is a hard solution of zinc and copper and with a crystal structure FCC. Systems of zinc- copper have about 38% zinc, and

b / Alpha plus beta brasses (α+β) contain around 50% zinc [9].

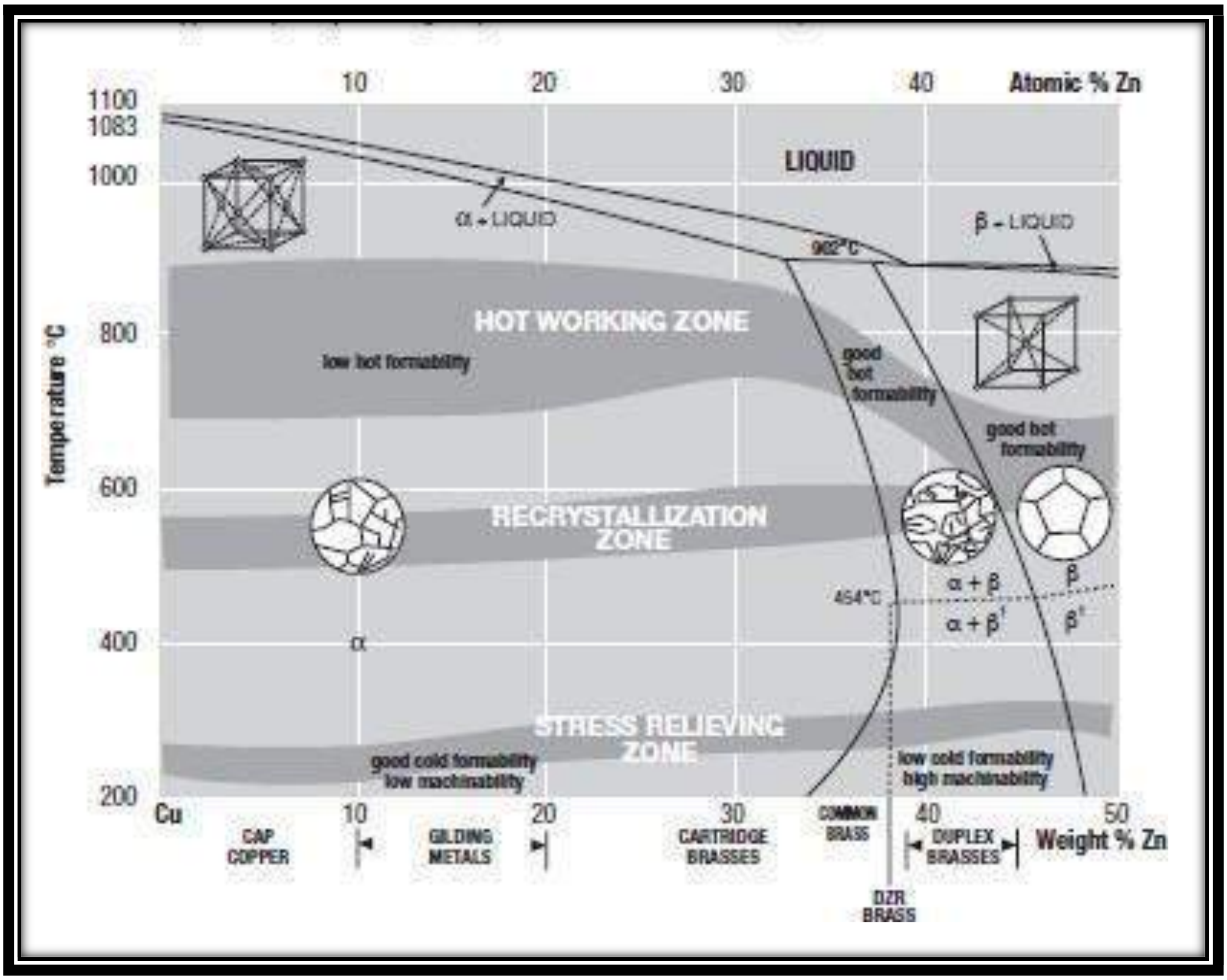


Fig (1-1): copper- zinc partial phase diagram [9].

Brass properties make it relatively noble and attractive. It has good mechanical and corrosion resistances, better resistance to biofouling, and high thermal and electrical conductivity. Brass has been widely used in the systems of water distribution, condensers, water treatment units, power plant condensers, desalination, shipboard condensers, petrochemical heat exchangers, and others. Dezincification of brass is one of the well-known and common processes by means of which brass loses its valuable physical and mechanical properties leading to failure of structure [10].

Dezincification, pitting corrosion, cracking of brass in water, and stress corrosion are studied widely. Dezincification or dealloying of brass can be seen without a microscope because of the distinctive color of alloy which is a reddish color which in turn contrasts with its yellowish color. In general, there are two kinds of dealloyings. Layer or uniform dealloying which takes place in alloys with high zinc in which the inside isn't affected while the outer layer is dealloyed and becomes dark; the second kind is Plug dealloying which is recognized by dealloyed dark plugs presence in the unaffected low zinc of alloys matrix [11]. Other elements may be added to modify properties such as strength, machinability, or corrosion resistance, although greater increases can be obtained by adding additional elements [12].

A well-known brass has 30% zinc and it is commonly known as ‘70/30’ or ‘cartridge’ brass, Cu-30%Zn – because of the ease with which the alloy can be drawn deeply for manufacturing cases of cartridge. Cases (up to 100mm diameter) begins as flat discs blanked from plate or strip and are formed successively to obtain its final shape by several operations, implemented at roomtemperature, which elongate the sidewalls and lowers their thickness. Cu-30%Znhas the best set of properties of minimal directionality, ductility, and strength, which gives it the ability of being cold drawn. Heat exchangers tubes are frequently manufactured from the brasses of alpha, often of Cu70/30Zn composition but have alloying additives which foster resistance for corrosion [13].

1.4 Aim of This Work

In this study, using alloying element aluminum with brass alpha (70%Cu-30%Zn) and after using Palm frond extracts as inhibitor. The used inhibitors were a bare plant (this inhibitor it has an almost cost free, available, nontoxic) to improve the corrosion resistance for this alloy. After that, the prepared samples by casting process were subjected to a number of tests to determine which is more effective in reducing the corrosion rate between adding aluminum by 1.5 wt. % or by the effect of adding organic inhibitor extracted from palm fronds. The tests included chemical analysis, microstructure, FTIR, and corrosion test by simple immersion test and Potentiostatic polarization,

CHAPTER TWO

Theory and Literature Review

Chapter Two

Theory and Literature Review

2.1 Introduction

Brass has been widely used in many industrial fields and investigating brass corrosion and inhibition is of great importance. Various inhibitors are used to decrease brass corrosion in different mediums [14]. One of the most important methods in the protection of copper and copper alloys against the corrosion is use of organic inhibitors [15].In general corrosion of brass tends to form a layer of zinc oxide which coats its surface. Insoluble film of cuprous chloride is adsorbed on the surface of the brass when dipping in chloride ion media [16].

2.2 Mechanical Properties of Brass

- Tensile strength: Brass has a low tensile strength.
- Hardness: with aluminum copper content and with cold working stresses, brass hardness increases.
- Ductility; the ductility of hammered copper alloys depends mainly on the extent of cold work. When heated, they all have high formability and lengthening ability. Low temperature on the other hand has minor effect on alloy ductility and they do not get fragile.
- Corrosion resistance: Alloys with approximately 15% of zinc may suffer from dezincification (a form of corrosion and weakening of brass objects in which zinc is dissolved out of the brass alloy), which causes porous, weak corrosion copper deposit. Dezincification resistance is greatly reduced by the adding a small quantity of arsenic to the alloy. Cracking dueto stress corrosion, especially by amines and ammonia, is another problem with the brasses. Alloys with more than 15% zinc are most liable to be influenced [9].

Corrosion

Metals corrosion is considered as one of the most challenging and serious problems worldwide. When metals contacts with various environments, like water, air, pollutants, or chemical products they start to degrade because of the interaction between the metal and its environment [17].

Metallic materials corrosion is classified into three groups :

1. Wet corrosion: in which the environment of corrosive is water or electrolyte solution. The process is electrochemical.
2. Corrosion: happens in other fluids like molten metals and fused salts.
3. Dry corrosion: in which the corrosive surrounding is a dry gas. Dry corrosion is also named as high temperature metal gas corrosion [18].

Two main areas are noticed in the corrosion of alloys and metals. The first one is where the alloy or metal is exposed to an electrolyte liquid, mostly water, and thus typically called aqueous corrosion. Second one is where corrosion happens in a gaseous environment, often called oxidation, High- Temperature Oxidation, or High-Temperature Corrosion, and here it is called as gaseous corrosion. Those two fields was (sometimes still are) referred to as dry corrosion and wet corrosion [19].

2.3 Type of Corrosion:

2.3.1 General corrosion

Is the most common form of corrosion types and it can be even or uneven as shown in Fig. (2-1). It is described by chemical or electrochemical reactions that occur on the metals surfaces. The metal becomes thinner and finally causes a failure. General corrosion can be prevented or decreased by the suitable choice of material or by use of cathodic protection or corrosion inhibitor [20].

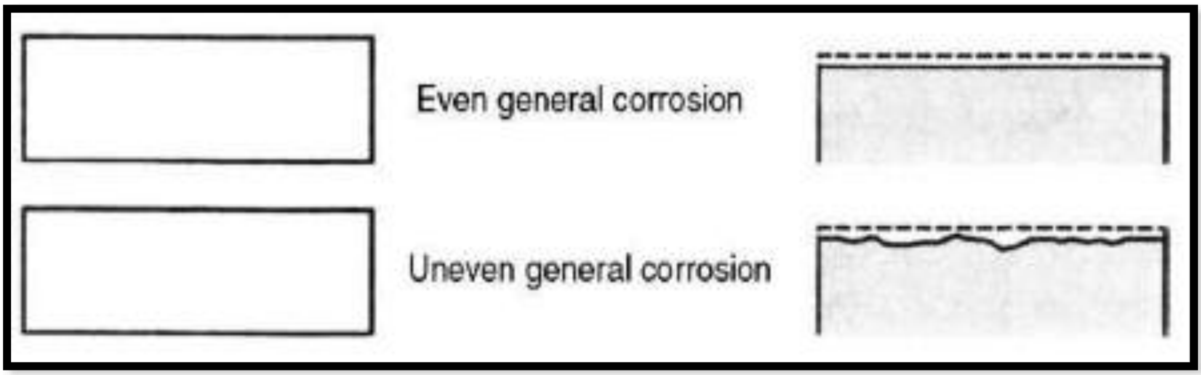


Fig. (2-1) General corrosion [20].

2.3.2 Localized Corrosion

The attack is characterized by the formation of severely corroded regions separated with sharp steps from neighboring areas with much less attack. Localized attack develops when the surface is partly covered with a protective film. The attack is usually associated with high flow rates. However, experiments have shown that localized attack can also be initiated and propagate under semi-stagnant conditions [21].

2.3.2.1 Pitting

Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Pitting corrosion can produce pits with their mouth open (uncovered) or covered with a semi-permeable membrane of corrosion products. Pits can be either hemispherical or cup-shaped [22], as shown Fig. (2-2).

Pitting is considered to be autocatalytic in nature; once a pit starts to grow, the conditions developed are such that further pit growth is promoted. The anodic and cathodic electrochemical reactions that comprise corrosion separate spatially during pitting. The local pit environment becomes depleted in cathodic reactant (e.g., oxygen), which shifts most of the cathodic reaction to the boldly exposed

Surface where this reactant is more plentiful. The pit environment becomes enriched in metal cations and an anionic species such as chloride, which electro migrates into the pit to maintain charge neutrality by balancing the charge associated with the cation concentration. [23]. Localized corrosion of copper, at least in the form of the pitting of copper water pipes, is a well-known phenomenon. Pit initiation involves the local breakdown of a Cu_2O film at grain boundaries or other surface defects. The pit propagates because of the permanentseparation of anodic and cathodic sites, with the anodic reaction localized in the bottom half of the pit under a porous Cu_2O membrane and the cathodic reaction (the reduction of Cu (II)) occurring in top half of the pit or (as the reduction of O_2)on the Cu surface around the periphery of the cap of corrosion products [24].

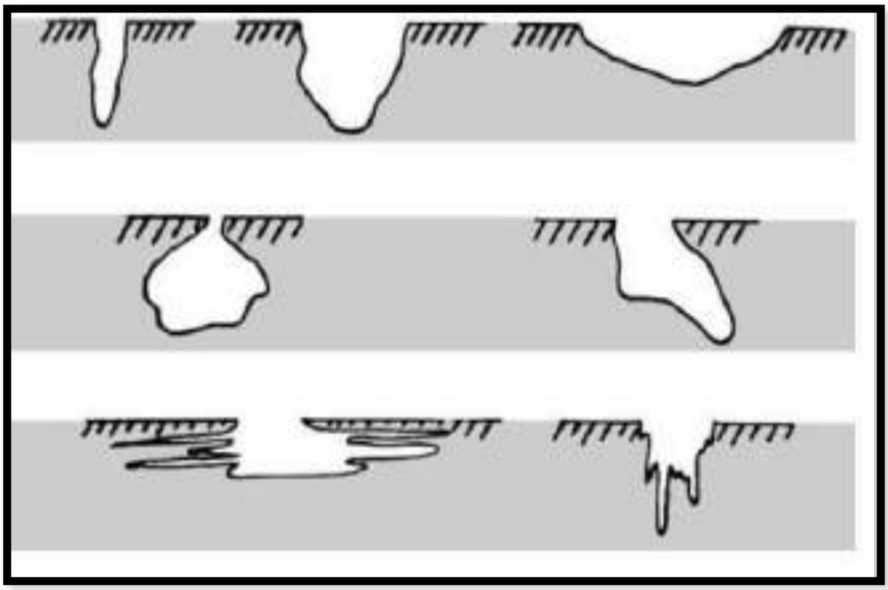


Fig. (2-2) Different shapes of corrosion pits [18]

2.3.2.2 Crevice Corrosion

Crevice corrosion occurs when part of the metal surface is shielded from the bulk environment. This may be because of deposits, or the crevice may be engineered such as those on a flange joint or under a washer on a bolt. Unlike the oxygen concentration cell that is required to initiate crevice corrosion on stainless steels, crevice corrosion of copper alloys depends on a copper ion concentration cell. As the metal corrodes, copper ions are released into solution, and in the bulk environment, they are either swept away or they precipitate as a copper compound such as copper oxide (Cu_20) or copper hydrochloride creviced area, there is a shortage of reactants to form copper compounds, and the copper ion concentration increases, making the metal in the creviced region cathodic to the metal outside the crevice. Corrosion occurs at the anodic region just outside the crevice, often along much of its length [12].

In the beginning of the reaction, the metal ions go into solution at anodic sites and oxygen is reduced to hydroxyl ions at cathodic sites. Corrosion is initially uniform over the entire area including the crevice. As the corrosion continues in the crevice, oxygen become depleted and cathodic oxygen reduction stops. Metal ions continue to dissolve at anodes inside the crevice, leading to produce a surplus of positive charges in the solution. Now, the negatively charged chloride (or any other anions) emigrate to the developing anodes to keep the electro neutrality. They form as a catalyst, accelerate the corrosion. At this point, the crevice corrosion is completely established and the anodic reaction continues with ferrous ions [Fe+2] going easily into solution [25], this is shown in Fig. (2-3).

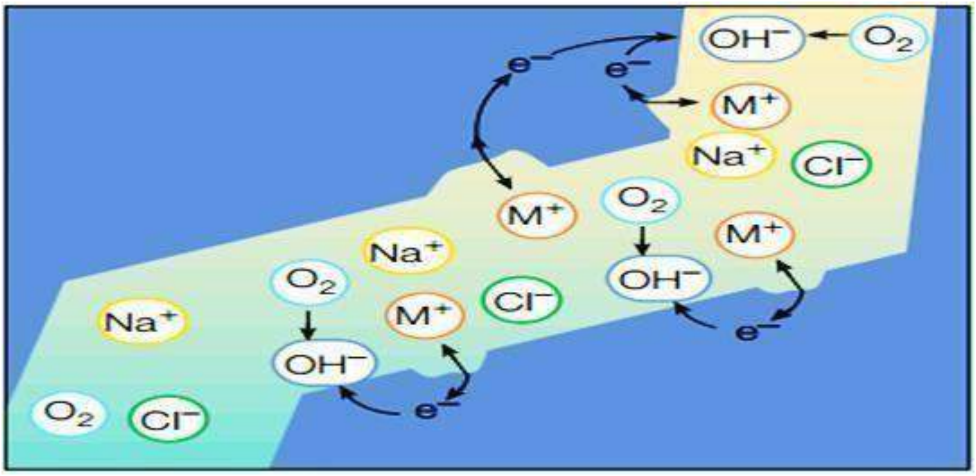


Fig. (2-3): Crevice Corrosion [25].

2.3.2.3 Galvanic corrosion

Galvanic corrosion tends to occur when dissimilar conducting materials are connected electrically and exposed to an electrolyte, figure (2-4). The following fundamental requirements therefore have to be met for galvanic corrosion:

1. Dissimilar metals (or other conductors, such as graphite).
2. Electrical contact between the dissimilar conducting materials (can be direct contact or a secondary connection such as a common grounding path).
3. Electrolyte (the corrosive medium) in contact with the dissimilar conducting materials [26].

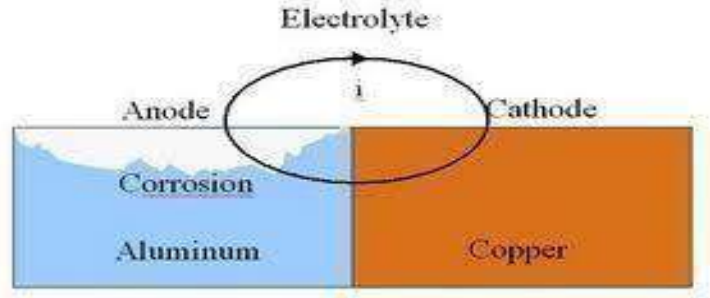


Fig. (2-4) galvanic corrosion [26].

2.3.2.4 Stress Corrosion Cracking

Stress corrosion cracking (SCC), or environmentally assisted cracking, requires a specific corrosive environment and a simultaneous stress for it tooccur. The environments that can cause SCC are often specific to a metal or alloy, for example, the cracking of titanium in methanol. There are several environments that can cause SCC of copper and its alloys, of which the best known is ammonia (NH_3). The stress to cause cracking can be an externally applied load due to service conditions or an internal stress due, for instance, to welding or cold working. SCC is not a new phenomenon; so-called season cracking of brass cartridge cases and other brass items has been known for over 150 years. The environment that caused the cracking was airborne ammonia, and the stress was the residual stress in the deep-drawn cartridge cases [12], as shown Fig. (2-5**).**

The factors determining the mechanisms and the course of development can be sorted into three main groups:

1. Environmental and electrochemical factors.
2. Metallurgical factors.
3. Mechanical stress and strain

The study of SCC is typically multidisciplinary, i.e. the description of the three groups of factors and their effects belong to three different technological disciplines, namely electrochemistry/corrosion, physical metallurgy and fracture mechanics [18].

Fig. (2-5) Stress corrosion of metal [26]**.**

2.3.2.5 Intergranular Corrosion

Intergranular corrosion refers to preferential corrosion along the grain boundaries. Grains are ‘crystals’ usually on a microscopic scale that constitute the microstructure of the metal and alloys. It has been defined commonly as a formof localized attack on the grain boundaries of a metal or alloy in corrosive media, which results in the loss of strength and ductility. The localized attack may lead to dislodgment of the grain. It works inwards between the grains and causes moreloss of strength than the same total destruction of metal uniformly distributed overthe whole surface . The attack is distributed over all the grain boundaries cutting the surface. Intergranular corrosion is less dangerous than stress corrosion, which occurs when stress acts continuously or cyclically, in a corrosive environment, producing cracks following mostly Intergranular paths [27]. This type of corrosion may have extreme effects on mechanical properties, resulting in a loss of strength and ductility ,this is shown in Fig.(2-6).

Fig. (2-6) Intergranular corrosion of metal [26].

2.3.2.6 Corrosion Fatigue

Corrosion fatigue is a process in which a metal fractures by fatigue prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels than would be otherwise required in the absence of a corrosive

Environment. Metals and alloys will crack in the absence of corrosion if they are subject to high cyclic stress for a number of cycles. The number of cycles for failure decreases as the stress is increased. Below a certain stress the metal will last indefinitely. This level is termed as ‘*Endurance Limit’* of the material. If, however, the material under cyclic stress is subject to a corrosive environment, the endurance limit of the material is sharply reduced. The premature failure of a material from the exposure to the combined action of corrosion and cyclic stress **is called ‘*Corrosion Fatigue*** [27].His coauthors have grouped forms of corrosion depicted graphically in figure (2-7) in the following three categories [18]

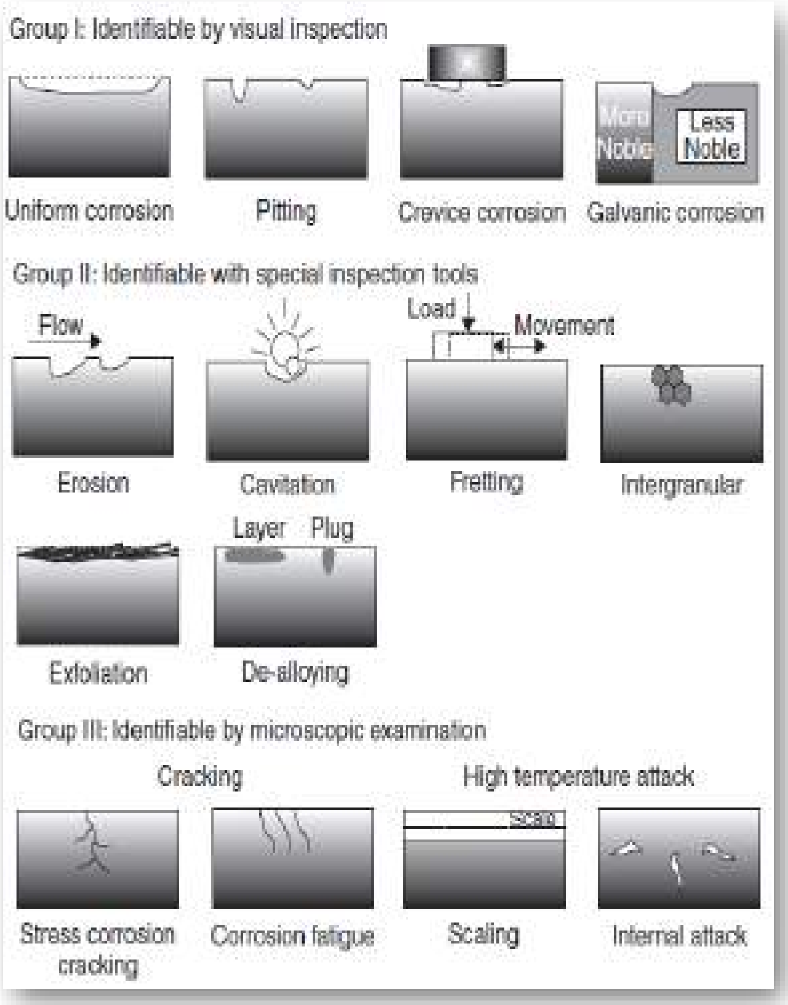


Fig.(2-7): Schematics of the common forms of corrosion[28].

2.4 Factors Affecting Corrosion in corrosion media

2.4.1 pH

In water that has air and lower than 5 pH, tubes will be quickly thinned and corroded, this is because the protective film will not be easily to form tubes that are made of copper alloy. Copper alloy gives good resistance for water whose air has been coming out and its pH is low also. Tubes made of stainless steel or copper- nickel alloy at high pH are more suitable to admiral tubes (71% copper, 28% brass and 1% tin) or aluminum-brass alloy tubes which get corroded at alkaline pH [29].

2.4.2 Oxygen and Sulfate

Soluble oxygen in water causes corrosion in the converter tubes. Sodium sulfites or corrosion preventive substances are added to the water, to reduce the amount of oxygen in it. Sulfates also produce calcium sulfate sediment byCalcium in water which is involved in creating corrosion. Copper alloy is not resistant in dirty waters whose oxygen is constantly used for corrosion and sulphate is also present [29]. It is readily that the effect of oxidizer additions or the presence of oxygen on corrosion rate depends on both the medium and metalsinvolved. The corrosion rate may be increased by addition of oxidizers, oxidizersmay have no effect on the corrosion rate, or a very complex behavior may be observed [30].

There are two compounds of corrosion for copper environments that have oxygen: CuO (cupric oxide) and Cu_2O (cuprous oxide). The quantity of cupric oxide and cuprous oxide has major effect on copper corrosion development [31]. In air saturated water, the initial concentration rate at the room temperature reaches high and this rate diminishes over a period of days as rust film is formed and acts as a barrier to oxygen diffusion [26].

2.4.3 Temperature

Cu-base alloys are liable to harsh corrosion under boiling heat transfer conditions. Rate of corrosion which is determined by the mechanism of corrosion for copper directly affects the service life at high temperature. Layers of corrosion product even can peel off because of corrosion and surface film growth and degrade copper. Copper degradation will cause temporarily failure and is very troubling. So, the behavior of corrosion and the copper stability in high temperatures are of great importance and it is important to evade corrosion products formation and the process of degradation of copper in order to expand its service life through studying the behavior of corrosion and copper stability [31].

As a rule, the degree of corrosion increases with increase in temperature, but increasing temperature also tends to drive dissolved gases out of solution so that a reaction that requires dissolved oxygen can often be slowed down by heating. There are numerous cases where metals satisfactory for cold solutions are unsuitable for the same solutions at elevated temperatures [32].

2.5 Types of Corrosion in Brass:

Corrosion happens when a material interacts with the surrounding environment and deteriorates because an electrochemical reactions consume the material via oxidation [33].

Copper based alloys are used in sea water system for applications like pumps, valves, fasteners, pipes, and heat exchangers. Relaying on the application and the need for mechanical features, Copper Alloys still widely used. They have good mechanical features along with good resistance to corrosion in sea water.

Nonetheless, certain types of corrosion may happen like localized corrosion [34]. A specific environment, passive material corrodes very little, even though it would otherwise corrode considerably. On the contrary, alloys show passivity is

Invariably quite active in the non-passive state. Some elements break down passive films, causing corrosion of metal where the film is broken [32].

Degradation of copper alloys surface forms adhering hydroxide and an oxide film which shorten metal transportation of ions of the layers interacting with the medium that promoting the protection of the metal surface [35]. Corrosion environment variables, including fluid velocity, temperature, and composition, can have a decided influence on the corrosion properties of the materials that are in contact with it [36].

2.5.1 Dealloying /Dezincification

DE alloying, also known as selective leaching, is a rare corrosion form in which one element extracted from a metal alloy and as a result the structure is altered. Dezincification is the most known form of selective leaching, in which zinc is taken out from brass alloys or from alloys that have zinc [37] Dezincification of brasses takes place in either localized area on the metal surface, called plug type, or uniformly over the surface, called layer type. A plug of dezincified brass may blow out leaving a hole, while a water pipe having layer type dezincification may split open [38].

The most common example of selective corrosion is dezincification of brass, in which zinc is removed from the alloy and copper remains. After cleaning the surface, dezincification is easy to demonstrate because the Zn–depletedregions have a characteristically red copper color in contrast to the original yellow brass. Dezincification occurs in two forms, see Fig. (2-8).

a) Uniform (layer) dezincification, where the front of the selective attack moves more or less uniformly through the material. This form is favored by high Zn content and acidic solutions.

b) Localized (plug-type) dezincification, where the localization and form of attack are determined more or less arbitrarily. This type occurs more often in alloys with somewhat lower Zn content and in neutral, alkaline and slightly acidic solutions. The liability to dezincification increases with increasing Zn content and temperature and is promoted by a stagnant solution, porous surface layers and oxygen in the corrosive medium (but oxygen is not strictly necessary) [18].

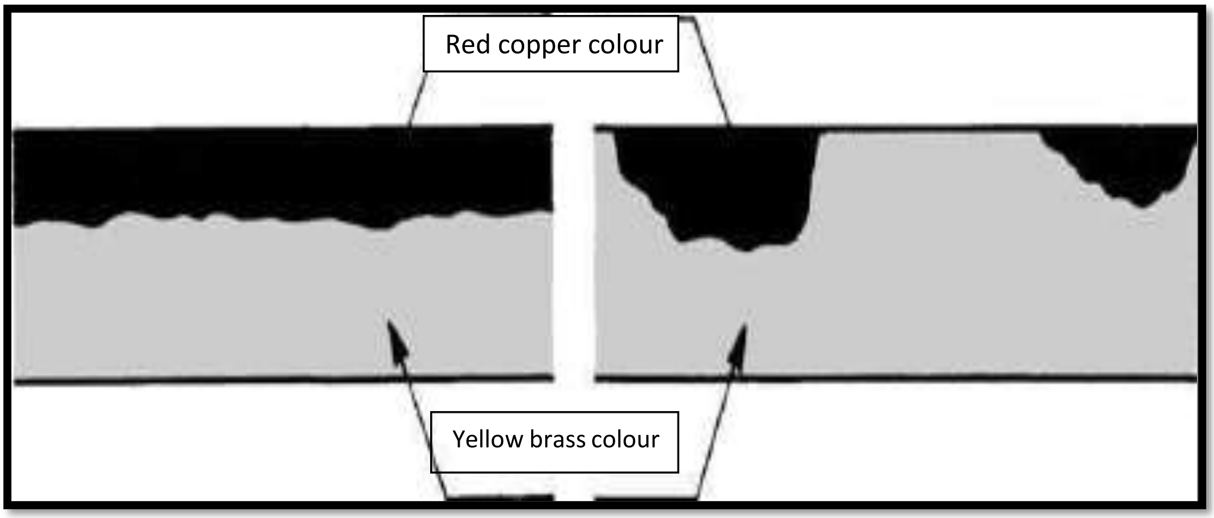


Fig. (2-8) a) Uniform (layer) dezincification and b) localized (plug–type) dezincification of brass [18].

These two attack types can be seen and in the type of uniform dezincification, leaching out over a wide area of the surface the active area is not localized to a specified point in the surface. Furthermore, Plug kinds of attack are localized; in a determined point on the surfaces and the surrounding areas do not effect. Dezincification may take place on the borders of grain, like α–βbrasses.

One group confirms that at the beginning the whole alloy is melted and after that, specific constituents are re-plated out of the solution that leaches the alloy. This is the dissolution basis and the redisposition mechanism.

$Zn \rightarrow Zn^{++} + 2e$ .... (2-1)

$2H^{+} + 2e \rightarrow H_2$ .... (2-2)

$CuCl + e \rightarrow Cu + Cl^{-}$ (I) dissolution .... (2-3)

$M \rightarrow Mn^{+n} + ne$ .... (2-4)

$H_2 \rightarrow 2H^{0}$ .... (2-5)

$Cu \rightarrow Cu^{++} + 2e$ (II) dissolution .... (2-6)

$Cu_2Zn \rightarrow Cu + Zn^{+2}$ (III) plating .... (2-7)

Fine copper dust is the deposits of copper that dissolves readily in any electrolyte. Zinc is leached out of the brass leaving behind a highly porous mass. The three steps involved above are:

First step: Dissolution of Cu and Zn (equations I and II),

Second step: - Zinc remains as a solution, and third step plates back of copper (equation III) [27].

2.5.1.1 Dezincification: Mechanism

The common mechanisms consist of three steps:

1- The zinc ions stay in solution, 2- the copper plates back on, and 3- the brass dissolves. Zinc is quit reactive, whereas copper is more noble. Zinc can corrode slowly in pure water by the cathodic ion reduction of H_2O into hydrogen gas and hydroxide ions. For this reason, dezincification can proceed in the absence of oxygen. Oxygen also enters into the cathodic reaction and hence increases the rate of attack when it is present. The amount of copper oxide is related to oxygen content of the environment. The porous nature of the deposit permits easy contact between the solution and the brass [39].

2.5.1.2 Examples of Dezincification

a- Type of Layer

Dezincification of uniform layer type happens on the inner surface of Admiralty brass heat exchanger tubes when exposed to water at pH = 8.0 and temperature range 31–49 °C.

(b) Plug type

It is found particularly in α-brass heat exchanger pipes. If the heat exchanger is not cleaned and dried, differential aeration cells are formed in which the brass dissolves. The corroded region is filled with the re-precipitated copper.

Dezincification resistant brasses can be made by adding about 1 wt. % of tin, aluminum, lead, or arsenic to the solid solution of brass to decrease the dealloying of zinc and form more protective oxide layers on the brass surfaces [27].

2.5.2 Cavitation

It is the process of vapor phase formation of a liquid when it is subjected to reduced pressures at constant ambient temperature. Other factors like temperature changes, velocity and turbulence play a role; the change of liquid to vapor is the same. When bubbles enter a region of lower temperature or higher pressure, they violently collapse giving a jet of liquid that produces a shockwave with a forces that upon impact has the ability to erode metal. In spite of the fact that the collapse is generally a low-energy event, it is highly localized [40]

cavitation corrosion happens at velocities of high flow and conditions of fluid dynamic causing variations of large pressure, for water turbines as often is the case, pump rotors, propellers, and the external surface of wet cylinder linings in diesel engines [18]. Solid boundaries absorb that impact energy, leading to elastic deformation, plastic deformation and eventually to fracture [41].

Cavitation starts mainly in four stages, first stage is incubation, small mass loss. However, pitting happens in ductile materials, whereas brittle materials will show pitting and cracking or cracking. Secondly stage, the process accelerates, and noticeable metal loss happens, this loss spreads gradually over the area of cavitation. In the third stage, the rate of metal loss is somehow stable, corresponding to metal loss over the cavitation area. In the fourth stage, the rate of metal loss lowers, either because the loss of metal is now so great that the local flow conditions have changed and the cavitation intensity is reduced, or because the metal surface is now protected by a layer of stagnant water [12], as shown Fig. (2-9).

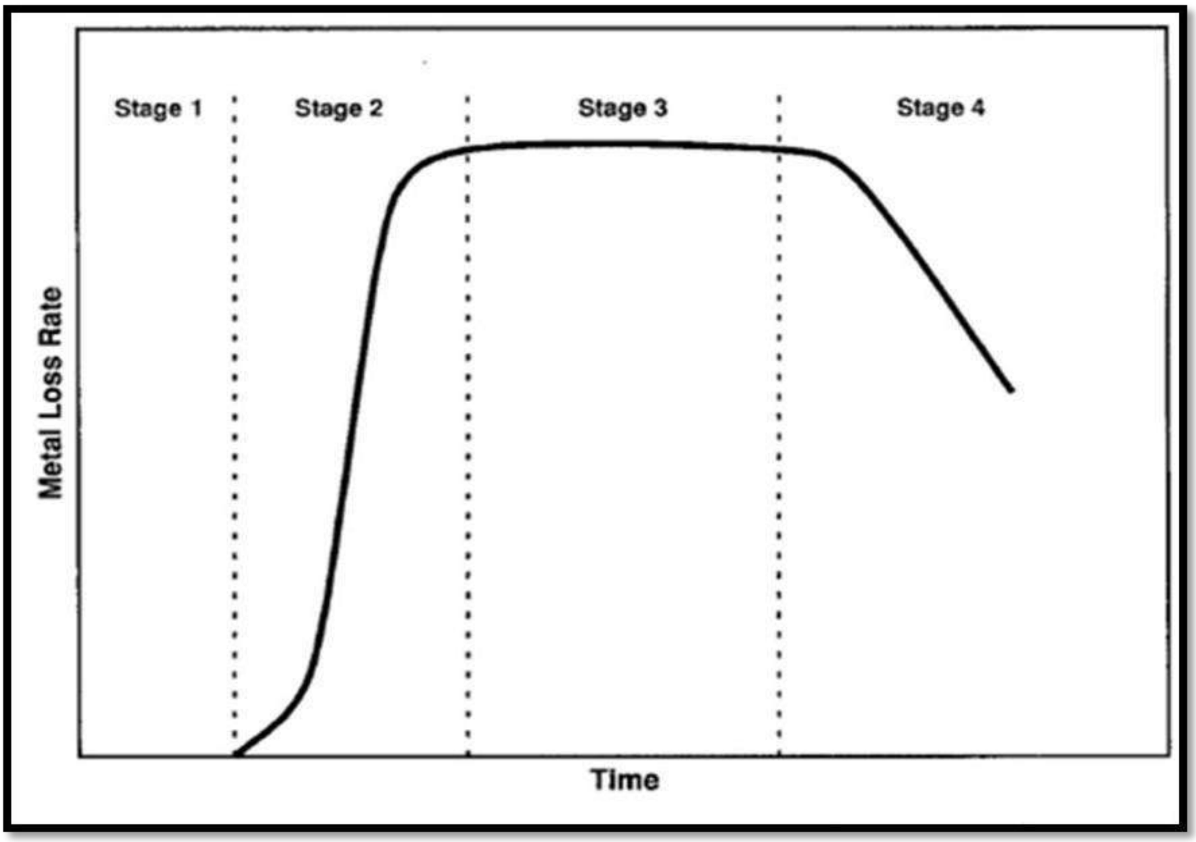


Fig. (2-9): Schematic showing the four stages of metal loss during cavitation [12].

When the pressure difference across an orifice is increased sufficiently, cavitation takes place in the exit flow. Cavitation begins when the corner of the inlet of an

Orifice is sharp sufficiently and the flow detaches from the walls of the orifice. At this stage a vapor region is formed inside the orifice [42].

Corrosion by cavitation is a form of erosion caused by the formation and rupture of vapor bubbles in the fluid near the metal surface, causing a sequence of pits in the form of small, but deep cracks [43], as shown Fig.(2-10) and (2-11).

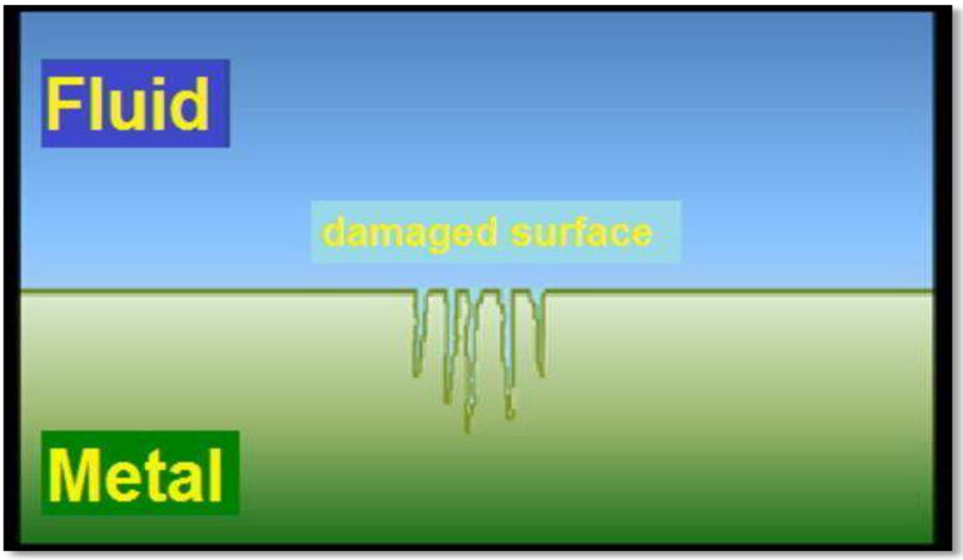


Fig. (2-10): Corrosion by cavitation [43].

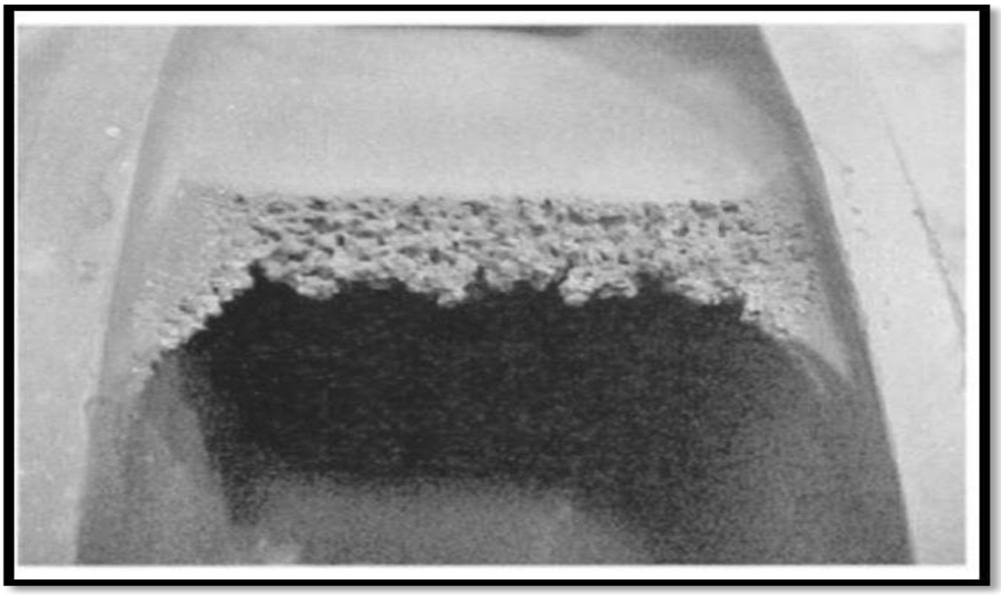


Fig (2-11): cavitation damage, showing typical jagged, honeycomb appearance [12].

2.5.3 Erosion-corrosion

Erosion–corrosion is the increase in the rate of degradation of the material caused by the combined action of electrochemical corrosion and mechanical wear processes. Corrosion is a material degradation process which occurs due to electrochemical action, while erosion is a mechanical wear process. When these two processes act together especially in the marine environments, it is known as erosion-corrosion. [44]. Erosion-corrosion, is the accelerated loss of metal due to the combination of: fast corrosion that follows the protective films removal and base metal erosion by solid particles, has been investigated for two-phase flow through bends using numerical techniques. A known cause of equipment failure is erosion- corrosion of two-phase flow through bends is commonplace in industry [45]. The attack looks like grooves taken out circular areas gully, depressions or waves shaped like a horseshoe, all these sometimes give directions. On occasion, attacks might be pits assembly. Ultimate holes because of progressive or thinning pits, and tearing because of failure of the thin wall in resisting the pressure of internal fluid are common. Equipment exposed to flowing fluid is under the risk of corrosion erosion, but the most commonly affected are piping systems and heat exchangers. Corrosion erosion can be affected by impingement, the presence of suspended solids, turbulence, temperature, prevailing cavitation conditions, and velocity. Attack acceleration is because of the removal or destruction of the film protecting it by mechanical powers, so contacting a surface of fresh metal that is anodic to the neighboring untraded film. A dense, hard adhering film, like that on stainless steel, can resist more than a brittle soft film, like the one on lead. Protective film nature depends wholly on the corrosive [46].

If the conditions are ideal, metal surface oxidation gives a barrier of Passivating diffusion. In combined attack by corrosion and erosion jointly, a second influence might affect the substrate which is the removal of the Passivating layer and that is affected by some variables like velocity, shape, loading in the gas flow, particle size, temperature, gas composition and angle of impingement [47].

All the factors that influence the resistance of material to erosion corrosion and their exact relationship are difficult to define. One property that factors in is hardness. In general, harder materials resist erosion corrosion better, but there are some exceptions. Surface smoothness, fluid velocity, fluid density, angle of impact, and the general corrosion resistance of the material to the environment are other properties that factor in. Equation 9 predicts the erosion rate of metals using some of these factors [48].

2.6 Corrosion Inhibitors

The corrosion of metals is a serious problem in many industries, installations and civil services such as water and sewage supplies. One of the most useful and practical methods that is used to control and protect metals against corrosion is the use of inhibitors [94].

Metallic surfaces corrosion can be reduced or controlled by the adding chemical compounds to the corroding. The name of this corrosion control is inhibition and the added compounds named as corrosion inhibitors [46]. The inhibitors are now used for the corrosion protection of metals, production and refining of oil, the heat exchanger, energy facilities, and conservation of machinery, missile technology, machinery and other industries. Under inhibitors are substances which include the introduction of the corrosive environment, usually in small quantities, can greatly reduce the speed of electrochemical corrosion of metals and alloys [5].

The effective type of corrosion inhibitors for these applications is film-forming inhibitors. Nowadays, surfactants are widely used and find a very large number of applications in the petroleum industry. This is attributed to their significant capability to influence the properties of surfaces and interfaces [5].

There are two types of corrosion: Layered type and local corrosion. In the first type of corrosion, the corrosion of the surface takes place all over the surface and is generally observed in brass rich in zinc. In local corrosion there are small local pits and holes formed on the surface, and there is very little corrosion on other parts of the surface. The region of the surface where these pits and holes are formed has a porous structure and is highly weakened. The metal is easily broken from these regions. One of the most widely used inhibitors for the protection of copper and brass [5]. Inhibitors are chemicals that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain levelof protection. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion [5].

Corrosion lies in controlling it by reducing the rate at which corrosion reaction proceed. Among the various conventional methods available to prevent the corrosion of metals in corrosive environments is the used of corrosion inhibitors. This method is gaining wide industrial acceptance, due to low its processing cost and ease of application [9].

Brass is susceptible to a corrosion process known as dezincification and this tendency increases with increasing zinc content of the brass. During the past decade, many techniques have been used to minimize the dezincification and corrosion of brasses one of the most important and practical methods in the corrosion protection of metals is the use of organic inhibitors to protect the metal surface from the corrosion environment, especially in aggressive media [9].

Inhibitors are chemicals when added in small portions into a system can protect metals from corroding. Inhibitors usually protect metals by adsorbing themselves to the substrate and thus provide protection through the formation of a passive layer [5].

A protective layer of the inhibitor is expected to deposit on the surface of copper enhancing its corrosion resistance towards sulfide attack. In addition, the specificity of the method is also addressed through its application to metals other than copper [05].

2.6.1 Corrosion Inhibitors Properties

(i) Strong adsorption onto metal surface

(ii) Increasing or decreasing the anodic and/or cathodic reaction

(iii) Decreasing the diffusion rate for reactants to the surface of the metal

(iv) Decreasing the electrical resistance of the metal surface.

Numerous factors including price tag and quantity, easy availability and most importantly safety to environment and its species need to be considered when choosing an inhibitor. Inhibitors of organic origin can be divided it into two major parts.

1. Synthetic/Organic inhibitors 2. Green inhibitors [05].

2.6.2 Mechanism of Inhibition

CIs action mechanisms are

- Through adsorption, a film is formed which is adsorbed onto the surface of the metal.
- Through inducing corrosion formation products like iron sulfidewhich is a passivizing species.
- Through changing characteristics of media, producing precipitate that can protect, eliminate or inactivate aggressive constituents.

It is well known that by adsorption organic molecules stop corrosion, a barrier is formed between the environment and the metal. So, the molecule polar group is linked directly to metal and the end of the nonpolar is oriented in a vertical direction to the surface of the metal, which stops species of corrosion, thus a barrier is established against electrochemical and chemical attack by fluids on the metallic surfaces [43], as shown Fig. (2-12).

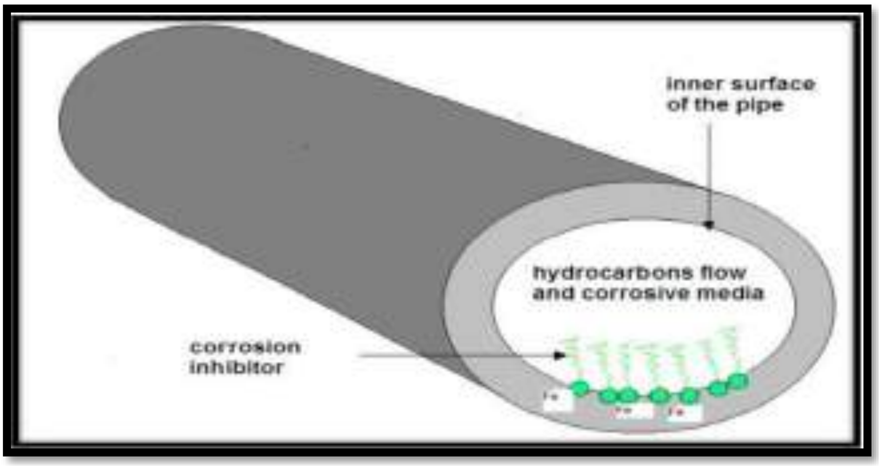


Fig (2-12): Representation of a CI adsorbed into a metal surface [43].

When brass undergoes corrosion, a zinc oxide layer is initially formed which passivates the brass surface. When brass is dipped in a media containing chloride ion, an insoluble film of cuprous chloride is adsorbed on the brass surface. The copper ions can pass into the solution by disproportionation reaction or it can dissolve with the formation of complexes with $CuCl_2^-$ The formation of stable Cu_2O is possible inside the pores of CuCl layer [16].

2.7 Types of Corrosion Inhibitors:

In general, the inorganic inhibitors have cathodic actions or anodic. The organics inhibitors have both actions, cathodic and anodic and the protective by a film adsorption [**04**], as shown Fig. (2-13).

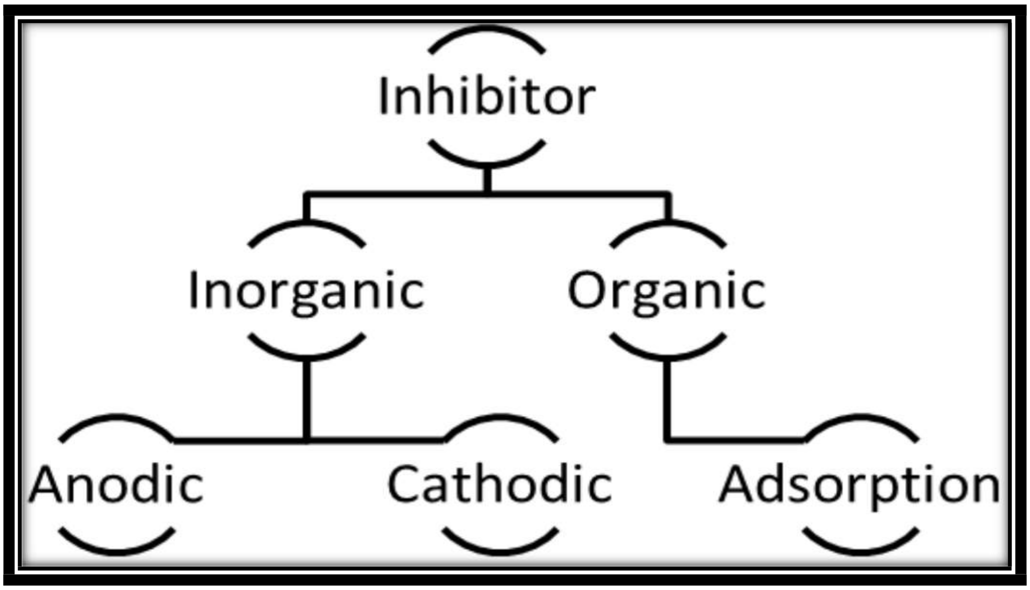


Fig (2-13): Classification of inhibitors [**95**].

2.7.1 Anodic Corrosion Inhibitors

Consumption rate is decreased by anodic inhibitors as a result of impeding anodic responses. An anodic inhibitor moves the harmony of the consumption procedure to the passivation zone creating development of a thin undetectable passivation oxide film on the anodic destinations, which builds the anode potential and discourages the oxidation procedure. Diminishment of the compelling anode range brings about reduction of consumption rate. anodic inhibitors have a genuine hindrance: at low focuses, they cause increment of erosion rate, thusly it is critical to maintain a strategic distance from abatement of the inhibitor content underneath the ideal level. The accompanying mixes are utilized as anodic inhibitors: chromate $(CrO_3)^{2-}$, nitrite $(NO_2)^{2-}$, molybdate $(MoO_4)^{2-}$, and orthophosphate $(PO_4)^{3-}$ [55].

2.7.2 Cathodic Corrosion Inhibitors

Cathodic inhibitors lessen the erosion rate because of hindering cathodic responses. A cathodic inhibitor causes development of insoluble mixes hastening on the cathodic locales in type of an obstruction film. The successful cathode range is one of the variables of galvanic erosion. In this manner its diminishmentbrings about lessening of consumption rate. The accompanying mixes are utilizedas cathodic inhibitors: zinc salts, calcium salts, magnesium salts, and polyphosphates [55].

2.7.3 Mixed Inhibitors

Blended inhibitors work by diminishing both the cathodic and anodic responses. They are normally film shaping intensifies that cause the arrangement of hastens at first glance blocking both anodic and cathodic destinations by implication Hard water that is high in calcium and magnesium is less destructive than delicate water as a result of the propensity of the salts in the hard water to accelerate on the surface of the metal framing a defensive film The most widely recognized inhibitors of this classification are the silicates and the phosphates. Sodium silicate, for instance, is utilized as a part of numerous residential water conditioners to keep the event of rust water. In circulated air through hot water frameworks, sodium silicate secures steel, copper and brass [55].

2.8 Factors affecting corrosion inhibitor performance

There are many factors which influence the inhibitors performance to reduce the corrosion effect. The following sections will describe more:

2.8.1 Inhibitor Concentration

The concentration of the inhibitor should be sufficient to be most effective in the metals protection. It has been found that the insufficient concentration can lead to increase the corrosion rate, i.e. localized corrosion attack. The concentration of inhibitors is controlled by many factors such as disposal problems, economics and availability of tools for monitoring inhibitors concentrations [**55,55**].

2.8.2 Temperature

Temperature acts as an important role in influencing the inhibitor performance and structure, physically and chemically. It also affects the corrosion environment so that the inhibitor work will be affected also [**64,65**]**.** For organic compounds which show inhibitive properties, the effect of temperature varies according to inhibitors.

Some organic compounds are better inhibitors at elevated temperatures presumably due to increase in adsorption at higher temperatures, others are more efficient at room temperature [66].

2.8.3 pH Effect

Inhibitor efficiency is reduced with decreasing pH. The pH is the direct reflection of the amount of hydrogen ions present in the solution. As corrosion rate decreases, the amount of hydrogen ions also decreases causing pH increment. The ideal of water pH with respect to corrosion inhibition of should be in the range of (6.8) to (7.3) [67].

At pH 7 the film grows slowest on oxides and the resulting film thickness is thin. However, this type of film has the most polymerised structure, and thereby provides the best corrosion protection. At pH 2 the film grows rapidly and a thick film formation occurs. The structure of these films are least polymerised, and their structure offers less protection for the copper underneath. Films grown at pH 3 act as cathodic inhibitors of the hydrogen evolution process, but they do not inhibit the oxygen reduction process. The failure to inhibit the oxygen reduction suggests that the film is be least somewhat permeable to oxygen [68].

2. 9. Inhibitor Efficiency

The inhibition efficiency was calculated, using the following equation [69]:

$$\mathbf{IE\ (\%) = [(i_{cor} - i_{cor\ (inh)}) / i_{cor}] * 100} \text{..} (2\text{-}8)$$

Where:

i_{corr} the corrosion current density values without inhibitor.

and $i_{corr\ (inh})$ the corrosion current density values with an inhibitor

2.10. Literature Review

Nawal, (2006) [70] used an organic inhibitor derived from palm fronds faction Al_Barbn to reduce corrosion in different corrosion media (tap water, brine, and acid solution) of low carbon steel sample (0.18% C). Inhibitor was added to the media in different ratio (0.5, 1.5, and 3) Vol %. Different methods have been used to measure corrosion such as simple immersion rate, erosion, polarization and testing atomic absorption. The test results showed the efficient of inhibitor to reach to 86.66% in tap water, in brine solution 78.94%, and 98.47 in the acid solution at a concentration of 3% of the inhibitor. The researchers also studied the effect of temperature on the efficiency of inhibitor at different degrees of temperature (40, 50, and 60) °C. Result showed that the efficiency of inhibitor increases with the increasing temperature (33.33, 71.42, and 88.8) % respectively. Atomic absorption examination of efficiency results to (0.98, 0.78, and 0.86) at 3% in the tap water and brine and acid respectively.

Avramovic & Antonijevic, (2011) [12] Investigated brass corrosion behavior from dezincification mechanism aspect of cold-deformed Cu- 42%Zn brass were tested in a solution of acid sulphate at pH-value 2 with additional ionsof chloride and inhibitors of corrosion with potentiostatic polarization method. Thiourea (TU), benzotriazole (BTA), ethylene diamine tetra acetic acid (EDTA),hydrazine sulphate (HS) and 2-butin- 1,4 diole (DS-3) have been used as effective acid corrosion inhibitors. Increase of a concentration of the Cl^- ions, except for value of

$5 \cdot 10^{-2}$moldm^{-3}. causes a noticeable value increase for current densities of corrosion. In solution without inhibitors, dezincification process and dissolution of anode of Cu- 42%Zn brass has been developed in the whole scope of tested potentials, and pointed out the instability of forms on their surface. Studies results show that only theorem, 10^{-2}wt.% concentration, inhibit brass corrosion in solutions of chloride. In concentration of 10^{-1}wt.% inhibitor benzotriazole inhibit brass corrosion with more than 94%. inhibition efficiency. The film significantly improved the ability of protecting the surface of the brass to corrosion in the solutions of chloride. The films were modified, the corrosion protection and quality were rapidly improved, with benzotriazole.

Raj& Rajendran. (2011) [16] investigated corrosion inhibition of brass in natural seawater by thiadiazole derivatives using electrochemical impedance spectroscopic techniques and potentiodynamic polarization. It was found that the efficiency of inhibition of thiadiazole derivatives, namely, 2-amino-5-ethyl-1,3,4-thiadiazole(AETD), 2-amino-5-ethylthio-1,3,4-thiadiazole(AETTD) and 2-amino- 5-tert-butyl-1,3,4-thiadiazole (ATBTD) rises with increase in concentration. Thiadiazole derivatives adsorption on the surface of brass exposed to solutions containing inhibitor has been confirmed using FT-IR spectra and EDX/ SEM spectra. Adsorption of these inhibitors on the surface of brass followed Langmuir adsorption isotherm. Analysis of ICP-AES confirms that dezincification was minimized to a large extent with existence of these inhibitors.

Rani & Basu,. (2012) [5] Investigated The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. Investigations of corrosion inhibiting abilities of tannins, alkaloids, organic,amino acids, and organic dyes of plant origin are of interest. Development of computational modeling backed by wet experimental results would help to fill this void and help understand the mechanism of inhibitor action, their adsorption patterns, the inhibitor metal surface interface and aid the development of designer inhibitors with an understanding of the time required for the release of self-healing inhibitors. The present paper consciously restricts itself mainly to plant materials as green corrosion inhibitors.

Al-Sultani et. al., (2013) [71] Investigated Carbon steel, the most widely used engineering material, despite its relatively limited corrosion resistance used in large tonnages in marine applications, nuclear power transportation, chemical processing, petroleum production and refining, pipelines, mining, construction and metal processing equipment.

The main objective of the present work involved the study of the inhibitive properties of natural product as spearmint plant extract as a safety and an environmentally friendly corrosion inhibitor for low carbon steel in (3.5% NaCl) solution. Results showed when the immersion model in (3.5%NaCl) solution that contains the inhibitor with concentration of (15% in volume), it's getting decrease in lost weight, indicating a layer of adequate oxide on the surface of steel, indicating that the amount of loss weight decrease with increasing concentration of inhibitor and this shows the damper on his ability to form a protective layer.

Branzoi et al., (2013) [72] Investigated the Effect of some new organic polymers as green corrosion inhibitors for brass in cooling water system. Pure metals and alloys react chemically/electrochemically with corrosive medium to form a stable compound, in which the loss of metal occurs. The compound so formed is called corrosion product and metal surface becomes corroded. Among the several methods of corrosion control and prevention, the use of organic corrosion inhibitors is very well known. Using the microwaves energy new organic polymers were synthesized by radicalic polymerization. These new organic compounds have anticorrosive and antiscale properties and for this reason, were used for cooling water systems protection. The inhibition activity analysis of these new organic polymers was made by assuming that the mechanism of inhibition by organic molecules is chemisorptions and that the energetic of the corrosion process per se is unaffected by the addition of substituents on the parent compound. We presume that these new organic polymers inhibit corrosion of carbon steel by a protective mechanism, forming insoluble iron complexes and repairing the porous oxide layers. The methods employed were potentiodynamic polarization, electrochemical impedance spectroscopy, scanning electron microscopy (SEM) and metallurgical microscopy techniques. The addition of the organic inhibitors led in all the cases to inhibition of the corrosion process. The inhibition efficiency was high in all the studied cases. The corrosion parameters obtained from polarization curves and from EIS spectra are in good concordance and point out the inhibitory action of these new organic polymers. The adsorptions of the organic compounds on the carbon steels surface obeyed Langmuir’s isotherm. Further characterization using Fourier transform infrared spectroscopy (FT-IR) demonstrates the adsorption of organic inhibitors and the formation of corrosion products on the carbon steels and the brass surface. The inhibition process was attributed to the formation of the adsorbed film on the metal surface that protects the metal against corrosive agents. The EIS measurements have confirmed this protection and pointed out the formation of adsorption layers on the electrode surface.

. **Adetunji et. al.,** (2014) [73] studied the fossil fuel influence like kerosene, diesel and petrol, on brass corrosion performance. Samples have been prepared for the study by cutting brass into 1 cm2 coupons and put them in plastic containers containing kerosene, diesel, and petrol. The rate of corrosion for a specific period of immersion ranged between 120-720 hrs. Was determined. Results showed that brass is resistant to corrosion after long contact in selected liquid fossil fuels. In petrol, brass has the highest corrosion rate, kerosene is second and least is diesel. After ten days, immersion samples photomicrographs have confirmed this also.

Khan et. al., (2014) [74] Experimented the effect of normal load and orientation on copper and zinc alloy, i.e. brass, by calculating the weight loss due to wear. To do so, a multi-orientation pin-on-disc apparatus was designed and fabricated. Experiments were carried out under normal load 05-20 N, speed 2000 rpm. Results show that the with- increasing load weight loss increases at all angular positions. The loss in weight is maximum at zero degree (horizontal position) and minimum at ninety degrees (vertical position) for a particular load. When the test specimen is held at 0° angle and minimum wear occurs when the specimen is held at 90° angle for given applied load, maximum wear occurs. For all positions, the circumferential distance travel is constant and for all loads but loss of the mass still varies.

Gowrani, (2014) [75] studied brass corrosion behavior in the presence of inhibitor namely 5-methyl benzotriazole (MBTA) in 3% NaCl medium. MBTA inhibition efficiency was measured by electrochemical and chemical techniques. Studies showed that MBTA markedly decreases the brass corrosion in 3% NaCl solution. This reduction in the rates of corrosion enhances with MBTA concentration. So that 71% inhibition was achieved with 150 ppm MBTA. Studies of Polarization also showed that MBTA act as mixed type inhibitor.

Fouda et. al., (2014) [76] Studied indole influence and 2-oxyindole on the rate of corrosion of α-brass in 1M HNO_3 using weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic, and techniques of modulation of electrochemical frequency (EFM). The study revealed that the compounds investigated act like inhibitors. Efficiency of inhibition rises with increasing the concentration of the inhibitor, but lowers with lowering the temperature. Adsorption of these compounds on the α- the surface of the brass follows Langmuir's adsorption isotherm. The electrochemical results revealed that all the compounds that have been investigated act as mixed-type inhibitors. Some thermodynamic parameters for the processes of corrosion were discussed and determined. The results obtained from electrochemical and chemical and techniques were in good agreement.

Florina & Viorel (2015) [4] have been study the inhibitory effect of PASAC1, PASAC 11 and PASAC13 on the corrosion behavior of brass in cooling water system at temperature of 25°C was studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), FTIR spectroscopy and metallurgical microscopy techniques. three types of organic inhibitors obtained by radicalic polymerization, i.e., PASAC1 (urea and maleic anhydride at molar rapport 1:1.5 at temperature of 140°C), PASAC 11 (polyaspartic acid and H_3PO_4 molar ratio 1:0.05 at temperature of 170°C), PASAC13 (polyaspartic acid 0.07 M and H_3PO_4, gravimetric ratio 1/1.5 with trisodium citrate at temperature of 200°C) was selected. The result of these polymers concentration on inhibition efficiency, the corrosion rate and surface coverage is investigated. Results show that these organic inhibitors exert a strong inhibiting effect on brass corrosion and acts as a mix-type inhibitor. The inhibition efficiency of organic polymers may be due to either the adsorption of inhibitor molecules building a protective film or the formation of an insoluble complex of the inhibitor adsorption obeys the Langmuir model. Further, characterization using FT-IR demonstrates the adsorption of organic inhibitors and the development of corrosion compounds at brass surface. EIS results confirm its corrosion inhibition ability.

Babouri et al., (2015) [8] investigated the protective efficiency of a new class of ‘green’ corrosion inhibitors on Copper-Zinc alloy (Brass). The inhibition effect of cerium carbonate (CAC) on Brass in 3% NaCl solution was investigated at room temperature both by potentiodynamic polarisation and impedance spectroscopy (EIS) methods and weight loss measurements. The surface analysis was made by scanning electron microscope and micro-Raman spectroscopy. The electrochemical measurements showed that the CAC decreases the density of the corrosion current and thus acts as a mixed type inhibitor. The CAC inhibits the corrosion of Brass by blocking the active sites of the metal surface with a maximum inhibitory efficiency of 84%, obtained with the concentration of 100 ppm of the inhibitor. The corrosion rate decreased by a factor of 3.5 in the presence of CAC, suggesting that the investigated method is promising. The mechanism of inhibition effect is attributed to adsorption of Ce-hydroxides in the excess of OH- production from the cathodic reactions of water reduction and O_2. This hydroxide precipitates subsequently as a barrier against the corrosion of the active regions .

Peter et al., (2015) [58] studied the corrosion of metals and its alloys employed in service is an inescapable but a controllable process. One of the practical methods for controlling the impact of corrosion of metals and alloys especially in aqueous environments is by using corrosion inhibitors which are composed mainly of organic or inorganic substances. However, the toxicity of organic and inorganic corrosion inhibitors to the environment and humans has compelled the search for safer corrosion inhibitors called ‘green corrosion’ inhibitor due to their properties like non-toxicity, biodegradability, and low cost. The use of natural gums as environmentally safe corrosion inhibitor for metal and alloys has in recent times received tremendous attention by several researchers. Also quantitative structure activity relationship approach has been used to establish the correlations between a number of quantum chemical parameters and the molecular structures of some gum extracts major components. This approach has aided in understanding the component of the gum extracts responsible for imparting the inhibition effect since there are several components of the gum which could act in synergy to inhibit the metal corrosion. This review paper presents an overview of works published on natural gums as green corrosion inhibitors. It also discusses the use of computational chemistry tools in understanding the inhibition mechanism of gum extracts components which is often difficult to determine using experimental means.

Ramdé et. al., (2016) [77] studied sulfamethoxazole corrosion inhibition action (SMX) on aesthetical brass in synthetic acidic rain water by means of electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, optical microscopy, fourier transformed infrared spectroscopy (FT-IR), and scanning electron microcopy (SEM). It was discovered that SMX inhibits brass corrosion and the efficiency 1f inhibition was risen with increasing concentration. About 84% efficiency of maximum inhibition has been obtained at the higher concentration of SMX in the synthetic acidic rainwater. Testing Long time immersion revealed that the efficiency of inhibition rises with immersion time as indicated the increase of total impedance. Characterization of the surface performed by SEM analyzes and FT-IR, optical allowed to establish that SMX work as inhibitor by protective adsorbed layer formation.

CHAPTER THREE

Experimental Work

Chapter Three

Experimental Work

3,1 Introduction

In this chapter materials, is devoted to prepare and examine the (A, B, and C) samples by casting process. Mechanical tests were used to characterize the properties of (A, B, and C) samples, Microstructure observation and corrosion tests were also conducted. Samples of these alloys were prepared and tested by Spectrom MAXx.

3.2 Melting and Casting

In order to prepare the samples (A, B, and C), melting and casting processes have been used. Samples used in this work are shown in the Table (3-1). They consist of brass as a base metal with addition of Al (B sample), Al with 1.5 wt% as listed in table (3-1), and using gas furnace in the casting laboratory in theCollege of Materials Engineering / Babylon University.

The melting temperature of copper is 1083 °C and zinc is 419.6 ˚C, while the melting temperature of alloys is 906 °C for this the zinc were added (5%) aspercentages compensatory before casting to compensate the missing of zinc. The melted alloy was mixed by ceramic rod to homogenous the melting alloy.

During the melting process, aluminum wire was used to keep proportion of the alloying elements (Al) were added to reference brass alloy after modifying the weight percent of copper and zinc to give the percent's.

In the melting process, cylindrical steel die open from both sides was used to prepare two groups of samples (A, B, and C); One with diameterof (14) mm and thickness of (1.7 to 2) mm used for hardness, XRD, microstructure observation, inhibitor corrosion and simple immersion tests. Each sample was drilled with a hole of (1) mm in order to hanging up in 3.5 wt.% NaCl solution while the other groups of samples have diameter of (13) mm and thickness of (5) mm used for polarization test. Before casting process, die was heated and graphite was used as lubricantthey were added in small amounts to ensure sample eject from the die. Later all samples were subjected to homogenization treatment at 500 °C for 4 hrs.

3.3 Samples Preparation

The cylindrical samples were cut up in order to prepare samples (A, B, and C). All samples were grinded by using (180, 220, 400,600,800,1000, 1200, and 2000) grit silicon carbide papers; then polished with a diamondpaste of 15 µm to get a bright mirror finish for the final step.

3.4 Analysis of Chemical Composition

Chemical composition OF alloys (A, B, and C) was determined using metal analysis by SPECTROMAXx (Germany) the results are shown in Table (3-1).

Fig. (3-1) SPECTROMAXx device

Table (3-1) composition of the used alloys

The Alloy	Cu%	Zn%	Al%	Other element %
A reference & C	69.53	29.96	_	0.51
B	69.65	28.41	1.53	0.41

3.5 Microstructure Observation

Microstructure of samples was detected by using optical microscope shown in figure (3-2) at 400x magnification. The samples were tested after grinding of up to (3000) grit and finally polished by 0.25µm diamond paste. To study the microstructure of the samples, they were etched using ($FeCl_3$ 5gm+alcohol.95gm).

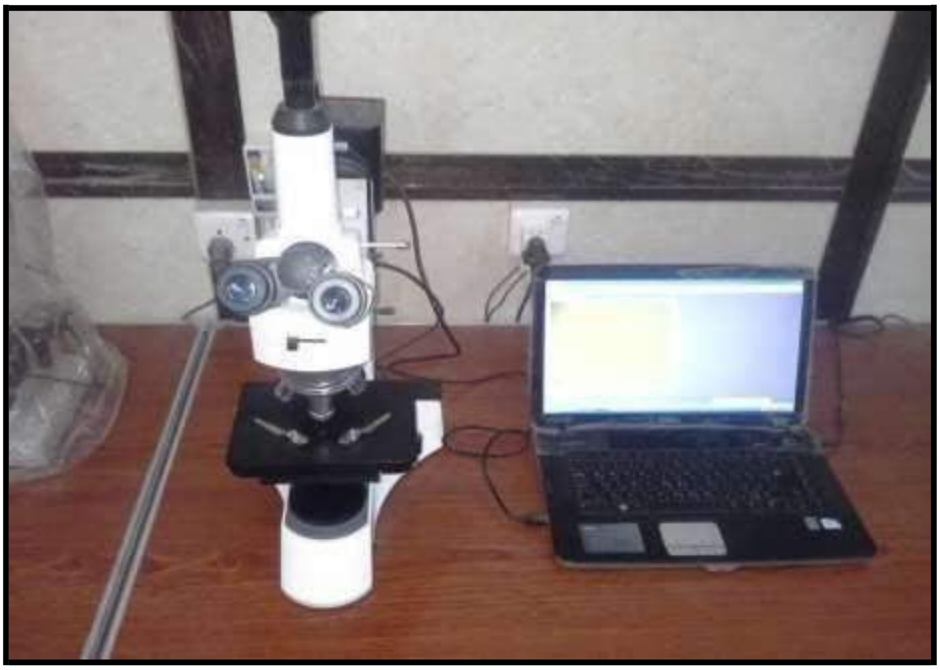


Fig. (3-2): Optical microscopy

3.6 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra has been conducted using (BRUαKER ALPHA.P) at Babylon university/college of Engineering., as shown in figure(3-3) , FT- IR spectrum of demonstrates the presence of many chemical functionalitygroups in an inhibitor [Palm frond extract].

Fig. (3-3): Fourier transform infrared spectroscopy (FTIR).

3.7 Corrosion Tests

3.7.1 Simple Immersion Method

This test is accomplished by immersing the samples (A, B, and C)in salty water (3.5% NaCl solution). The weight change was recorder every (2) hours. Before immersion process, all samples were weighted with sensitive weighting balance with accuracy (±0.0001) gm and calculated of the surface area. After each immersion process sample was taken out of salty water, dried with air dryer and weighting. For each experiment, the change of weight was calculated and recorded. The corrosion rate was determined by the following relationship:

$$\text{Corrosion rate } (g/mm^2 * hrs.) = \Delta w / (Area * Time) \qquad (3\text{-}2)$$

Where:

Δw = weight loss (g),

A=sample area (mm^2) and

Time = immersion time

(hour)

On the other hand, the sample reference (A) it was immersing in an inhibitor after immersing in salty solution and at the same conditions. The used inhibitors were a bare Palm frond extract 3% grows in most gardens evenin those of the houses.

3.7.2 Potentiostatic Polarization

Potentiostatic technique is another corrosion measurement technique used to observe the anodic and cathodic behaviors (i.e. monitoring the corrosion reactions on specimen of desired metal). Polarization tests wereperformed by Potentiostatic type (winking M lab 200, Germany). Using standard electrochemical cell9 with open necks for working electrode (brass alloys), auxiliary electrode (Pt. electrode) and saturated calomel electrodeSEC reference electrode. The corrosion resistance of the specimens (A, B, and C) was studied in salty solution at room temperature. Corrosion current densitymeasurement is obtained by using the following equation (3-3) [55]:

$$i = I_{corr} / A \qquad \ldots\ldots (3\text{-}3)$$

where: i_{cor} = corrosion current density,$\mu A/cm^2$, I_{cor} = total corrosion current, μA, and A = exposed specimen area, The electrochemical system used is shown in figure (3-4).

Fig. (3-4): shows the electrochemical system

Figure (3-5) shown Potentiostatic test for the sample reference (A) immersed in an inhibitor. The used inhibitors were a Palm frond extract plant grows in most gardens even in those of the houses.

Fig. (3-5) Potentiostatic test in an inhibitor

CHAPTER FOUR

RESULTS AND DISCUSSION

Chapter Four

RESULTS AND DISCUSSION

4.1 Introduction

This chapter deals with the results and discussion of the experimental work. It includes microstructure examination, electrochemical test which include, simple immersion, Potentiostatic Polarization test, (A) reference sample test in an inhibitor at room temperature and in (50-55) ˚C.

4.1.1 Microstructure

Light optical microscope was used to obtain the microstructure of the etchedsamples (A, B, and C), figure (4-1) illustrates the microstructure of *α* brassat 400X.

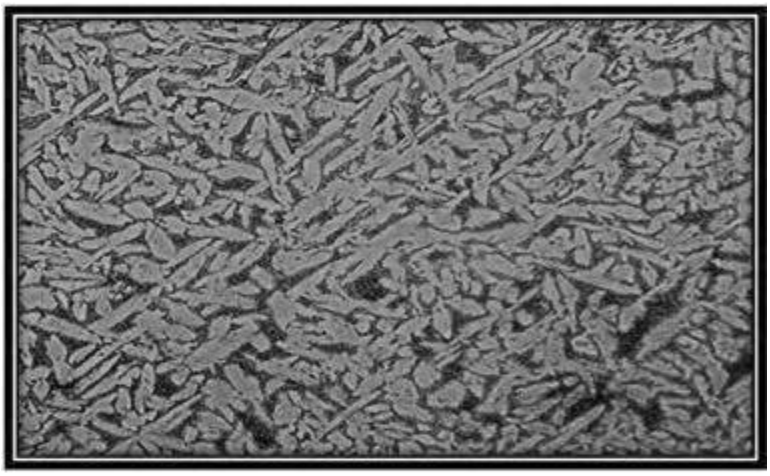


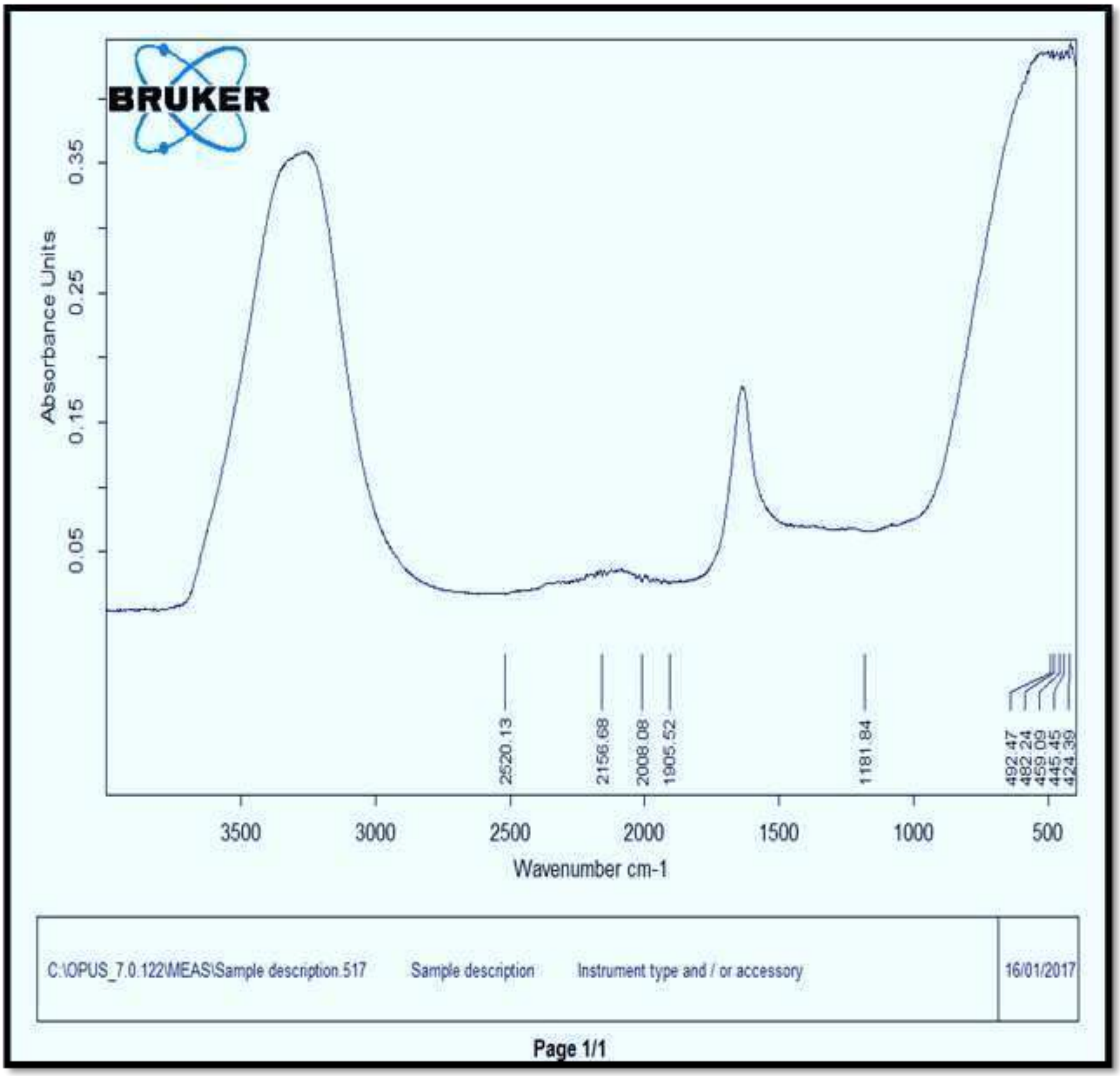
Fig (4-1) Microstructure of Alpha brass alloy
At 400 X

4.1.2 Analysis of the inhibitor:

Fourier Transform Infrared spectroscopy(FTIR) was used to analyses the inhibitor. FTIR is described as a technique for materials analysis. Fig. (4-2) represents the relationship between the absorbance and wave number of inhibitor extraction active groups. The O-H stretch appeared between (3500-3200 cm^{-1}) alcohols, phenols. The C≡N stretch appeared between (2260-2210 cm^{-1}) nitriles. While The C=O stretch around (1760-1665 cm^{-1}) indicates that the presence of carbonyls and C=O stretch shows at between (1750-1735 cm^{-1}). These peaks show saturated aliphatic, and C-Br stretch appeared between (690-515 cm^{-1}) alkyl halides. See also (Table 4.1)

The presence of double bonds in the structure means that this organic compound may be an effective corrosion inhibitor. The existence of the double bonds makes the inhibitor tends to adsorb on the surface of the metal significantly and thus be able to prevent the metal corrosion [45].

From the FT-IR results noted that the [organic material Palm frond extract] contains different atoms such as oxygen and nitrogen and is common in other research[**55,54**], these atoms allows adsorption on the surface of the metal, and they areable to form bonds with the metal surface and thus reduce the corrosion rate.



C:\OPUS_7.0.122\MEAS\Sample description.517 Sample description Instrument type and / or accessory 16/01/2017

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Fig. (4-2): Fourier Transform Infrared (FTIR) spectrometry

Table (4-1): Wavenumbers of different active groups

Positive Number cm^{-1}	Active Group
3200-3500	**O-H**
2210-2260	**C≡N**
1665-1760	**C=O**
1735 -1750	**C=O**
515-690	**C-Br**

4.2. Corrosion Test

4.2.1. Simple Immersion Test

The immersion test simulates the corrosion environments and the degree of acceleration. This test was conducted in salt water solution (3.5% NaCl) at room temperature, figure(4-3) showed the variation of weight loss with immersion time for all prepared samples.

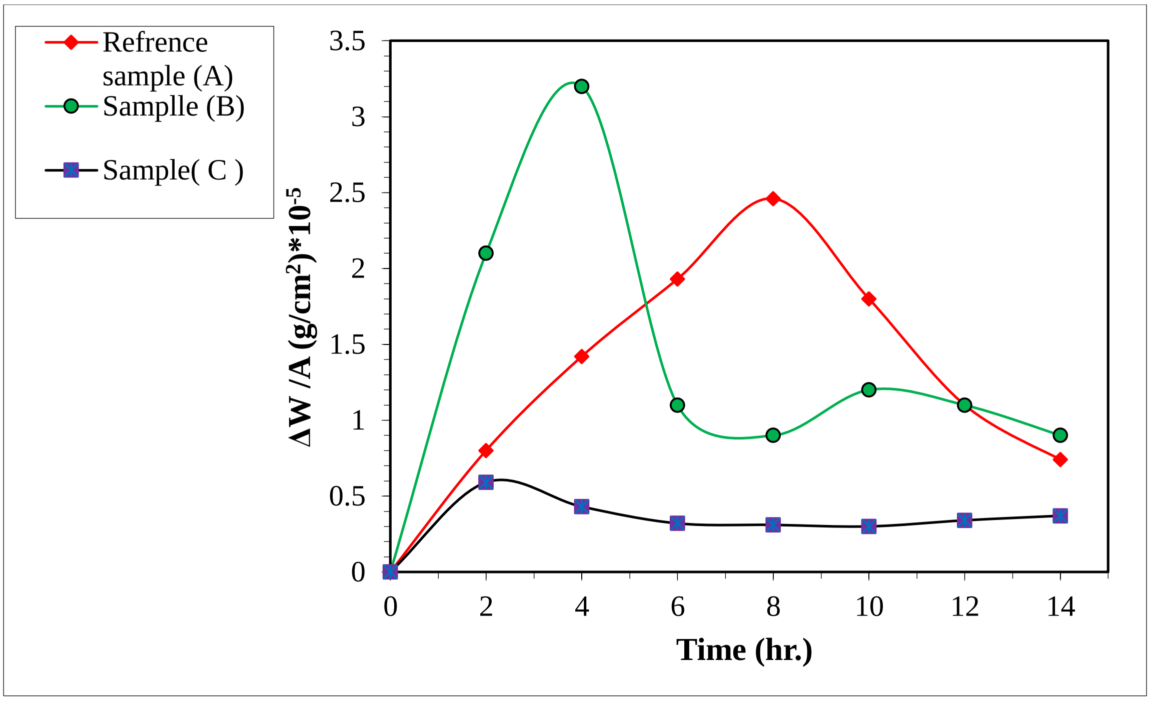

Fig. (4-3) Simple immersion test of prepared samples in salty water (3.5% NaCl)

As shown in the figure, the weight loss of sample A increases with increasing time. This behavior is expected since brass is unable to build a protective layer and it suffers from selected leaching. In case sample(B), theweight loss increases with time, then decreases and eventually exacted to follow a steady state. This is because the addition of (Al) to brass reduced theselective leaching behavior and helps to build a protective oxide rich in Al_2O_3. It is clears from fig above, that it is possible to enhance corrosion resistance of brass used in heat exchanger by the addition of Al as alloying elements, in spite of fact of high cost of those elements and the additional cost comes from processing of these alloys elements. This technique is costly tedious, and time consuming process. However, the more effective, cheaper, (almost free) and available appears to be economic and better selection technique to avoid corrosion in heat exchangers, is the use of inhibitors to combat corrosion in heat exchangers. The used inhibitor was a bare (organic material Palm frond extract) plant grow in most gardens even in those of the houses.

Figure (4-3) shows the effect of inhibitors on weight loss of the reference sample (A) in tap water at room temperature

4.2.2 Potentiostatic Polarization

Polarization curves for samples A, B, and C are illustrated in figures (4-4) to (4-6) respectively. Test was conducted with and without inhibitor to understand the corrosion behavior in such environments. Corrosion parameters observed from these curves, $E_{corr.}$, $I_{corr.}$ Are listed in Table (4-2).However, the corrosion currents of all samples were determined by Potentiostatic Polarization method and listed in Table (4-2).Ascan be seen in this Table , the corrosion current of the reference sample(C) inthe inhibitor was only (4.627 x10^{-5} A). This value is approximately equals to that obtained in simple immersion. This result may be a suitable evidence to support the measurement. Table (4-5) illustrates inhibitive efficiency (I.E.) to alpha brass (A) in salt water and an in inhibitor (C).

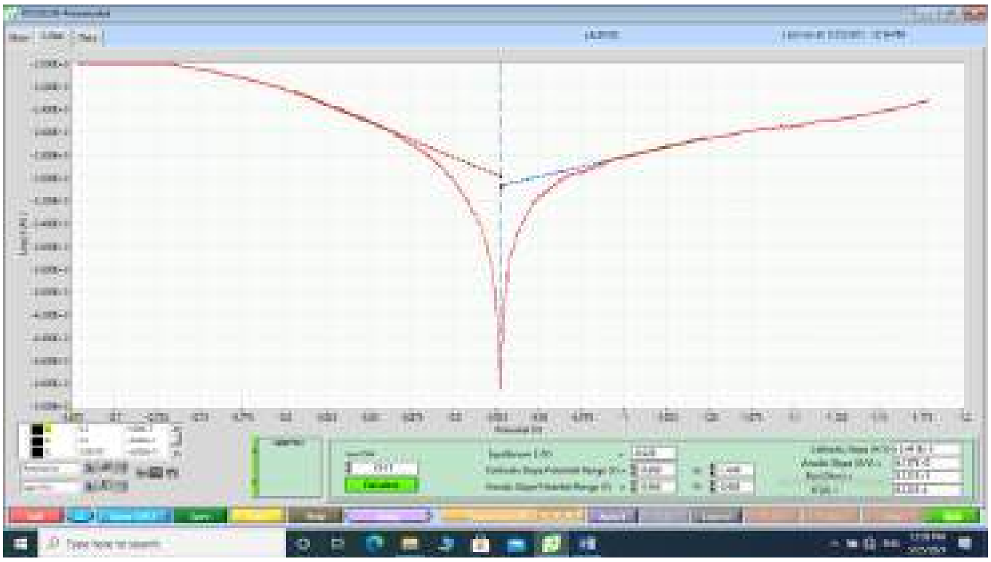

Fig. (4-4) Potentiostatic Polarization curve of reference sample(A) in salty water solution

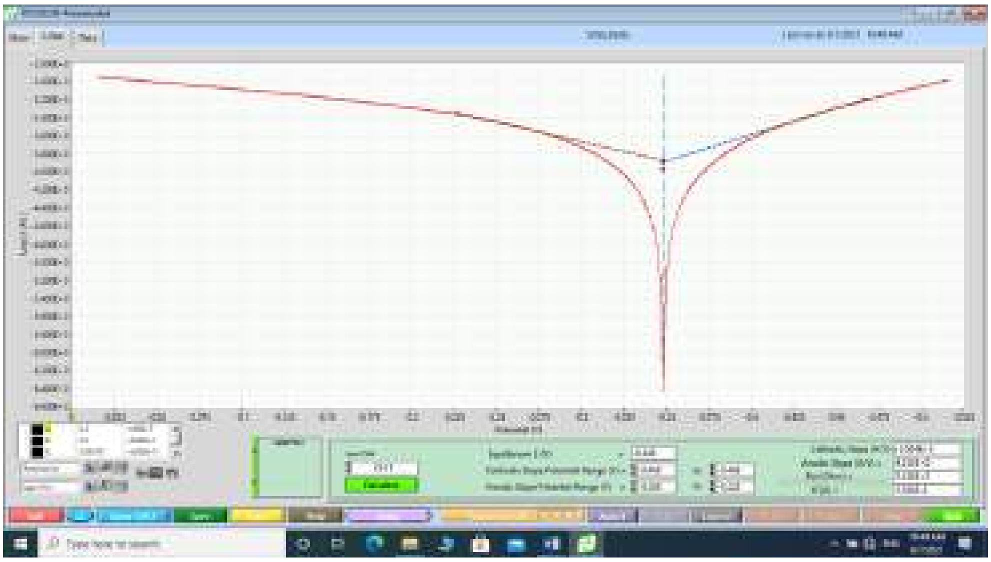

Fig. (4-5) Potentiostatic Polarization curve of sample(B) in salty water solution

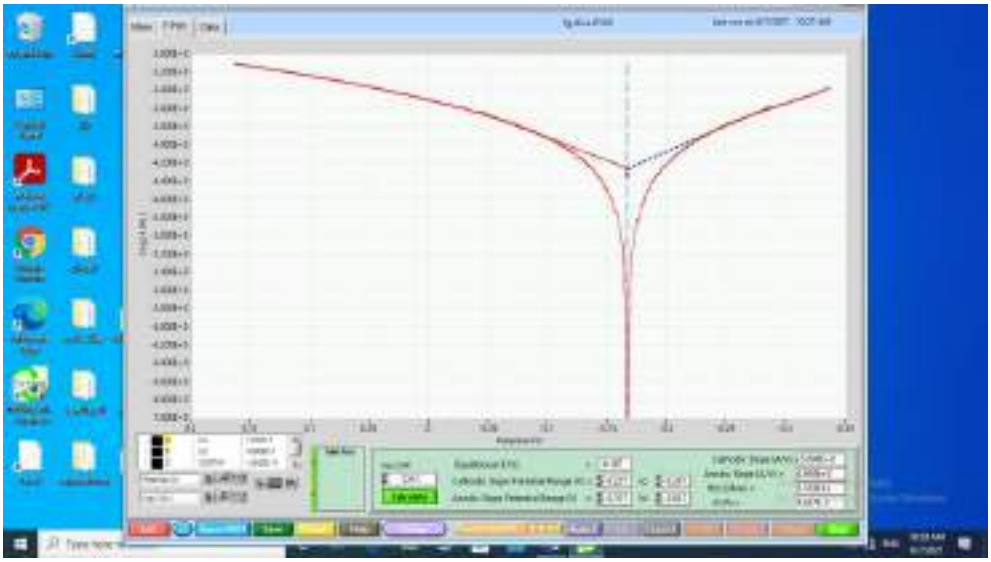

Fig. (4-6) Potentiostatic Polarization curve of sample(C) in salty water solution

Table (4-2) illustrates corrosion parameters (E corr., I corr., current density and Icor/Icor reference)

Alloys in water	$E_{corr.}$ (V)	$I_{corr.}$ x10^{-5} (A)	$I_{corr.}/I_{corr.reference}$
A (reference)	- 0.928	82.321	/
B	- 0.348	10.542	0.13
C	- 0.167	4.627	0.05

CHAPTER FIVE

Conclusions and Recommendations

Chapter five
Conclusions and Recommendations

5.1 Conclusions

The following conclusions may be drawn from this work:

1. The used inhibitor provide great protection to brass used in heat-exchangers against corrosion .
2. Using the inhibitor reduced the corrosion current to a value of only about (0.05) with respect to the reference sample.
3. The best value of corrosion current obtained from the costly alloyed samples (B)was ($10.542\ x10^{-5}$ A) compared with that of the reference sample($82.321x10^{-5}$A)

4.

5.2 Suggestions for further work

1. Studying the inhibitor acting of the in other media.
2. Investigate the effects of inhibitor concentration.
3. Investigate the effects of a range of temperatures, on the efficiency of the inhibitor

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