Corrosion Inhibitors for Cooling/ Heating Water-based Systems

By

Hawa Alajaili

Department of Chemical Engineering
McGill University
Montreal, Quebec
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ABSTRACT

Corrosion control of metals is of technical, economical, and environmental importance. One of the most effective, practical and economical ways for minimization of metal corrosion is by corrosion inhibitors. Corrosion inhibitors often play an important role in water treatment systems, chemical manufacturing, heavy manufacturing, oil and gas exploration and production, petroleum refining, and processing industries where they have always been considered to be the first line of defence against corrosion. Corrosion inhibitors interfere with the corrosion mechanism in order to prevent or mitigate it. Determining the most effective corrosion inhibitor for a given environment is essential, therefore, inhibitors' cost, toxicity, availability and their friendliness to the environment should be taken into account. Here, we report on recent achievement in design and selection of inhibitors that are used in cooling and heating water systems.

Résumé

Le contrôle de la corrosion des métaux est d'une importance technique, économique et environnemental. L'un des moyens les plus efficaces, pratiques et économiques pour la prévention de la corrosion des métaux impliques l’utilisation d’inhibiteurs de corrosion. Les inhibiteurs de corrosion jouent souvent un rôle important dans les systèmes de traitement de l'eau, fabrication de produits chimiques, l'industrie lourde, l'exploration et la production pétrolière et gazière, le raffinage du pétrole, et les industries de transformation où ils ont toujours été considérés comme la première ligne de défense contre la corrosion. Les inhibiteurs de corrosion interfèrent avec le mécanisme de corrosion afin de l’empêcher ou l’atténuer. La détermination de l'inhibiteur de corrosion le plus efficace dans un environnement donné est essentiel, par conséquent, le coût, la toxicité, la disponibilité des inhibiteurs et l’impact sur l'environnement doivent être pris en considération. Dans ce rapport, nous rapportons sur la réalisation récente dans la conception et la sélection des inhibiteurs qui sont utilisés dans les systèmes d'eau de refroidissement et de chauffage.

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CHAPTER 1

1 INTRODUCTION

Corrosion of construction metals such as stainless steel, carbon steel and aluminum appears as one of the biggest industrial problems. The presence of water is one of the main reasons of internal corrosion that occurs in pipes and storage tanks, to name but a few. Hence, internal corrosion is considered as a concern in many industries. It is not only costly, but it also negatively impacts the environment and jeopardizes people's safety. The cost of replacing corroded materials of, for example, civil structures is usually expensive and a risky maneuver which may not always succeed. Corrosion costs in the United States amounts to approximately \$350 billion per year depending on the recent estimation by the Battelle Institute. [1, 2]. Moreover, it has been evaluated that approximately 5% of an industrialized nation's income is spent on corrosion protection and the upkeep or substitution of products lost or contaminated as a result of corrosion [3].

Corrosion is an electrochemical process that occurs due to the presence of anodic and cathodic sites on the material's surface, arising from the heterogeneous nature of the bulk material and its surface. The presence of an electrolyte and electrical connection is also fundamental for electrochemical corrosion to occur. In addition, the bulk material and its surface represent the anode, cathode and the electrical connection. On the other hand, for instance, humid air and aqueous solution constitute an electrolyte that completes the corrosion circuit. Corrosive species could be in a liquid form such as water, aqueous solutions and acids; or in gaseous (or vapour) form such as hydrogen sulfide (sour corrosion) and carbon dioxide (sweet corrosion); or gases dissolved in liquids [3]. In other industries, corrosion could also occur for instance, during material processing using acid solutions. These processes are referred to as pickling in which acids are used for cleaning equipment like storage tanks and boilers to remove rusts, scales and other corrosion products [4-8].

Corrosion plays a significant nuisance in cooling and heating water systems. It is the major reason of failure of closed-loop systems. Corrosion in closed-loop systems is caused by the reaction between dissolved oxygen and the substrate metal, galvanic activity between two different metals, low pH, or from the byproducts of bacterial activity. The dissolved oxygen in the water will start to react with steel bearing metals in the system as the temperature of the water increases. Corrosion results in the formation of metal oxides, which affect the water quality by turning it to black water or brown sludge. This phenomenon has a significant economic effect. Many drinking water and process water transporting pipelines have corrosion troubles in open and closed tubes or cooling and heating processes. This is due to the fact that metals, such as stainless steel, carbon steel, copper and aluminum are liable to corrosion and as a result of poorly conditioned water.

Carbon (mild) steel as construction material is widely used due to its economic viability and fair quality. However, the major drawback of using mild steel is its low resistance to corrosion in these environments [2].

Mild steel is a commonly used metal in the cooling water system that is most susceptible to corrosion. Other metals in general, such as copper, stainless steel and aluminum alloys also do corrode but the electrochemical process is slower compared to mild steel. However, in media other than water and in presence of dissolved gases, such as H_2S or NH_3, the corrosion of these metals is more severe and destructive than mild steel.

Aluminum is the second after iron in terms of production and consumption. It is one of the most significant metals that have inclusive domestic and industrial applications [9, 10]. Aluminum and aluminum alloys are widely used due to their lightweight, recyclability, formability, conductivity and corrosion resistance. In many cases, aluminum and carbon steel are exposed to harsh environments and are susceptible to corrosion [11].

Metal corrosion in water transporting systems such as cooling water as the electrolyte is of concern in industry [12]. Eliminating any one of the previously mentioned corrosion factors (anodic/cathodic surface sites, or the electrolyte) results in the termination of the electrochemical corrosion processes. Unfortunately, in reality, it is impossible to fully achieve that. Nevertheless, there are some methods known that are capable of reducing the influence of one or more of these factors. Many techniques are currently used and some are in research to ultimately reduce the kinetics of the electrochemical process that controls the corrosion.

In order to minimize corrosion, several preventive measures must be employed. One of them is the use of various corrosion inhibitors [13-18]. Examples of the most widely used corrosion inhibitors include chromates, nitrites, molybdates, and orthophosphates. The inhibitors reduce corrosion by interaction with the metal surface and decrease the rate of electrochemical corrosion reactions. However, most of the well-known inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atom [2, 19]. The corrosion inhibition efficiency of these molecules depends especially on their capabilities to adsorb onto the metal surfaces and on the adoption a surface orientation that would represent a diffusion barrier to corrosive species [20-23]. Research has determined that these molecules adsorb on the metal surface by forming a protective film after displacing water molecules [23-25].

Unfortunately, the corrosion inhibitors that are still in use are both expensive and pose health risks [26, 27]. Therefore, there is an increased urge to develop cheap and environmentally friendly corrosion inhibitors. Recently, the research about ‘‘green’’ corrosion inhibitors addressed the goal of using cheap, effective molecules of low environmental impact.

1.1 OBJECTIVES

The purpose of the proposed research is to report on various strategies used for corrosion control in cooling and heating water systems, utilizing previous research papers and experimental results, with the specific focus on using corrosion inhibitors.

The first part of this thesis consists of a theoretical basis of corrosion and corrosion control and literature review on the general use of inhibitors for corrosion control of construction metals.

The second part focuses on corrosion control in water treatment systems. Experimental data and results from various literatures are used to evaluate overall quality and potential industrial application of such corrosion suppressing methods.

CHAPTER 2

2 BACKGROUND

2.1 CORROSION

In general, corrosion is the attack on the metal leading to the deterioration or loss of its properties through chemical or electrochemical reaction with its surrounding environment. Since corrosion is a natural phenomenon, it is often difficult to eliminate completely.

Electrochemically, corrosion is a process involving the movement of electrons across the surface between a metal and the electrolyte solution in which it is immersed. Any electrochemical reaction requires four elements, all of which must be in contact: (1) the anode, (2) the cathode, (3) the conductive material, and (4) the electrolyte. If any of these four are absent or are not in direct contact with each other, then corrosion cannot occur. Electrochemical reaction is the result of electrical energy passing from a negative area to a positive area through an electrolyte medium. Thus, the corrosion process can be chemical in nature or electrochemical due to a current flow, and requires at least two reactions that must occur in a particular corrosive environment.

2.1.1 Anodic Reaction

An anode is an electrode during which positive electric shipment fluxes. Therefore, the corrosion anodic reaction is usually called the oxidation reaction where the metal is being oxidized and loses electrons.

For instance, the corrosion of mild/carbon steel [28] can be represented by the following set of equations (Figure 1):

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^{-} \tag{2.1}$$

wich might be later oxidized into ferric ion, depending on the potential:

$$\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + e^{-} \tag{2.2}$$

Next, the ferrous ions may be deposited on the steel surface as:

$$\mathrm{Fe}^{2+} + 2\mathrm{OH}^{-} \rightarrow \mathrm{Fe(OH)}_2 \tag{2.3}$$

which results in the formation of 'rust', $Fe(OH)_2$, usually noticeable on several industrial and civil constructions. In the presence of carbonates in the electrolyte, ferrous ions can form a corrosion scale [14, 15]:

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \tag{2.4}$$

The solid products of the corrosion are able to slow down the corrosion process. On the other hand, they also result in the penetration of the electrolyte to the surface, which eventually increases the corrosion.

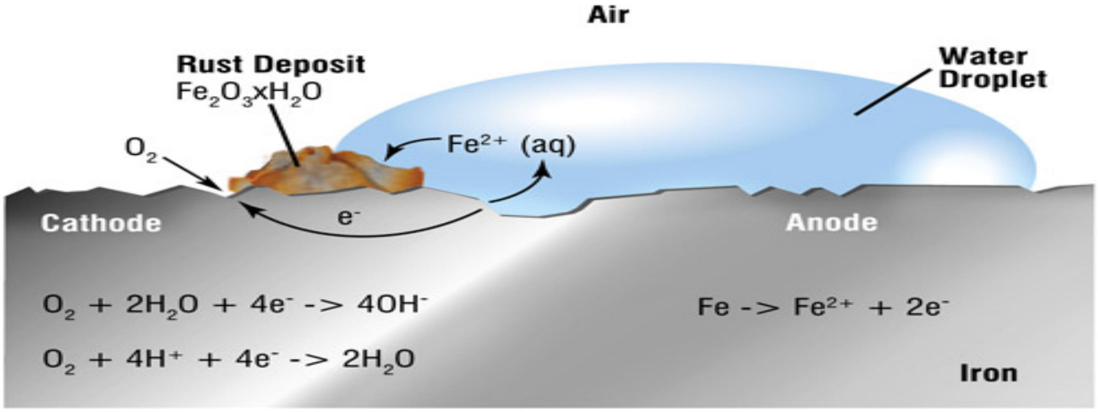


Figure 1. Formation of rust as a result of corrosion of Iron [29].

2.1.2 Cathodic Reaction

Cathode is a negative electrode at which a reduction reaction occurs. The oxidation and reduction reactions are complementary given the fact that electrons produced in oxidation reactions (Eq. (2.1 and 2.2)) are consumed in reduction reactions. Furthermore, it is essential that the cathode and anode be either two different metals or two different sides of the same metal. The main cathodic reaction that occurs in the absence of oxygen and in an acidic aqueous environment is hydrogen evolution: [3]:

$$2H^+ + 2e^- \rightarrow H_2 \tag{2.5}$$

On the other hand, in an alkaline aqueous solution, the reaction occurs as: [23]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2.6}$$

The more favorable cathodic reaction in the presence of dissolved oxygen is:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{2.7}$$

while in the alkaline environment, the reaction is:

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \tag{2.8}$$

all of which denote *reduction* in the chemical concept [28, 30].

2.2 TYPES OF CORROSION

In order for corrosion to occur, an anodic and cathodic sites must be formed. This can be caused by many reasons such as the presence of impurities or composition differences in the metal, localized stresses and surface discontinuities. Rapid changes in the environment condition such as temperature, oxygen and salt concentration also accelerates the formation of such sites. The corrosion is said to be uniform when anodic and cathodic sites migrate on the metal's surface. This happens when local differences on the metal are not too large which creates fouling problems rather than equipment failure.

2.2.1 Uniform or General Corrosion

Uniform corrosion is defined as a type of corrosion attack (deterioration) that is more or less consistently dispersed over the entire surface of a metal. It is also known as loss of material over whole surface when displayed to moist air or electrolyte for a period of time. However, it is not considered as the most dangerous form of corrosion because it is easy to anticipate. This type of corrosion includes the rusting of iron or discoloring of silver as the most common corrosion type in world. The oxidation and reduction reactions occurs randomly over the surface, as previously mentioned [28]. Hence, the expression "uniform corrosion" indicates that the anodic and cathodic locations are almost inherent [31].It is also relatively easy to control uniform corrosion to adequate levels through proper selection of materials and the application of corrosion control methods.

In contrast to uniform corrosion, localized corrosion poses a more serious industrial threat. In this occasion, the anodic site is stationary as the electrochemical reaction occurs. Localized corrosion comes in many forms including pitting, leaching, galvanic corrosion, crevice corrosion, stress corrosion cracking (SCC) and microbiologically influenced corrosion (MIC). Corrosion that arises from erosion is also studied but is debated on which corrosion category it belongs to.

2.2.2 Pitting Corrosion

One of the most destructive types of corrosion is pitting. This form of corrosion is promoted by large variations in surface conditions which causes the anodic and cathodic sites to be stationary. Further deterioration occurs at slow or stagnant environmental condition (low flow velocity) and by the accumulation of chloride ions. Pits of varying sizes are formed where it entraps the solution and isolates it from the bulk environment. This increases the corrosion rate as the pits start forming excess of positively charged cations. For that reason, the presence of chloride anions, that attract the cations further damages the substrate. Hydrolysis reaction that lowers the pH by producing H^+ ions accelerates the rate of corrosion. Pitting corrosion is also difficult to predict even in controlled environments such as laboratory testing. An illustrative example of pitting corrosion can be seen in Figure 2.

Figure 2. Pitting corrosion inside a crude oil pipeline in saltwater and carbon dioxide environment [32].

2.2.3 Selective Leaching

Corrosion of an alloy where only on element disintegrate is referred as selective leaching. For example, the removal of zinc from copper-zinc alloys is termed dezincification, a commonly occurring issue in cooling systems (see Figure 3). The conditions that accelerates steel corrosion are no different to brass where it is generally used in cooling systems. Dezincification is therefore promoted by low pH (<6.0) and high concentration of free chloride anions (<1.0 ppm) [33]. Graphitization is another example of selective leaching occurring in gray cast iron alloy. During the electrochemical reaction, the carbon (2-4%) becomes the cathode, while the anode is iron. The result is iron leaching away while the carbon is left behind untouched [33]. It is important to emphasize that the carbon must be “free” in the structure for leaching to occur. White cast iron does not have free carbon and thus does not corrode by the same method. This form of corrosion can also occur in other alloy systems where some elements such as aluminum, chromium, cobalt, etc are vulnerable to selective leaching.

Figure 3. Dezincification of Admiralty brass [34].

2.2.4 Galvanic Corrosion

A common type of corrosion termed galvanic corrosion, occurs when two different metals are in contact in an electrolyte. Both metals must be in contact with the solution to form the electrical circuit and conduct electricity as can be seen in Figure 4. The electric potential difference between the two metals is the main driving force for this type of corrosion.

For example, galvanic corrosion plays a dominant role in cooling systems where both copper and steel alloys are employed. Since iron (steel) has a more negative standard potential than copper, it will corrode – the system will, in essence, behave like a battery.

In marine environments, where water is a good electrolyte, galvanic corrosion is frequently observed in connections of aluminum-copper and mild stainless-steel. Aluminum and its alloys poses a grand risk to galvanic corrosion due to aluminum being a thermodynamically more active than other materials (more negative standard potential). Similarly to other forms of corrosion, the corrosion of aluminum (and its alloys) is even higher when the electrolyte contains free chlorine or other aggressive species.

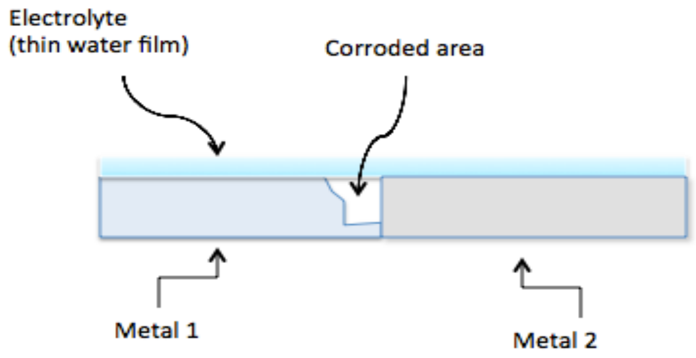


Figure 4. Schematic showing galvanic corrosion.

2.2.5 Crevice Corrosion

Corrosion can also be present in a metal that is in contact with a non-metallic material such as wood or plastic. As the name suggest, a crevice is formed in between the contact area of the metallic substrate and the other material (in a 'pocket', or 'crevice'). The electrochemical process is however diffusion controlled where mobility of the ions of the electrolyte is slow. This leads to a concentration gradient of oxygen levels inside the crevice that is dramatically different from its outside. The electrochemical reaction inside the crevice consumes every available oxygen while oxygen is abundant outside the crevice. The anode is therefore the metal side in contact with crevice white the cathode is the metal side in contact with the oxygen-rich solution outside the crevice.

Crevice corrosion is most commonly found in underneath deposits and narrow cracks or corners where oxygen levels are suppressed. Without the oxygen in these crevices, formation of the protective passive film layer cannot occur. Areas that are secluded from the bulk environment are the most vulnerable to localized crevice corrosion.

The electrolyte found in pitting corrosion are often very similar to the one present in crevice corrosion as they both are highly concentrated and have low pH. The mechanism of these two forms of corrosion are the same and thus any condition accelerating the corrosion of one also applies to the other. Stainless steel and aluminum alloys that rely on passivation for a method of protection against corrosion are at high risks in crevice corrosion. The oxide film gets destroyed in crevices where the solution is very acidic and contains free chlorine ions. Figure 5 shows a typical example of crevice corrosion.

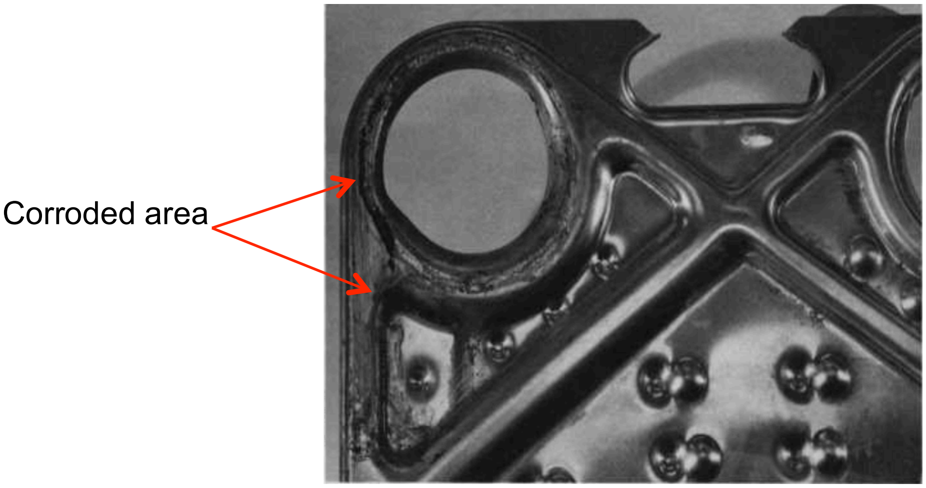


Figure 5. Crevice corrosion in several areas under the gasket of 316 stainless heat exchanger plates in seawater [35].

2.2.6 Erosion Corrosion

Erosion corrosion is a form of corrosion resulting from a turbulent flow between a corrosive solution and the metal. The shear stress on the metal's surface created by either a fast flowing fluid or the substrate itself is in motion results in abrasive wear. Often the surfaces of such corroded metals are shiny, an indication that some material is being actively removed from its surface. An illustrative effect of erosion corrosion can be seen in Figure 6. Grooves and rounded holes that are smooth and have a distinct directional pattern are great indication of erosion corrosion. Often, corrosion of this form arises from a turbulent liquid flowing over the metal and thus can be called turbulence corrosion. Naturally, a more abrasive solution that contains for example, bubbles and suspended solids further aggravates this type of corrosion.

Erosion corrosion initially starts with the formation of a corrosion product and the creation of the protective oxide layer. This layer quickly vanishes due to the abrasive and turbulent nature of the flow. The exposed metal surface then undergoes electrochemical corrosion process aided by the harsh nature of the moving electrolyte. This further leads to the formation of pits that can be distinct in pattern caused by the flow of liquid or gas at the surface of the metal. Major factors affecting erosion corrosion are the flow conditions (velocity, turbulence, chemical and physical compositions). In addition, erosion corrosion can often be localized form of corrosion where the fluid abruptly changes direction.

Figure 6. Corroded metal by erosion corrosion [36].

2.2.7 Stress Corrosion Cracking (SCC)

Stress corrosion cracking or simply stress corrosion arises from the simultaneous combination of applied physical force and corrosive environment. Metals under static or applied tensile stress are prone to such corrosion. The formation of “cracks” is a usual indication that the metal under constant load and in a corrosive solution underwent SCC. Stresses can originate from external loads, centrifugal forces or temperature. Another common source of stress is inside the metal that is induced by cold working or heat treatment. The formation of cracks can be visible on the plane of the metal where tensile stresses are applied normal to that plane. Cracks can propagate along the grain boundary following the grains of the material or trans-granularly following the edge of the lattices. Branching of cracks is also a common observation. Figure 7 shows a typical piece of metal that underwent SCC. Materials that underwent this form of corrosion are often employed in manufacturing, fabrication and heat treatment. Uneven distributed stresses and cyclical forces are the main drivers for SCC in metals found in manufacturing. Internal stresses are formed in processed and treated metals. Such metals and alloys have been through cold working, quenching, bending or pressing and are vulnerable to SCC.

Uneven stress inside the material creates points of varying electric potential. In order to minimize these stresses, corrosion takes place. The anode forms around the point of high stresses while areas under lower stresses becomes the cathode. Materials that form a protective layer inside a typical corrosive environment to prevent additional corrosion cannot do so under applied or static stress.

Cracks formed as a result of SCC can take form of intergranular propagation where the cracks advance along the grain boundaries or trans-granular propagation where cracks are found along individual grains. Often times the surface of the corroded metal is free from visible cracks while fine cracks with extensive branching can be found inside the metal. In corrosive environments, the dissolved corrosion products and the absence of any protective layer makes materials with SCC vulnerable to rapid failure.

As previously mentioned, periodic variation in temperature also induces internal stresses. Materials used in cooling systems such as stainless steels and brasses are susceptible to SCC due to being exposed to different water temperatures. For example, higher temperatures significantly increases stainless steel's weakness to SCC. High stresses coupled with a corrosive environment makes aluminum alloys used in cooling systems susceptible to SCC via intergranular corrosion. The presence of free chlorides ions and elevated temperatures (> 20 °C) of the water poses SCC threats to high strength aluminum alloys [37].

Figure 7. Stress corrosion cracking [38].

2.2.8 Microbiologically Influenced Corrosion (MIC)

Microbiologically Influenced Corrosion (MIC) or simply bacterial corrosion or bio-corrosion is the deterioration of a material due to microbial activity. Microorganisms can adsorb at the metal's surface and form colonies that can further produce corrosive compounds. In many cases, a biofilm is observed at the surface of the substrate as a results of bacteria producing polymeric materials from their cells. The biofilm enhances the formation of a cathode and an anode leading to electrochemical corrosion. Biofilm formation contributes to corrosion via three ways: by physical adsorption, bacterial production of corrosive by-products and depolarization of the corrosion cell. In addition, physical deposition can further create unfavorable compound gradient between the metal's surface and outside the biofilm. For example, bacterial deposits in a pipeline creates low oxygen levels inside the biofilm compared to the rich oxygenated solution leading to accelerated corrosion. Figure 8 shows deposited microbial corrosion inside a pipeline.

Bacteria can range from being aerobic at the water surface or be anaerobic deposited at the metal-biofilm interface. Bacteria can produce highly corrosive compounds such as organic or inorganic acids leading to an electron flow. For example, some microorganisms such as anaerobic sulfate-reducing bacteria transforms organic sulfur compounds present in the solution into hydrogen sulfide (S^{-2} anion), an excellent electron acceptor. The product of this cathodic reaction includes the formation of H_2 gas contributing to hydrogen embrittlement of the metal.

MIC is also an issue encountered in water cooling systems, most notably when the flow is relatively stagnant. Underground systems are also in danger of bacterial corrosion due to the soil being rich in microorganisms and nutrient. Temperatures less than 40 °C and pH between 5 and 9 coupled with low redox potential of the soil indicates anaerobic conditions where MIC is more pronounced [37].

Figure 8. Microbiologically Influenced Corrosion inside the walls of a pipeline [39].

2.3 CORROSION OF CARBON STEEL

Mild (carbon) steel is widely used in industrial processes because of its easy accessibility and its low cost. Examples of industrial applications include water pipelines [40, 41], cooling water systems [42], oil pipelines, gas distribution networks, air conditioning systems, boilers etc. In these industrial institutions, the steel is widely used as a building material. Due to its low cost, mild steel is specially preferred. However, the main problem is that mild steel is susceptible to different forms of corrosion due to its low resistance, as previously described. Therefore, it must be protected versus corrosion in particularly destructive media.

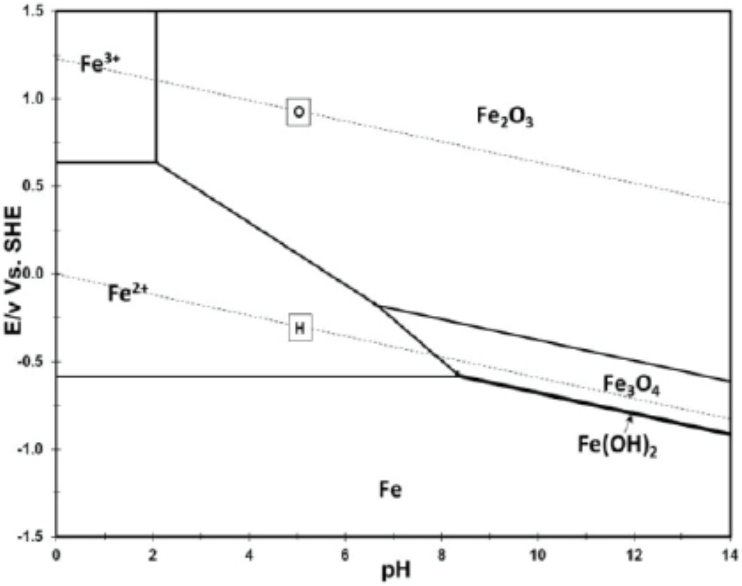


Figure 9. Pourbaix Diagram for H_2O-Fe system at 25 °C [43].

Since the main composition of steel is iron, the corresponding Pourbaix diagram (as shown in Figure 9) for Fe is used to determine the behaviour of this material at 25 °C. Three main regions can be associated with different corrosion types such as immunity, passivation and active corrosion. The region where the potential is independent of the pH corresponds to the immune state where no corrosion does not occur. Passivation is illustrated by the Fe_2O_3 region where thermodynamics favour the creation of the protective oxide layer. Corrosion takes place at the Fe^{2+} region of the Pourbaix diagram where solid iron is oxidized into Fe^{2+} and/or Fe^{3+}.

2.4 CORROSION OF ALUMINUM

Aluminum is a highly reactive material to most surroundings, inside or in the open air. Aluminum is relatively soft, lightweight, has good thermal conductivity and has a very high resistance to corrosion. It quickly forms a thin and intense oxide layer that safeguards the fundamental material very well. Because of these features, aluminum is the most used metal after steel in many industries due to its low cost and easy accessibility for applications such as, tanks, pipeline, and boilers. Although aluminum has a good sturdiness versus many chemicals, it suffers from severe corrosion in aggressive environments, and it has to be protected.

Aluminum suffers mostly from localized corrosion due to the separation of the anodic and cathodic reactions. The galvanic cell size is in addition limited by the resistance of the solution. The anodic electrochemical equation where metal dissolution occurs can be written as:

$$Al \rightarrow Al_3^{+} + 3e^{-} \tag{2.9}$$

while the cathodic reaction is oxygen reduction:

$$O_2 + 2\ H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad (2.10)$$

Or hydrogen reduction in acidified solution such as in a pit environment as a result of aluminum ion hydrolysis:

$$2H^{+} + 2e \rightarrow H_2 \qquad (2.11)$$

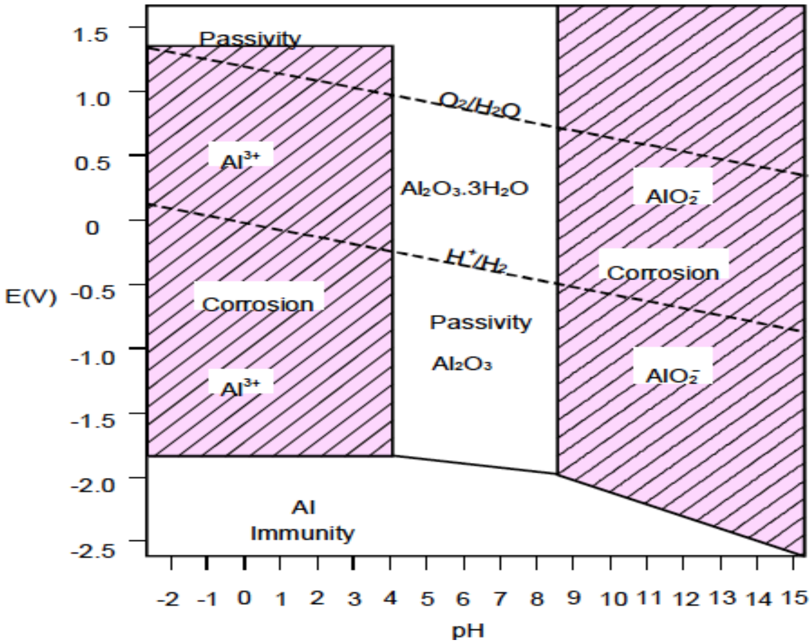


Figure 10. Pourbaix Diagram of Aluminum in Water at 25 °C [44].

Figure 10 represents a Pourbaix diagram for aluminum showing its electric potential as a function of pH. At low potentials, the Al immunity region dominates where the metal is relatively inert. At low pH values corrosion takes place with the dissolution of aluminium cations. The same could be said for high pH values where aluminium anions are formed. pH values between 4 and 8.5 is where passivity takes place with the formation of a stable oxide layer.

2.5 METHODS OF CORROSION PROTECTION

There are many ways to reduce or control corrosion. Therefore, the use of the method depends on various parameters, for instance, the type and the site of the corrosion, the workable use of the surface to be protected, the local environment, etc.

2.5.1 Proper Selection of Materials

There are many major factors affecting the selection of materials, including the chemical formula of the compound, Mechanical, physical and chemical properties, manufacturing requirements, service requirements, cost of the material, cost of processing, and availability of the material. All these major factors have a major impact on the selection of materials. Therefore, one of the most essential tasks is the proper selection of the materials.

2.5.2 Cathodic Protection

Cathodic protection (CP) is a technique used to minimize the corrosion rate of a metal surface by making it the cathode of an electrochemical circuit. This is achieved by sweeping the potential of the metal in the negative direction, which can be acquired by using sacrificial anodes or by an external impressed current. Cathodic protection is a reliable, active and an economic method for protection of a wide range of buried pipelines, water storage tanks, marine structures including ships hulls and submarines against corrosion [45]. However, it is used for protection against external corrosion: e.g. it can protect a buried pipeline from the external corrosion, but does not protect against the internal corrosion of the pipeline, where other corrosion protection techniques are required.

2.5.2.1 Types of Cathodic Protection

The two types of cathodic protection systems: sacrificial anodes and impressed current. They differ in the way the electrons are transferred. In the first one, electrons are transferred in a spontaneous process due to the large potential difference between the two metals while in the later one the electrons are forced to move from the anode to the cathode. In the next two subsections, both methods are discussed in details with case studies presented as examples.

2.5.2.1.1 Sacrificial Anodes

A sacrificial anode is an anode electrically connected to the system to be protected. It is made from a metal alloys with a more "active" voltage (more negative reduction potential / more positive electrochemical potential) compared to those of the metal structure. Three main metals that are used such as sacrificial anodes, magnesium, aluminum and zinc to protect the structures metals (e.g. iron or carbon steel). The difference in potential between the two metals means that the sacrificial anode corrodes, so that the anode material is consumed in preference to the structure. The sacrificial anode will corrode and therefore, the target system will be protected since it becomes a cathode. The sacrificial anode technique uses the natural potential difference that exists between the structure (cathode) and a second metal (anode) in the same environment to provide the driving voltage as shown in Figure 11. Therefore, no power source is employed. Moreover, the dissolution of the second metal, that is, the sacrificial anode, provides the source of electrons for cathodic polarization of the structure [46].

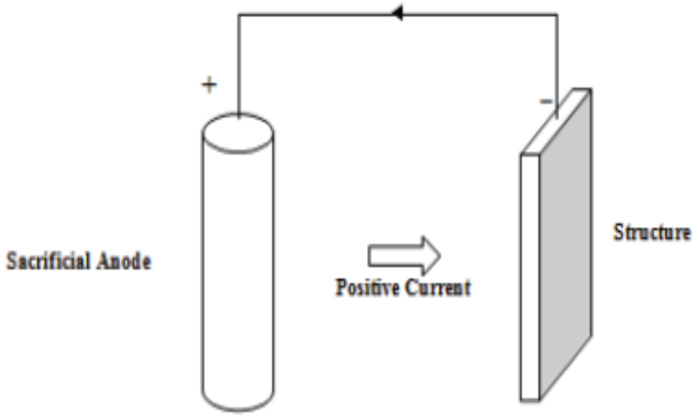


Figure 11. The use of a sacrificial anode for CP [46].

Sacrificial anodes have been widely used for protecting such metal structures as ships hulls, oilrigs and pipelines. On large structures the anodes must be placed at intervals to ensure that the whole surface is protected. Therefore, the use of a sacrificial anode is electrochemically equivalent to cathodic protection since it causes the potential of the surface to become more negative.

Cathodic protection by sacrificial anode has acquired general acceptance as a means of preventing and protecting metals from corrosion. This is because it has the features of being simple to install, independent of a source of external electric power, appropriate for localized protection and less liable to cause interaction on neighbouring structures [47]. This is accomplished by changing the electrode potential of the metallic structure so that it lies in an exterritorialy region, within this region, the metal is in the stable form of the element and corrosion reactions are therefore impossible [48].

2.5.2.1.2 Impressed Current

Impressed current type cathodic protection systems supply cathodic current to the system to be protected, from an external power source. Therefore, this form of corrosion protection is applied by connecting the negative terminal of a DC power source to the structure to be protected and the positive terminal to an anode. Because the driving voltage is provided from a DC source and not electric potentials, the anode does not need to oxidize and an inert anode can be used such as mild steel, ferrosilicon, graphite, lead alloys, magnetite and platinized titanium anodes. The circuit includes a power source, an auxiliary or impressed current electrode, the corrosive solution, and the structure to be protected (Figure 12). The power source drives a positive current from the impressed current electrode through the corrosive solution to the structure. The structure is thereby cathodically polarized (i.e. its potential is lowered), and the positive current returns through the circuit to the power supply. Thus, to achieve cathodic protection, the impressed current electrode and the structure must be in both electrolytic and electronic contact.

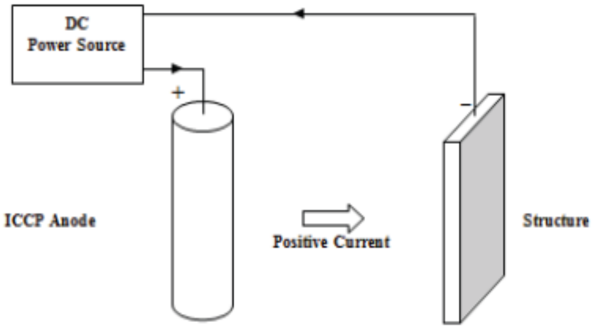


Figure 12. The use of an external power supply to provide CP [46].

There are three major advantages of using impressed current cathodic protection (ICCP), one being that the DC power sources can provide much higher driving voltages than sacrificial anodes (100 to 10,000 times higher) and can protect larger areas. The second major advantage is that the anodes that are used, such as graphite, are inert and do not need to be constantly replaced. The final advantage is the degree of control over the electron transfer that ICCP has; the current can be increased or decreased as needed. ICCP is what is usually found on all pipelines as it does not have to be constantly monitored like sacrificial anodes and there is more control over the electron flow [49]. Also, using radio-waves, it could be controlled remotely.

2.5.3 Corrosion Inhibitors

A corrosion inhibitor is a chemical substance which, when added to a corrosive environment, continuously or intermittently decreases the rate of corrosion attack. In addition, inhibitors are considered the first line of defense against corrosion. It is a widely used method for corrosion control of the primary material used in the construction of cooling water systems and other industrial water distribution systems. However, many of the corrosion inhibitors that are being used in the industries are toxic, such as sodium chromate, acetylenic alcohols etc. Therefore, due to these reasons, there is an increasing interest in exploration and utilization of eco-friendly inhibitors, known as green corrosion inhibitors. Green corrosion inhibitors are (bio)organic compounds that are neither toxic and are biodegradable. They act by adsorption on the metal surface by forming a film that minimizes the interaction between the surface and the corrosive environment.

2.6 CLASSIFICATION OF CORROSION INHIBITORS

Inhibitors are chemicals that react with a metal surface, or the environment this surface is exposed to, providing the surface a definite level of protection [50]. Inhibitors often act by adsorbing themselves on the surface to be protected, forming a film on the metallic surface and thus protecting it influencing the anodic or cathodic polarization behavior, decreasing the movement or publishing of ions to the metallic surface, and rising the electrical resistance of the metallic surface [45, 50].

On the other hand, removing the corrosive species in the medium can control corrosion. Inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called environmental conditioners or scavengers [45]. They can be classified into liquid and vapor phase inhibitors and also called volatile corrosion inhibitors (VCI). They are compounds transported in a closed environment to the site of corrosion by volatilization from a source [50].

Liquid-phase inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on whether they inhibit the anodic, cathodic, or both electrochemical reactions [45].

2.6.1 Anodic Corrosion Inhibitors

Anodic corrosion inhibitors usually work by the formation of a preventative oxide film on the surface of the metal causing a large anodic transformation of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors: oxidizing anions, such as chromate, nitrite, and nitrate, that can passivate steel in the absence of oxygen and, the nonoxidizing ions, such as phosphate, tungstate, and molybdate, which require the presence of oxygen to passivate steel. These type of inhibitors are the most effective and the most widely used in recirculation-cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers [45].

2.6.2 Cathodic Corrosion Inhibitors

Cathodic corrosion inhibitors act by either reducing the rate of cathodic reaction itself or stimulating selectively on the cathodic surface areas to limit the diffusion of reducible species to these areas. In addition, cathodic inhibitors are effective at forming protective inhibitor films at cathodic corrosion sites so as to prevent oxygen reduction of cations such as magnesium, zinc, and nickel. The rates of the cathodic reactions can be decreased by the use of "cathodic poisons”. Cathodic poisons are substances that intervene with the cathodic reduction process. Examples include arsenic, antimony, sulfur, selenium, tellurium, and cyanide which prevent the hydrogen atoms from forming hydrogen gas. However, cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking. Hydrogen can be absorbed as well by the metal during aqueous corrosion or cathodic charging. The corrosion rates can also be decreased by the use of oxygen scavengers that react with dissolved oxygen, such as sulfite and bisulfite ions that can combine with oxygen to form sulfate. Some cathodic inhibitors, such as composites of arsenic and antimony, act by making the recombination and discharge of hydrogen more difficult.

2.6.3 Organic Inhibitors

Organic inhibitors act by decreasing both the cathodic and anodic reactions, but as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors commonly have heteroatoms. They protect the metal by adsorbing to the metal surface. Therefore, such compounds commonly sediment on the surface blocking both anodic and cathodic sites indirectly. Oxygen, Nitrogen, and Sulfur are found to have higher basicity and electron density and thus work as corrosion inhibitors because availability of non-bonded (lone pair) p-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. Oxygen, Nitrogen, and Sulfur are the active centers for the process of adsorption on the metal surface [51]. Therefore, the corrosion inhibition efficiency of the homologous series of organic substances differing only in the heteroatom is ordinarily in the following order: $P > S > N > O$ [52, 53]. However, the efficiency of an inhibitor depends on the characteristics of the environment in which it acts. It also depends on the nature of the metal surface and electrochemical potential at the interface. The structure of the inhibitor itself is another factor, which includes the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface [54-62]. The use of organic compounds containing polar groups including oxygen, sulfur, and especially nitrogen to decrease corrosion attack on steel has been studied in some detail. The existing data show that most organic inhibitors absorb to the metal surface by displacing water molecules on the surface and forming a compact barrier.

The performance of organic inhibitors is related to the magnitude to which they adsorb and cover the metal surface. Organic inhibitors protect the metal in three possible ways: physical adsorption, chemisorption and film forming. The physical adsorption (physisorption) process is one in which there are van derWaals (electroattractive) forces of interaction between gas or liquid molecules and electrically charged metal surface. On the other side, chemical adsorption (chemisorption) occurs due to a charge transfer, where the adsorbed species must have a dipole in the molecule. In addition, it ordinarily takes place through donation of electrons from species with loosely bonded electrons, such as multiple bonds, or unpaired electrons in functional groups that contain atoms such as O, N, S, P, to the vacant d-orbital of transition metals (substrate), or π-electrons in aromatic rings [51]. Therefore, the force of the chemisorption bond depends onto the electron density on the donor atom of the functional group and also the polarizability of the group. Therefore, when an H atom attached to the C in the ring is substituted by a functional group (–NH2, –NO2, –CHO, or –COOH) it improves inhibition [63]. The electron density in the metal at the point of attachment changes leading to the obstruction of the cathodic and/or anodic reactions. In addition, straight chain amines containing between three and fourteen carbons have been examined. Inhibition increases with carbon number in the chain to about 10 carbons, but with higher members, only a slight increase or even a decrease in the ability to inhibit corrosion occurs. This is due to the reduced solubility in aqueous solution with increasing length of the hydrocarbon chain. However, the presence of a hydrophilic functional group in the molecule would increase the solubility of the inhibitors.

Also, the performance of an organic inhibitor is linked to the chemical structure and physicochemical properties of the compound like functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule. The inhibition could be due to (i) adsorption of the molecules or their ions on anodic and/or cathodic sites, (ii) increase in cathodic and/or anodic over voltage, and (iii) the formation of a protective barrier film.

In general, the adsorption of an organic inhibitor on a metal surface depends on the structure of the inhibitor, on the surface physico-chemical properties of the metal, on the nature and surface charge of the metal, and on the kind of electrolyte [45, 50]. Inhibitors such as imidazolines, amines, diamines, pyrimidines are well-known corrosion inhibitors for metals and alloys in various corrosive media [64]. For example, the general chemical structure of an imidazoline inhibitor is shown in Figure 13.

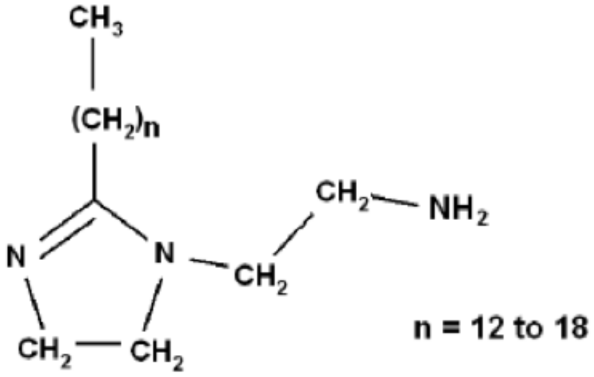
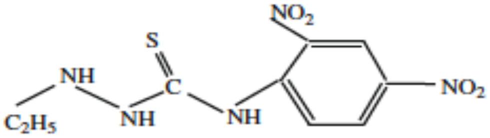


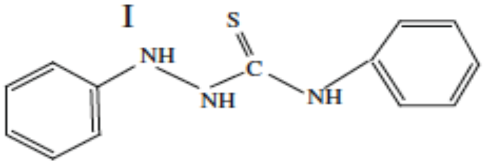
Figure 13. General chemical structure of imidazoline [52].

The following examples were noted on literature review. Ortega-Toledo et al. [53] studied the CO_2 corrosion inhibition of high-strength pipeline steel by hydroxyethyl imidazoline, as corrosion inhibitor in saltwater. The results showed that this inhibitor was an anodic-type inhibitor and the greater inhibitor efficiency (62%) was reached at concentration 25 ppm. Liu et al. [54, 55] studied an electrochemical behavior of carbon steel in saltwater saturated with carbon dioxide (CO_2) by using a new synthesized imidazoline derivative inhibitor. They found the inhibition efficiency of the inhibitor increased with increasing the inhibitor concentration, yielding a maximum value of 80%. Also, they found that the imidazoline ring and heteroatoms are the active sites of the inhibitors. Badr [56] studied the corrosion inhibition of carbon steel in 2 M HCl by some thiosemicarbazide derivatives namely, 1-ethyl-4(2,4-dinitrophenyl) thiosemicarbazide (I), 1,4-diphenylthiosemicarbazide (II), 1-ethyl-4-phenylthiosemicarbazide (III). The chemical structures of thiosemicarbazide are presented in Figure 14. It was found that the essential effect of these compounds as corrosion inhibitors was due to the presence of free electron pairs in the inhibitor structure. The results show that the higher corrosion inhibition efficiency (~75%) was found by using the inhibitor 1-ethyl-4(2,4-dinitrophenyl) thiosemicarbazide (I), which provided a better surface coverage.



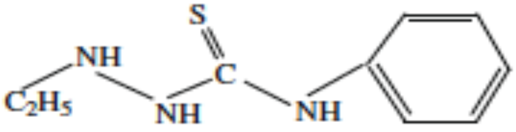
1-ethyl-4-(2,4-dinitrophenyl)thiosemicarbazide

I



1,4-diphenylthiosemicarbazide

II



1-ethyl-4-phenylthiosemicarbazide

III

Figure 14. Chemical structure of inhibitors: (I) 1-ethyl-4(2,4-dinitrophenyl) thiosemicarbazide, (II) 1,4-diphenylthiosemicarbazide (II) and (III) 1-ethyl-4-phenylthiosemicarbazide [56].

Moretti et al. [57] studied the inhibition effects of tryptamine (TA) as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid (H_2SO_4) in the temperature range 25-55 C°. Tryptamine is a derivative of the tryptophan, relatively cheap molecule, non-toxic and easy to produce in purity greater than 99%, which is one of the standard amino acids. TA was found to be an effective iron corrosion inhibitor, even at 55 C° and over a period of 72 h, but only at concentration 10^{-2} M, the maximum protection inhibition efficiency for both 25 and 55 C° ranged from about 95% to 98%.

Yildirim and Cetin [58] synthesized and evaluated the inhibition effect of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivative on carbon steel corrosion in 2 M HCl and mineral oil medium. The authors found these inhibitors provided a good corrosion protection (~90%) and showed maximum efficiencies at the critical concentration (50 ppm).

Ashassi-Sorkhabi et al. [59] studied the inhibition effect of three amino acids (alanine, glycine and leucine) against steel corrosion in 0.1 M HCl solution. The authors found these amino acids were physically adsorbed on the metal surface and the inhibition efficiency depended on the type of amino acid and its concentration. Inhibition efficiency depended on the type of amino acid and its concentration. The results obtained increasing inhibitor concentration, its adsorption to metal surface increases and also its inhibition efficiency, ranging from 28 to 91%.

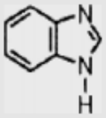
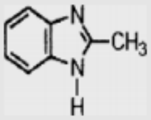
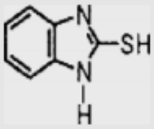
Hluchan et al. [60] studied corrosion inhibition of iron in 1 M hydrochloric (HCl) solution, by amino acids. The authors studied twenty-two different common amino acids, and the best result was obtained with 3,5-didiodotyrosine, with an inhibition efficiency of 87%. In addition, they concluded that amino acids with longer hydrocarbon chains showed greater inhibition efficiency.

Saliyan and Adhikari [61] synthesized a new corrosion inhibitor, quinolin-5- ylmethylene-3-((8-(trifluoromethyl)quinolin-4-yl)thio)propanohydrazide (QMQTPH), and tested as corrosion inhibitor for mild steel in 1 M and 2 M HCl. The results show that the high corrosion inhibition efficiency was (~91%). Also, they found the inhibition efficiency increased with increasing inhibitor concentration in the range 10-5 - 10-3 M, but slightly decreased with increasing temperature.

Abiola et al. [62] studied the corrosion inhibition of Gossypium hirsutum L. leave extracts (GLE) and seed extracts (GSE) of aluminum in 2 M NaOH. They found the inhibition efficiency increased with increasing concentration of the extracts. Results showed GLE gave 97% inhibition efficiency while the GSE gave 94% at the highest concentration. Therefore, the leave extract (GLE) was found to be more effective than the seed extract (GSE).

Aljourani et al. [63] studied the inhibition ability of benzimidazole, 2-methylbenzimidazole and 2-mercaptobenzimidazole against the corrosion of mild steel in 1 M HCl. The chemical structures of benzimidazole are presented in Table 1. The results show 2-mercaptobenzimidazole provided a higher inhibition effect (~90%), and was attributed to the presence of sulphur and nitrogen atoms in the same time in the molecular structure of the inhibitor.

Table 1. Benzimidazole derivatives chosen to be studied as corrosion inhibitors for mild steel in 1 M HCl [63].

Inhibitor	Structure
Benzimidazole	
2-Methylbenzimidazole	
2-Mercaptobenzimidazole	

A. Yurt et al. [64] synthesised newly three Schiff bases—MP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]phenol), MBP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]-4-bromophenol), MCP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]-4-chlorophenol)—on the corrosion behaviour of aluminum in 0.1 M HCl. The results show that the corrosion inhibition efficiency (~84%) was found by using the inhibitor MCP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]-4-chlorophenol), (~80%) MBP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]-4-bromophenol) and (~67%) MP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]phenol). MCP and MBP are the most effective ones, since they have electronegative atoms such as chlorine and bromine as substituent on the benzene ring of Schiff bases as can be seen in Figure 15. Also, the results show that inhibition efficiencies increase with increase in inhibitor concentration.

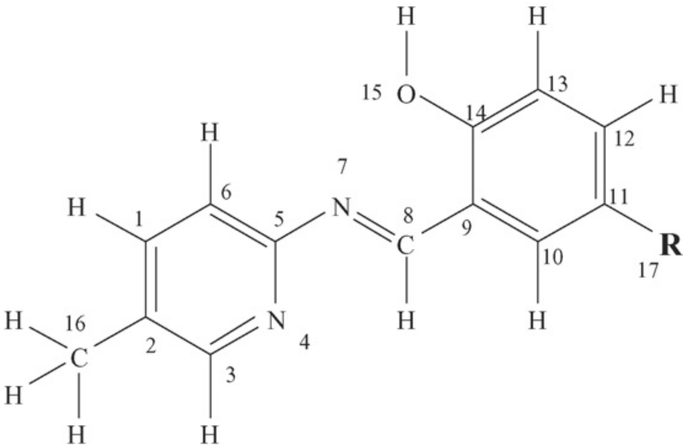


Figure 15. Chemical structure of inhibitors: MP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]phenol); R = H; MBP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]-4-bromophenol); R = Br; MCP (2-[2-aza-2-(5-methyl(2-pyridly))vinyl]-4-chlorophenol); R = Cl [64].

2.7 SELECTION OF THE CORROSION INHIBITOR

Inhibitors must be chosen after taking into account the nature and combinations of metals present, the nature of the corrosive environment, by selection of suitable physical properties for the operating conditions in terms of flow, temperature, and heat transfer. In addition, the presence of sulfur, oxygen, nitrogen, phosphor and multiple bonds or aromatic rings in the inhibitor molecule is preferred. Therefore, this leads to increased adsorption of the compound on the metal surface and to the strength of the inhibition efficiency [65, 66]. Furthermore, it should be non-toxic, and prevent causing a health risk [67-69].

2.8 ADSORPTION OF CORROSION INHIBITORS

Preventive absorbed film is formed over the whole metal surface if an adsorption inhibitor is used. Hence, the film helps to protect electrochemical reactions between metal and aqueous ions. Some of the organic compounds are proper to work as adsorption inhibitors. So to understand the mechanisms of corrosion inhibition, the adsorption behavior of the organic adsorbate molecules (inhibitors) on the metal surface needs to be known. Though, the adsorption process, depends upon (1) the topography, uniformity and phisico-chemical properties of the metal surface, (2) the chemical structure of the organic molecule, (3) the distribution of the charge in the molecule, and (4) the aggressive medium [70, 71].

2.9 TOXICITY OF CORROSION INHIBITORS

Since many corrosion inhibitors have been used in different industries to control corrosion, a number of them that are still in use are considered toxic and harmful for the environment. For instance, sodium chromate was extensively used as an additional for the inhibition of corrosion in aqueous heating and cooling systems. Unfortunately, it is no longer in use because it is suspicious to be a carcinogen [72-74]. Another example, acetylenic alcohols are extensively used as acidizing inhibitors because of their trade feasibility and effectiveness. However, these inhibitors suffer from defects: they are efficient only at high concentrations, they are considerably toxic, causing problems of treating and get red of waste, and they produce toxic vapors under acidizing process conditions [75]. Thus many common corrosion inhibitors that are still in use are toxic [76], it remains a major aim to find inhibitors of the non-serious type for the prevention of metals against corrosion [65]. Hence, it is extremely important to study environmentally friendly molecules that could be used as possible corrosion inhibitors.

2.10 ENVIRONMENTALLY FRIENDLY INHIBITORS

In recent years, the safety and environmental affairs related to the use of corrosion inhibitors become universal concern because a number of corrosion inhibitors that are still in use are health hazards. Therefore, there has been an increasing trend in developing more environmentally-friendly corrosion inhibitors.

For example, Fares et al. [3] studied the inhibitor effect of a pectin natural polymer, acidic media, as a green corrosion inhibitor on the surface of aluminum metal in 2.0 M HCl. They showed that pectin natural polymer is a good corrosion inhibitor on the surface of aluminum metal in this acidic electrolyte, yielding a maximum inhibition efficiency of 91%.

Ghareba and Omanovic [77] studied the inhibitor effect of 12-aminododecanoic acid (AA), as a corrosion inhibitor for carbon steel (CS) in 0.5 M HCl. They showed that 12-aminododecanoic acid (AA) inhibits both partial corrosion reactions, with a slightly stronger inhibition of the anodic corrosion reaction for carbon steel in this acidic electrolyte, yielding a maximum inhibition efficiency of 98.8% and standard Gibbs energy of adsorption was −26 kJ mol^{-1}.

Hmimou et al. [78] studied the inhibitor effect of 2-propargyl-5-p-chlorophenyltetrazole (PCPT), acidic medium, as a corrosion inhibitor for mild steel in 1M HCl. They showed that 2-propargyl-5-p-chlorophenyltetrazole (PCPT) has good inhibiting properties for mild steel corrosion in this acidic electrolyte, yielding a maximum inhibition efficiency of 98% at 5×10^{-4} M

Omanovic and Roscoe [79] studied the possibility of using SAMs of linoleic acid (LA) on a 316L stainless steel surface as corrosion inhibitors. They found that the adsorption of LA onto the stainless steel surface results in an almost saturated coverage and high inhibition efficiency (95 %) towards corrosion. LA has been found to act as a mixed-type inhibitor and its inhibitory effect was explained on the basis of a self-assembled blocking mechanism.

Ibrahim and Mohamed [80] studied the inhibition effect of fig leaves extract as a corrosion inhibitor for mild steel in 2 M HCl solution. The authors found the change in free energy and the activation energy values indicate that the adsorption is physical. Inhibition efficiency of as high as 87% were achieved for fig leaves extract of above 200 ppm.

Xianghong et al. [81] studied the inhibition effect of sodium molybdate (Na_2MoO_4) as a corrosion inhibitor for aluminum in 1.0M H_3PO_4 solution. The results show that Na_2MoO_4 is a good inhibitor, and the inhibition efficiency obtained by three methods is higher than 84% at 20 mM. The adsorption of Na_2MoO_4 obeys the Freundlich isotherm at lower concentrations (1–7 mM), while the Langmuir isotherm describes the adsorption at higher concentrations (7–20 mM). Polarisation curves indicate that Na_2MoO_4 acts as an anodic inhibitor.

Mobin et al. [82] studied the effect of corrosion inhibition behavior of nitrogen-containing amino acid L-Histidine (LHS) on mild steel in 0.1 M H_2SO_4 solution in the temperature range of 30-60°C. Also, they studied the effect of the addition of very small concentration of surfactants, sodium dodecyl sulfate (SDS), and cetyltrimethyl ammonium bromide (CTAB), respectively on the corrosion inhibition behavior of LHS. They found LHS noticeably decrease the corrosion rates of mild steel, with the maximum inhibition efficiency (IE) being 71.09% at 30 °C in the presence of 500 ppm of LHS. Furthermore, the IE of LHS is synergistically increased in the presence of SDS and CTAB.

Anejjar et al. [83] studied the effect of potassium thiocyanate (KSCN) on the corrosion of carbon steel in 1 M HCl. The results obtained revealed that the compound is a good mixed type inhibitor with predominant cathodic effectiveness. Also, they studied the effect of temperature on the corrosion behavior with the addition of optimum concentration of KSCN in the temperature range 298–328 K. It was found that the value of inhibition efficiency decreases slightly with the increase in temperature.

Ayşe Ongun Yüce et al. [84] studied the effect of corrosion inhibition behavior of 2-amino-4-methyl-thiazole (2A4MT), as a corrosion inhibitor for mild steel (MS) in 0.5 M HCl. The results show that 2A4MT yields an excellent inhibition activity against the corrosion of MS in 0.5 M HCl solution. In addition, the high inhibition efficiency is attributed to the adherent adsorption of the 2A4MT. The authors found the inhibition efficiency increases with inhibitor concentration but decreases with the temperature increase.

Ostovari et al. [85] studied the inhibition effect of henna extract (Lawsonia inermis) and its main constituents (lawsone, gallic acid, a-D-Glucose and tannic acid), as a mixed inhibitor for corrosion of mild steel in 1 M HCl solution. Also, the authors studied the effect of the addition of henna extract and they concluded that the latter shifts the pitting potential of mild steel to more positive values indicating an increased resistance to pitting corrosion. They also found all the examined henna constituents act as mixed-type inhibitors for corrosion of mild steel in 1 M HCl with good inhibition efficiencies in the following order: lawsone > gallic acid > a-DGlucose (dextrose) > tannic acid, and the inhibition efficiency increases with increase of inhibitor concentration to attain a maximum value of 92.06% at 1.2 g/l henna extract.

Abiola et al. [86] studied the inhibition properties effect of Gossypium hirsutum L. leave extracts (GLE) and seed extracts (GSE) as green corrosion inhibitors for aluminum in 2 M sodium hydroxide (NaOH). They found the inhibition efficiency increased with increasing concentration of the extracts, and the GLE gave 97% inhibition efficiency while the GSE gave 94% at the highest concentration. Therefore, the leaves extract (GLE) was slightly more effective than the seeds extract (GSE) in reducing the corrosion rate of aluminum in NaOH solutions.

CHAPTER 3

The previous chapter of the thesis presented some general aspects of corrosion and corrosion protection. In this chapter, emphasis will be put on corrosion and corrosion protection in water-treatment systems.

3 WATER-TREATMENT SYSTEMS

Closed water systems are present in many of today's facilities such as hospitals, cities and factories. In developed countries, consumption of water is alarmingly high. Closed systems have their function of either heating or cooling water. Many innovative and sustainable efforts are being done to reduce water consumption in domestic and industrial processes. For that reason, closed water systems also clean the water and recycle it for reuse. Reducing water consumption by this method however adversely increases the concentration of inorganic salts dissolved in the water. The water becomes more electrolytic and hence increases the corrosion rate of the vessels and piping equipment. Components commonly found in closed water loops that are affected by corrosion include: boilers of varying operating pressure, cooling system, piping and various tanks.

3.1 BOILERS

Boilers are specialized vessels operating at various pressures designed to heat water or produce steam. In residential buildings, hot water produced by the boiler is essential and has many usage as service water. Commercial buildings use boilers that are powered by natural gas. Boilers can also have electric resistance heaters or be fueled by oil fired burners. Applications such as adsorption cooling, kitchens, laundries, sterilizers typically make use of steam generated by boilers.

The widespread use of boilers in today's buildings comes to no surprise since they are very efficient at heating (~95%) and have a long work life. They make for an effective method of heating buildings during cold times and require little to no moving parts (pumps) in case of steam. The shortcoming of such boilers is manifested by high fuel costs and requirement of regular maintenance.

3.1.1 High Pressure Boilers

Boilers are fabricated to operate at specific designed pressures, for high-pressure boilers that amounts to operating steam pressures above 80 bar [87]. Main use of high-pressure boilers is found in industrial application such as power generation in thermal power plants.

High-pressure boilers are operated in an efficient manner where only latent heat of vaporization is supplied to generate steam. Typically, the feed water is heated to saturation level with the help of waste heat incoming from a different stream. For that reason, less energy is required for high-pressure boilers to supply steam.

Typically, high-pressure boilers are equipped with two super heaters in series and operate at pressures 80 to 300 bar and steam temperature generated from 450 °C to 585 °C [87]. Steam at these conditions is essential to drive turbines optimally. In addition to an increase of thermal efficiencies, it reduces the moisture content during the expansion stage in the turbine.

Modern high-pressure boilers transfer their heat via radiation, conduction and convection. The equipment receiving the heat is divided into several parts in order to be easily located inside the furnace. Forced water circulation is a feature shared by many high-pressure boilers in order to increase evaporative capacity and heat transfer. Thus high-pressure boilers require less heat of vaporization that allows compact design for additional floor spacing.

Using feed water at high velocities, scale formation is reduced and uniform heating is maintained. Simple and efficient control system allows for quick steam flow and temperature adjustment without worrying of overheating.

3.1.2 Low-Pressure Steam and Hot Water Heating Systems

Low-pressure boilers heat an circulate water to approximately 90 °C and generate steam to pressure of ~1 bar [33]. These heat systems are typically closed loops that require little maintenance. Some boilers can operate at moderate pressures between 2.4 – 24 bar as long as the pressure is maintained above saturation to keep the hot water in the liquid state.

Dissolved oxygen and low pH are major concerns that lead to corrosion in low-pressure operating boilers. Inhibitors such as molybdate nitrite are added to alleviate corrosion. Some systems with high dissolved oxygen content make use of oxygen scavenger such as sodium sulfite combined with a synthetic polymer to control corrosion and formation of deposit.

3.2 BOILER SYSTEM CORROSION

Corrosion issues inside boilers can arise from various sources, one them are dissolved gases. Oxygenated water is the main cause of the formation of pits due to its localized nature (see Figure 16). Dissolved CO_2 is typically found in condensate systems as opposed to water distribution systems that also causes corrosion. Copper and copper bearing alloys are specifically susceptible to water containing ammonia combined with dissolved oxygen. In many cases the corrosion manifests into harmful deposits that reduce heating efficiencies and decrease the working life of the boiler.

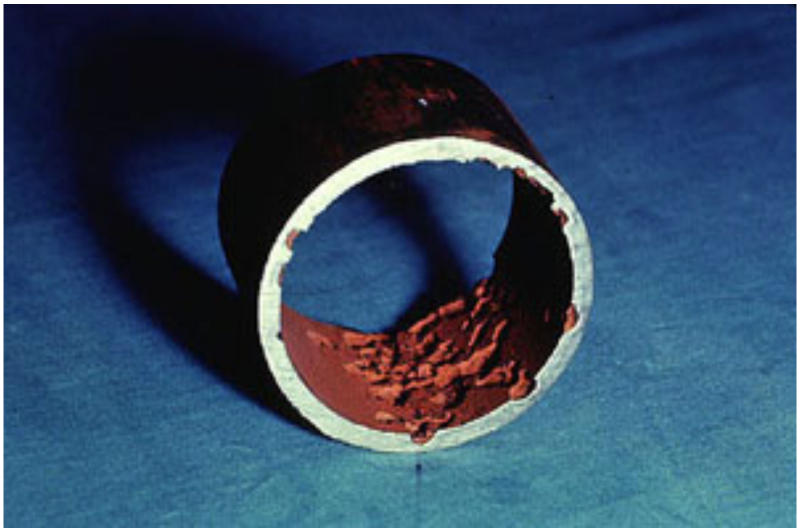


Figure 16. Tube severely damaged by oxygen [33].

3.2.1 Boiler deposits

Steam generating boilers are mostly affected by formation of deposits arising from corrosion products. Lose of heating control such as overheating can be an issue due to high accumulation of material along the boiler's wall. The need for downtime and maintenance costs become exacerbating as a result of such corrosion. Feed water containing dissolved metals and ions such as calcium, magnesium, iron, copper, aluminum and silica are major factors contributing to boiler deposits. Deposits are generally classified by the form they take: scale deposits or sludge. Scale deposit is the accumulation of material crystallized directly on the surface of the substrate (pipe or tube see Figure 17). On the other hand, sludge is typically precipitated elsewhere then with flowing water, transported to the metal's surface.

3.2.1.1 Boiler scale

Boiler scale is manifested by typical precipitation where temperature controls the solubility limit of a compound. Salts that are soluble in boiler (hot) water have limited solubility limit and precipitate on the walls of piping as soon as critical solubility temperature is reached. Scaling is manly found in water containing high calcium and magnesium salts which are less soluble hot than cold. In addition, silica content in relation with the pH (alkalinity) of the water also contributes to scaling.

Figure 17. Boiler scale onto the tube surfaces [88].

3.2.1.2 Boiler sludge

Boiler sludge is known as the deposit formed from suspended particles settling and adsorbing onto the walls of boiler tubes and other surfaces (see Figure 18). Compounds such as hydroxyapatite or magnesium silicate are typical sludge deposits. While condensate corrosion is the main cause of metal oxides such as iron oxide formation, makeup water and feed water also plays a role. Deposited metal oxides can adsorb on already present sludge and form a thick layer on the tube's surface decreasing heat transfer efficiencies.

Figure 18. Boiler sludge onto the hot tube surfaces [89].

3.3 COOLING SYSTEM

Many industrial equipment require heat removal for optimal operation. The use of a proper cooling system is therefore necessary to insure correct temperature control of an instrument and increase its work life. Such cooling water circuits have similar issues to boiler loops where corrosion and accumulation of scale deteriorate the life span of the equipment and piping. In addition, corrosion also reduces thermal efficiencies and can significantly increase maintenance costs.

3.4 COOLING SYSTEM CORROSION

Corrosion in cooling systems have two main repercussions: equipment failure and decrease of thermal efficiency. With excessive material deterioration, replacement of equipment becomes necessary, an expensive and daunting task. Accumulation of corrosion products and heat exchanger fouling (see Figure 19) significantly decreases heat transfer efficiency thereby increasing operational costs.

Figure 19. Corrosion in cooling system [90].

3.4.1 Cooling System Deposits

In addition to reducing thermal efficiencies, corrosion deposits also limit the water's flow rate of the water distribution system. Oxygen differential cells that accelerate corrosion also begin to form as a result of deposits. Depending on the water's composition and mechanism leading to deposits, accumulations can take form of thin adsorbing films to thick gels (see Figure 20). Deposit forming mechanism is a function of different parameter such as water properties (temperature, flow rate, composition, and residence time) and system metallurgy. For example, in system operating at high wall temperatures and low water velocities, heavy deposits are observed.

3.4.1.1 Scale deposits

Scale deposits in cooling water systems are formed via precipitation coupled with crystal growth at the surface of the substrate. When solubility of certain compounds exceed their limits at the specific temperature, precipitation occurs. For example, compounds such as calcium carbonate, calcium phosphate and magnesium silicate are frequently observed to form scale deposits at higher temperatures where the water is adjacent to a heat exchanger.

Scale formation is however not always dependant on temperature. Some rough metallic surfaces could trigger deposits of for example, calcium sulfate where crystal nucleation could easily take place. Low water velocities is also a factor in the formation of scale deposits. Furthermore, precipitation could be triggered by different pH values. The formation on corrosion cells on the metal's surface creates areas of high pH where many salts precipitate. Once solid compounds adhere to the surface, nucleation followed by rapid crystal growth dominates.

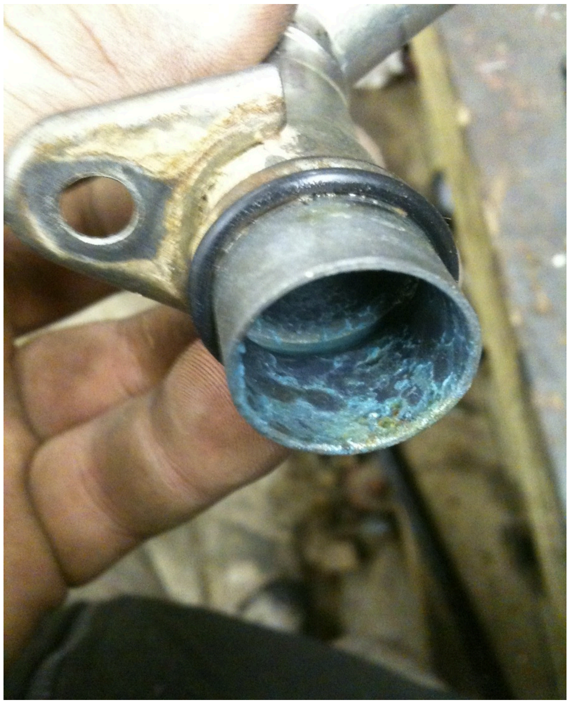


Figure 20. Cooling System Deposits [91].

3.5 CORROSION IN THE WATER TREATMENT SYSTEMS

Corrosion is the most widespread problem in the water-treatment systems such as heating and cooling. The major cause of failure of closed-loop systems is corrosion.

3.5.1 Closed Loop Systems

Closed-loops are basically big heat exchangers designed for heat transfer and are ubiquitous in buildings, industries, etc. Closed Loop Water Systems are designed that convey hot water, or cold water through buildings or equipment for heating or cooling purposes, and then return the water to the point of origin to restart the process. Many hot and cold loops are used for heating or cooling of internal spaces, such as private homes, or hotels, etc.

Corrosion can be caused by many factors, including the type of materials used, the age of the piping and fittings, the stagnation time of the water and the water quality in the system, low pH, oxygen and other gases interacting with the system metal, galvanic occurs between two dissimilar metals such as carbon steel and aluminum. All these cases might lead to a metal loss, which can result in leakage and failure of the system.

In water, the corrosion of metal fundamentally relies on the installation of water. Therefore, water that is used to fill closed loops systems for Cooling or Heating normally contains dissolved oxygen, very high chloride concentrations and other anions of metals.

Figure 21 is a schematic diagram of a typical closed recirculating heating system. The heat-exchange medium (water) is circulated between the heat source (boiler) and the heat sink (radiators). A typical radiator is made from mild steel and the heating modules in the boiler are made from aluminum.

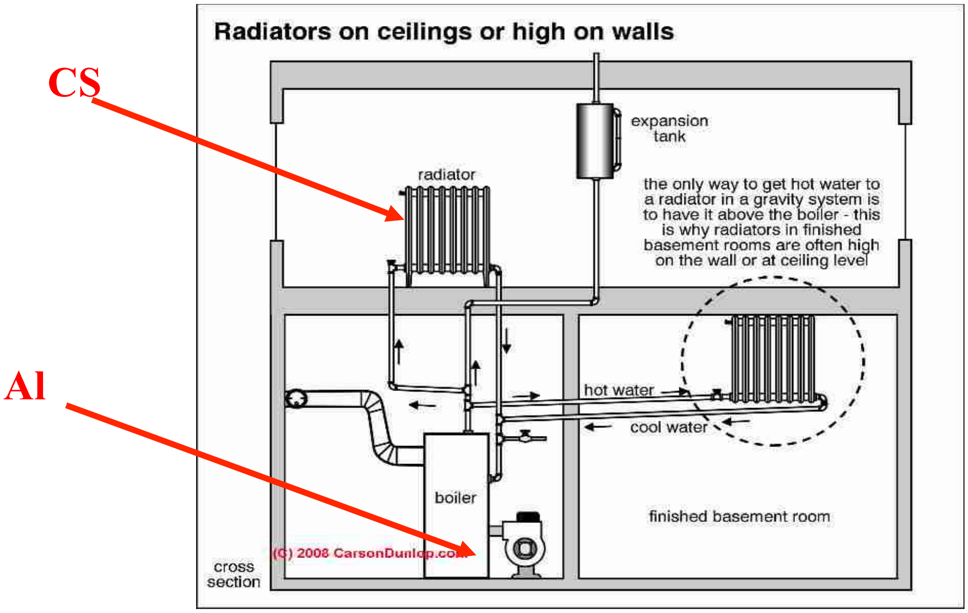


Figure 21. Schematic diagram of a closed recirculating heating system [92].

3.5.1.1 Corrosion of Carbon Steel in the Closed Loop System

One of the most extensively investigated metals for corrosion studies is carbon steel because of its widespread application in various corrosive environments such as cooling and heating systems, etc.

Carbon steel is used considerably in the manufacture of pipelines for heat exchanger tubes. Corrosion problems occur in these pipelines due to the harsh environment. The oxygen dissolved in the system water will interact with the iron content in steel radiators to produce rust and hydrogen. The rust, hydrogen and heat can also produce chemical reactions within the system. The end product, commonly seen, is ferric oxide rust.

3.5.1.2 Corrosion of Aluminum in the Closed Loop System

Aluminum has good resistance to corrosion, due to a preventative film of surface oxide, but perturbations in this film can lead to rockiness and then consequence to corrosion. Aluminum is considered as one of the most widely used system metals in household central heating systems. It is usually used to produce highly efficient boilers and radiators.

Aluminum is susceptible to corrosion at higher pH levels, and the use of normal boiler chemicals can be extremely harmful to the boilers. Therefore, these kinds of boilers are very susceptible to boiler water pH, and need to be chemically treated very accurately. Aluminum has a potential to undergo pitting attack at high pH levels. This potential, is the reason of several problems, particularly in systems with mixed metallurgy.

All of these systems include mild steel, aluminum and copper, and each of these metals request partially different treatment ways to ensure protection. In the case of aluminum and mild steel, the treatment ways are actually in contradiction with each other. Mild steel corrosion protection requires a high pH 10, while the protection of aluminum needs a much lower pH (8 to 9).

Therefore, boilers made with aluminum heat transfer components are increasingly used for new process manufacturing and industrial applications. They offer energy efficiency advantages, and are likely less expensive to manufacture than steel boilers. Aluminum is usually hard to chemically safeguard, because it is amphoteric. This means that it is very reactive at both ends of the pH spectrum. In addition, chlorides and heavy metals affect the sturdiness of aluminum. In drinking water, small holes in the aluminum can occur. When boilers and radiators fail, it is both disruptive and costly for homeowners but also cause major problems for installers.

Metal corrosion in water systems is of major concern in industrial applications because immoderate corrosion does not only lead to severe harm of installations, it also causes senior environmental pollution.

Hence, common problems arising from corrosion are lowering in heat transfer and water flow producing from a partial or complete clogging of pipes, pumps, valves, refineries, etc. Therefore, thermal and energy transfer of a heat exchange may get affected with large economic fallout. The cost of corrosion is always more importance than just the substitution of the heat exchanger or element.

Furthermore, gases that are usually found in water carrying pipelines are carbon dioxide (CO_2) and oxygen (O_2). These gases in a pipeline are the major causes of corrosion [75, 93].

When CO_2 dissolves in water, it yields carbonic acid, causing the formation of $FeCO_3$ [94-96].

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{3.1}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{3.2}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \tag{3.3}$$

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \tag{3.4}$$

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \tag{3.5}$$

3.5.1.3 Control of pH

Control of pH is crucial for the most of water treatment systems. Generally, when pH is less than recommended extents, the opportunities for corrosion increase and when pH is more than recommended extents, the opportunities for scale forming increase.

Decreasing the pH value in cooling water with mineral acid is easy and cost effective way to decrease the scaling potential for many common scale constituents, such as calcium carbonate and calcium phosphate. Solubility of potential scale forming minerals increases with reducing pH. However, adding acid because the solubility of this salt is almost independent of pH cannot effectively control Calcium Sulphate scaling.

Scale forming potential is reduced in acidic environment; however, decreasing pH value may increase the corrosion produced by water, as well as the solubility of calcium / corrosion inhibitor salts. Therefore, suitable pH control is required to provide an appropriate environment for both scale and corrosion inhibitors act effectively.

However, in most industrial systems there are huge temperature differences and it may be more suitable to control the pH value of the water (by acid addition such as Sulfuric acid), below that at which calcium carbonate will come out of solution, and to counter the offensive action by the use of a corrosion inhibitor. On the other hand, control can be accomplished by the use of chemical, such as inorganic polyphosphates, to delay scale formation at what would generally be scaling pH levels.

Generally, the higher the pH of the cooling water, the greater will be the propensity to form mineral salt deposits. Therefore, many control systems are operated at pH values slightly below the saturation-scaling index and corrosion is prevented by the use of an inhibitor.

3.6 CORROSION INHIBITORS IN HEATING SYSTEM

Corrosion inhibitors do not eliminate full possibility of corrosion but rather, reduce the corrosive ability of the water. Inhibitors introduced in closed loop systems can last the life time of a building if regular maintenance is done.

The two most commonly used corrosion inhibitors for hot water boilers are nitrite and molybdate. Molybdate is one of the most practical corrosion inhibitors, which has been proven to be capable of preventing the corrosion of different metals and alloys in a variety of corrosive media, especially when combined with other chemicals. In addition, molybdate works in conjunction with oxygen to form a protective oxide layer on ferrous metals, so it is not effective in the absence of oxygen. However, the main drawback of molybdate is its expense. Nitrite is also an effective inhibitor. However, in open systems it tends to be oxidized to nitrate. In addition, nitrite cannot be used in aluminum boilers, as it produces a very reacting and corrosive situation. Hence, use of nitrite will lead to serious damage to aluminum boilers. Also, a shortcoming of nitrite treatment is the propensity to promote microbiological growth.

Other corrosion inhibitors include chromate, silicates and orthophosphate. Chromate is an effective and economic aqueous corrosion inhibitor for steel, copper, and aluminum. However, the use of chromate has dropped recently and will probably be banned in the near future, due to its high toxicity. Silicates are found to be slow-effect inhibitors. Orthophosphate is not really an oxidizer per se, but transforms to one in the presence of oxygen. Polyphosphates form a polarizing film on the cathodes, although orthophosphate combine with calcium to form an iron phosphate film on anodic surfaces of ferrous metals. Due to its low cost, orthophosphate is extensively used as an industrial corrosion inhibitor.

For example, LaBrosse and Erickson [97] held a pilot research to determine effective aluminum corrosion inhibition. Closed loop inhibitors were investigated on a pilot scale hot water system with a maximum temperature of 160 °F. The pH was kept below 8.5 in most trials, due to specifications from aluminum boiler manufacturers. It was found that nitrite, silicate, and azole were ineffective at controlling aluminum corrosion in a multi-metal system at any pH, on the other hand, higher levels of silicate and azole with a molybdate adjunct provided effective aluminum corrosion inhibition at a pH range of 7.3–8.5. For a pH range of 8.5–9.7, molybdate or nitrate adjunct combined with silicate were found to effectively control both aluminum and carbon steel corrosion. It was also found that copper corrosion was successfully controlled with an azole product at any pH investigated.

Munn [4] studied modern inhibitor formations used for the protection of central heating systems against corrosion and scaling. New non-toxic nitrite free inhibitors were developed for central heating systems involving electrochemical testing of steel/copper couples under temperature cycling and of cast iron under nucleate boiling conditions. They found that an inhibitor based on molybdate and carboxylate could offer full protection of mild steel and copper and be economically viable.

Gaudreault et al. [98] studied green chemistry – with a special emphasis on tannin molecules for the protection of aluminum boilers. They used the pilot unit to investigate the corrosion inhibition efficiency on aluminum, mild steel and copper used in boilers, hot-water closed loop systems. Results show that TGWT tannins (TG 3000) protect aluminum surface from pH 7.0 up to 9.0, i.e. above manufacturer's specifications (pH = 7.0 to 8.5). In addition, corrosion inhibition efficiencies up 80% were obtained for aluminum (pH 7-9) and mild steel (pH 10-11). Figure 22 shows that it takes approximately 5 hours for TG 3000 to reach to the highest corrosion inhibition.

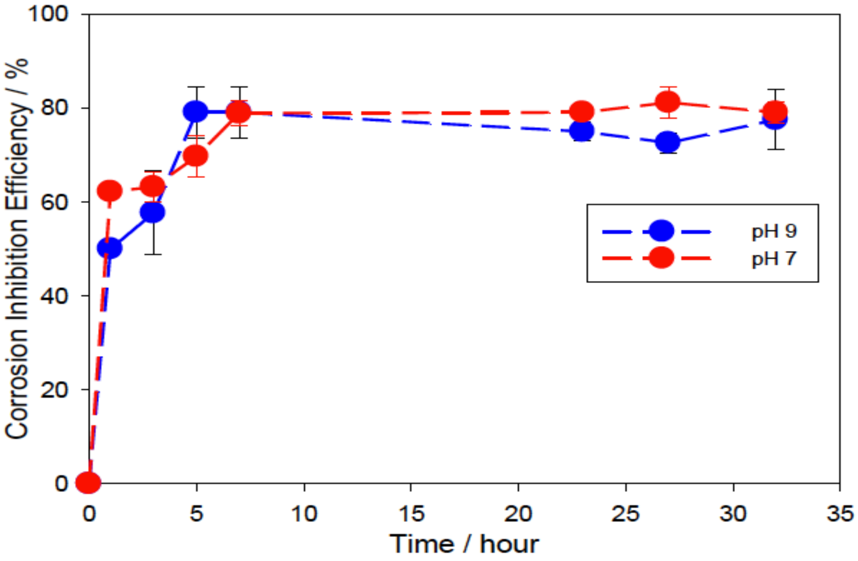


Figure 22. Corrosion inhibition efficiency of TG 3000 inhibitor as a function of time for Al 1100 at 72°F (22°C) at pH 7 (red) and 9 (blue) [98].

Also, Figure 23 shows the corrosion inhibition efficiencies of TG 3000 inhibitor for both Al 1100 and C1010, at various pH after one hour of incubation at 158°F (70°C). The results indicate that the optimum pH / corrosion inhibition efficiency of a closed loop aluminum/mild-steel boiler system, using tannin-based chemistry, would be about 9 or lower.

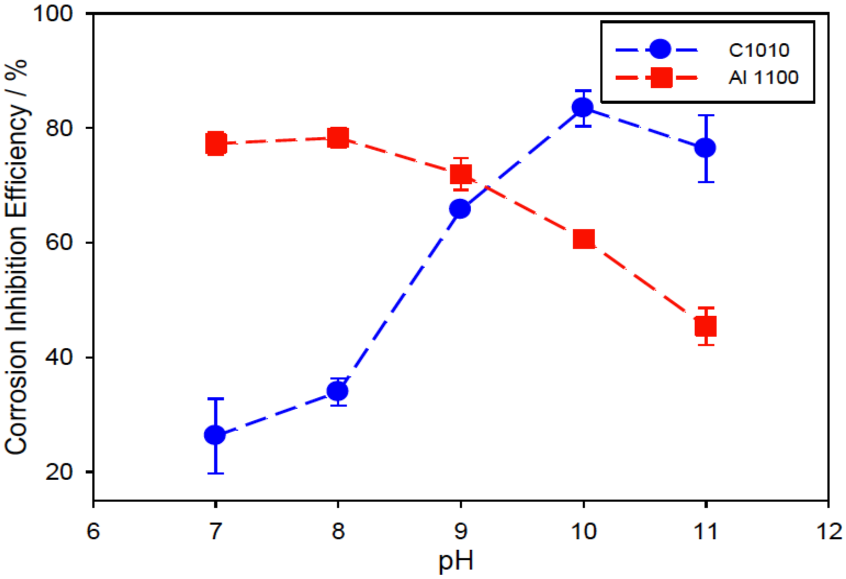


Figure 23. Corrosion inhibition efficiency (η) of TG 3000 inhibitor as a function of pH for C1010 and Al 1100 obtained by modeling EIS spectra at various pH after one hour of incubation at 158°F (70°C) [98].

3.7 CORROSION INHIBITORS IN COOLING SYSTEM

One of the most effective, practical and economical ways for prevention of metal corrosion in cooling system is the use of corrosion inhibitors. The water treatment chemistry at the correct time is extremely important because even simple problems can create significant costs. For instance, the failure of pipes or valves might lead to blocking of surface facilities. Water should be treated with a measured dose of the suitable chemicals and the water quality should be observed to make sure that the chemicals are operating effectively. Hence, injection of corrosion inhibitors through different locations of pipes to protect installations from failure is extremely important.

There are two major treatment methods for injecting inhibitors inside a well stream; the first method is to inject bottom a specified treater series enable continuous injection, and the second is to go at cyclic periods bottom the tubing with the well shut in [50].

For example, Abulkibash et al. [99] studied corrosion inhibition of carbon steel in cooling water system by 2-Phosphonobutane-1,2,4 tricarboxylic acid (PBTCA), either alone or in combination with polyvinylpyrrolidone (PVP). They found the inhibition efficiency at different inhibitor concentrations to increase with increasing PBTCA concentration as shown in Figure 24. A sizable betterment in the protection efficiency was accomplished by adding polyvinylpyrrolidone to the PBTCA solution. The study showed PBTCA and PVP works as a synergic inhibitor and found to increase the inhibition efficiency to 96.7%.

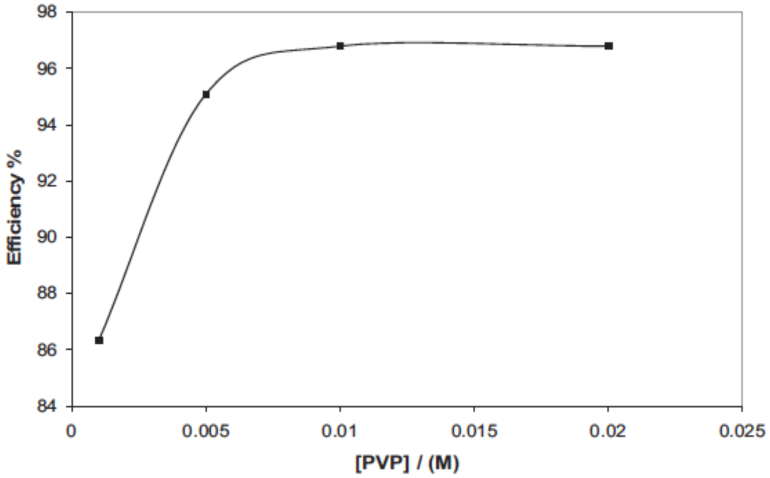


Figure 24. Effect of the concentration of mixture of 0.01M PBTCA with different concentrations of PVP on the protection efficiency of carbon steel in cooling water at 23°C [99].

The variation of protection efficiency with the concentration of PBTCA was investigated at various temperatures using weight loss measurements as shown in Figure 25.

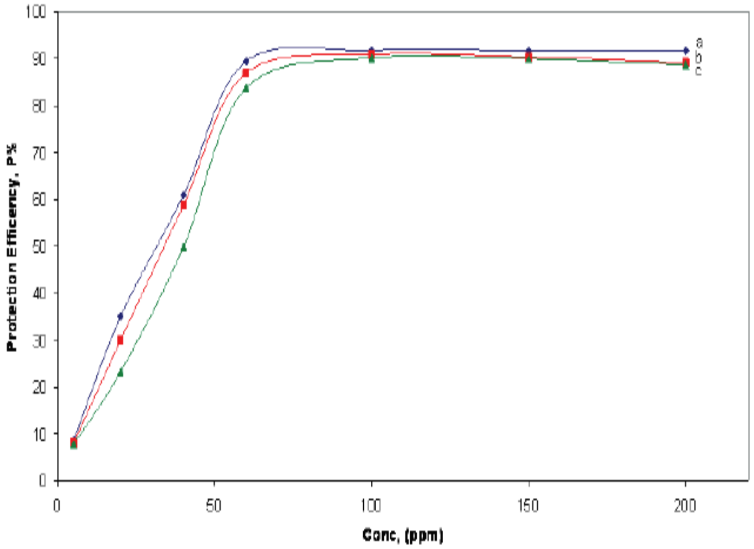


Figure 25. Variation of the protection efficiency with the concentration of PBTCA for carbon steel in cooling water: (a) 23, (b) 40, and (c) 60°C [99].

As Figure 25 shows, temperature has no significant effect on the performance of PBTCA. This may be due to the low phosphorus content of this compound, that it resists hydrolysis, and has high thermal stability at high temperatures [100]. A similar observation was made at high temperatures upon combining PVP with PBTCA as shown in Figure 26.

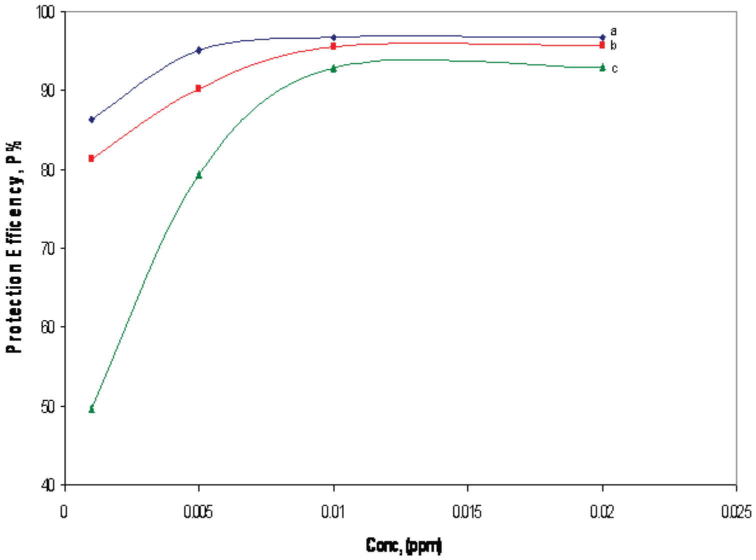


Figure 26. Variation of the protection efficiency with the concentration of mixture of (100 ppm PBTCA with different concentration of PVP) for carbon steel in cooling water at different temperatures: (a) 23, (b) 40, and (c) 60°C [99].

Badiea et al.[5] studied inhibition efficiencies of Ocimum basilicum and Cucurbita pepo extracts on low carbon steel corrosion in industrial cooling water. They found that the plant extracts chosen showed good performance as green inhibitors for low carbon steel in industrial water, and their inhibitive performance improved with increasing concentration up to critical values of 2.96 and 5.25 g L^{-1}, with inhibition efficiency of 82.02% and 77.86% for Cucurbita pepo and Ocimum basilicum at 30 and 40 °C, respectively at 1.56 m s^{-1}, as shown in Figure 27.

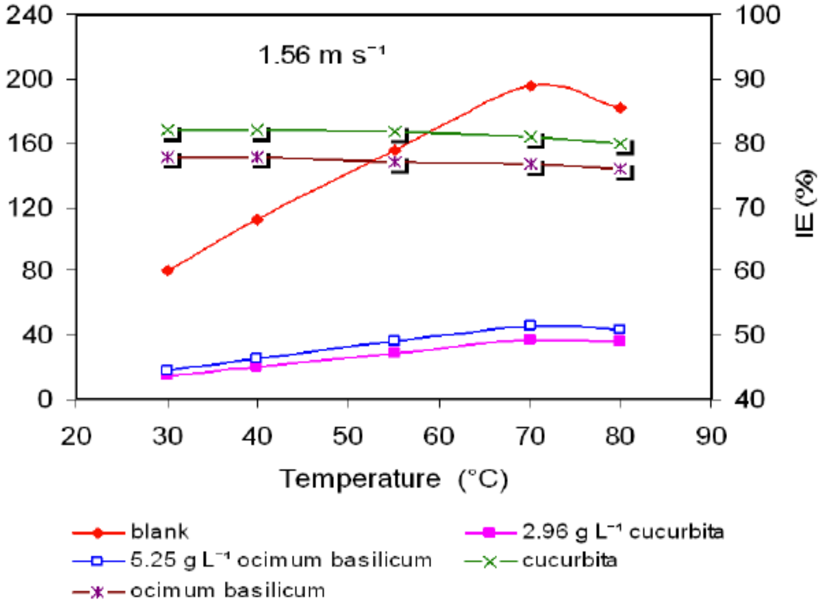


Figure 27. Effect of temperature on IE in absence and at optimum concentration of cucurbita pepo and Ocimum basilicum at 1.56 m s-1 [5].

Saremi et al. [6] studied the effect of molybdate concentration and hydrodynamic effect on mild steel corrosion inhibition in simulated cooling water. The authors found that molybdate was able of inhibiting the corrosion of mild steel in simulated cooling water. They found that the inhibition efficiency of molybdate was increased with increasing both its concentration and water circulation velocity. Therefore, these two factors seem to promote the adsorption of molybdate and oxygen ions on the metal surface, leading to the formation of a preventive layer with a greater charge transfer resistance and lower permeability.

Badiea et al. [101] studied effect of temperature and fluid velocity on corrosion mechanism of low carbon steel in presence the corrosion inhibition of 2-hydrazino-4,7-dimethylbenzothiazole in industrial water medium at different concentrations. The results showed that corrosion resistance increased by increasing the inhibitor concentration. The authors found the negative values of Gibbs free energy in the presence of 2-HMBT indicated that, the adsorption processes of inhibitor on low carbon steel in industrial water is chemisorption. Also, the activation energy increased with increasing the concentration of inhibitors leading to decrease of the pre-exponential factor, and the entropy of activation increased negatively in the presence of inhibitor. The inhibition efficiency of 2-HMBT reaches 82.07 % for low carbon steel in industrial water.

Mohana et al. [102] studied effects of sodium nitrite–borax blend on low carbon steel corrosion in industrial water medium at various temperatures, various inhibitors concentration of sodium nitrite and borax and at various rotational speeds of the specimens. They used an analytical grade $NaNO_2$ and $Na_2B_4O_7$ (Merck) as inhibitors. The inhibition efficiency of sodium nitrite-borax blend was found to be 75.82 % at 1627 rpm and 83 ppm $NaNO_2$ and 1660 ppm $Na_2B_4O_7$ at 30 °C. The inhibition efficiency of $NaNO_2$–$Na_2B_4O_7$ blend was found to be slightly decreased with increasing temperature at the optimum condition. Also, the higher concentration of inhibitors in industrial water decreased the apparent activation energy for corrosion of low carbon steel.

Touir et al. [103] studied the mechanism action of sodium gluconate (SG) for ordinary mild steel used for cooling water system treatment. Gluconate sodium (SG) and cetyltrimethylammonium bromide (CTAB) were used as corrosion, scale and biofilm inhibitors. Their molecular structures are presented in Figure 28. Result showed that the inhibition efficiency became more important with increasing temperature, at high concentration (10^{-2} and 10^{-3} M). This can be explained by the formation of a stable complex SG–Ca^{2+}. The obtained results show that SG is a very good inhibitor for corrosion and scale and remains effective in the presence of corrosion products.

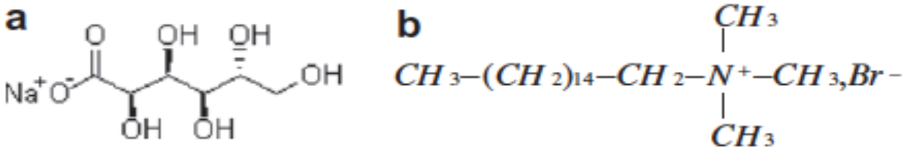
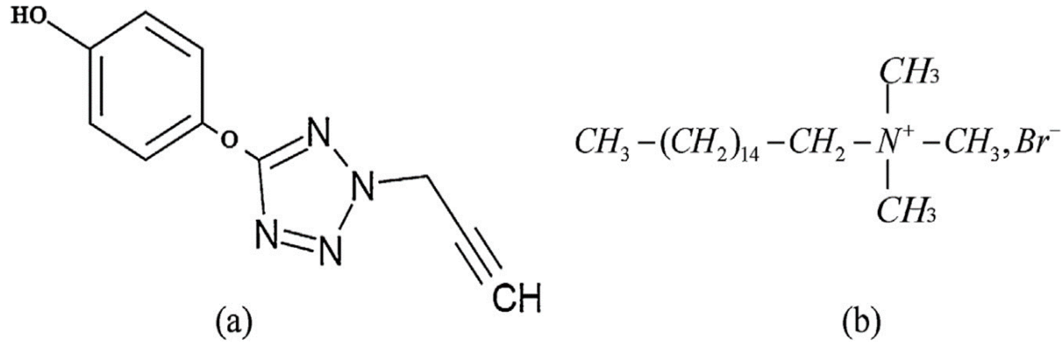


Figure 28. Chemical structure of inhibitors: (a) Sodium gluconate and (b Cetyltrimethylammonium bromide [103].

Touir et al. [7] studied the effect of phosphonate anion (PHOS) on the corrosion of ordinary steel in simulated cooling water. PHOS was studied in the concentration range from 7.5×10^{-5} to 10^{-3} M. Results showed that PHOS perform excellently as corrosion inhibitor for ordinary steel in simulated cooling water. They found that the inhibition efficiency of PHOS was increased with increasing both its concentration and water circulation velocity. Hence, these two factors seem to promote the adsorption of phosphorus and oxygen ions on the metal surface, leading to the formation of a protective layer with a greater charge transfer resistance and lower permeability.

Dkhireche et al. [104] have studied the effect of 2-propargyl-5-o-hydroxyphenyltetrazole (PHPT), as corrosion inhibitor for low carbon steel in simulated cooling water. The chemical structures of these two compounds are presented in Figure 29. Its inhibition efficiency was found to enhance with increase of the inhibitor concentration and immersion time due to the formation of the inhibitor film on the metal surface.



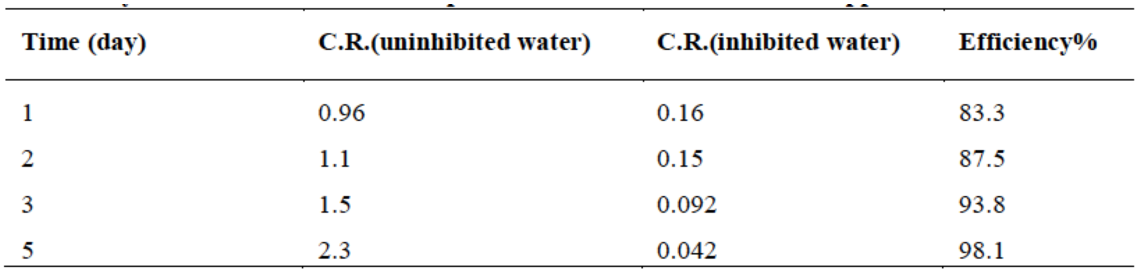
$$CH_3-(CH_2)_{14}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-CH_3,Br^-$$

Figure 29. Chemical structure of the inhibitors: (a) 2-propargyl-5-o-hydroxyphenyltetrazole (b) Cetyltrimethylammonium bromide (CTAB) [104].

Karim et al. [8] studied effect of corrosion inhibition of mild steel by sodium nitrite in simulated cooling water (SCW) containing chloride ion. The authors concluded that nitrite inhibited mild steel corrosion in near neutral and alkaline (pH 6 and above) SCW and accelerated corrosion in aqueous media (pH 4 and below). They showed that the inhibition activity increased with the increase of nitrite concentration up to 500 ppm, and afterwards remained more or less constant at pH 6 and above. In addition, in stagnant SCW, maximum corrosion inhibition was observed at pH 8 for all concentration of $NaNO_2$.

Dina Raheem [105] studied the effect of mixed corrosion inhibitors in cooling system by using carbon steel specimens. The carbon steel specimens immersed in mixture of sodium phosphate (Na_2HPO_4) used as corrosion inhibitor and sodium gluconate ($C_6H_{11}NaO_7$) as a scale dispersant at different concentrations (20,40, 60, 80 ppm) and at different temperature (25,50,75 and 100)ºC for (1-5) days. Hence, the author showed that the corrosion inhibitors efficiency was calculated by using uninhibited and inhibited water to give 98.1% as shown in Table 2. The results of these investigations also indicate that the corrosion rate decreases with the increase of corrosion inhibitors concentration at 80 ppm as shown in Figure 30 and at 100ºC for 5 days. In addition, Table 3 and Figure 31 showed that the corrosion rate increased with temperature.

Table 2. Efficiency of Mixture of Sodium Phosphate and Sodium Gluconate at 80 ppm [105].



Time (day)	**C.R.(uninhibited water)**	**C.R.(inhibited water)**	**Efficiency%**
1	0.96	0.16	83.3
2	1.1	0.15	87.5
3	1.5	0.092	93.8
5	2.3	0.042	98.1

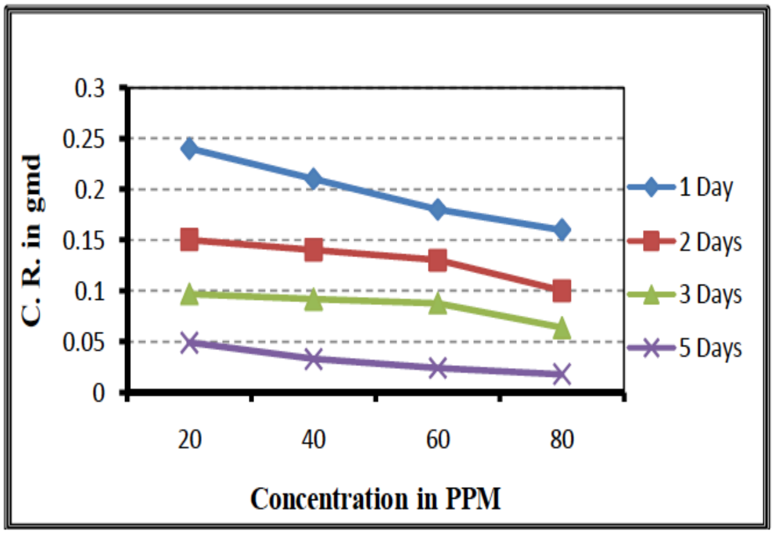


Figure 30. Effect of Concentration of Mixture Inhibitor on Corrosion Rate [105].

Table 3. Corrosion Rate of Carbon Steel in Mixture of Sodium Phosphate and Sodium Gluconate at 80 ppm Concentration and at Different Temperature [105].

Test no.	**Time /day**	**Temp. in °C**	**Weight/w1 in gram**	**Weight/w2 in gram**	**Δw**	**Surface area (cm)^2**	***C.R. in gmd**
1	1	25	47.1500	47.1511	0.0011	0.00652	0.16
2	1	50	47.1498	47.1415	0.0017	0.00652	0.27
3	1	75	47.1432	47.1445	0.0022	0.00652	0.34
4	1	100	47.1400	47.1414	0.0014	0.00652	0.23
5	2	25	47.2999	47.3008	0.0009	0.00415	0.10
6	2	50	47.2998	47.3014	0.0016	0.00415	0.20
7	2	75	47.1500	47.1539	0.0039	0.00652	0.30
8	2	100	47.1500	47.1515	0.0015	0.00652	0.20
9	3	25	47.2999	47.3007	0.0008	0.00415	0.064
10	3	50	47.1400	47.1417	0.0017	0.00652	0.09
11	3	75	47.1400	47.1429	0.0029	0.00652	0.15
12	3	100	47.3300	47.3312	0.0012	0.00415	0.12
13	5	25	47.3300	47.3303	0.0003	0.00415	0.018
14	5	50	47.1500	47.1506	0.0006	0.00652	0.02
15	5	75	47.1400	47.1409	0.0009	0.00652	0.028
16	5	100	47.2999	47.3002	0.000029	0.00415	0.014

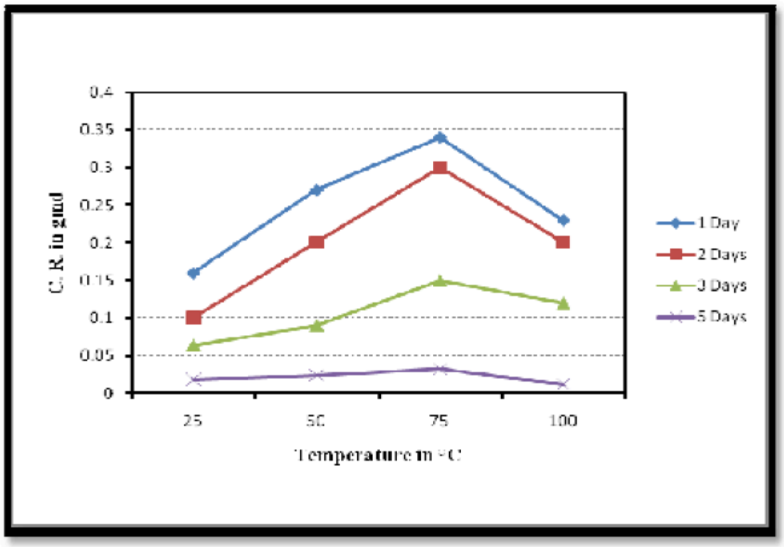


Figure 31. Effect of Temperature on Corrosion Rate at Different Times and at 80 ppm of Mixture Corrosion Inhibitors Concentration [105].

Also, Figure 32 showed the corrosion rate decreases with increasing time at constant concentration.

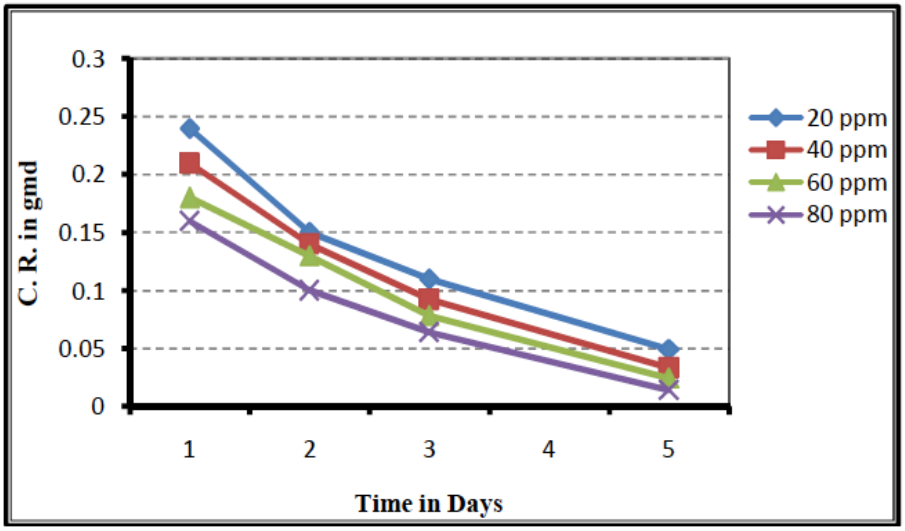


Figure 32. Effect of Time on Corrosion Rate with Different Concentration of Mixture Inhibitor [105].

CHAPTER 4

4 CONCLUSION

Mitigating corrosion in the industry is a necessity as the penalties of failures due to corrosion can be very costly. These failures might result in safety hazards too. There exist different methods of reducing corrosion in industries. Among these different techniques the most economically viable method is the use of corrosion inhibitors. Therefore, it is one of the most effective, practical and economical methods for prevention of metal corrosion in cooling and heating systems. Since inhibitors can easily be applied through batch and/or continuous treatments, partial or complete shutdowns in the plants can be minimized.

Based on previously displayed facts, numerous compounds can be used as corrosion inhibitors and the possibility of their application depends on a few factors. The presence of aggressive ions and pH are among the most important parameters for selecting the medium in which the inhibitor is applied.

The mechanisms of corrosion inhibition are different for different compounds. Molecular structure of inhibitor is the main factor determining its characteristics. Inorganic compounds act through oxide films formation. Organic compounds mostly act via adsorption on metal surface and complex formation. That is the basis of the adverse effect of high temperature on the efficiency of organic compounds. The toxicity of organic and inorganic corrosion inhibitors to the environment has prompted the search for safer corrosion inhibitors such as green corrosion inhibitors as other more environmental friendly corrosion inhibitors, most of which are biodegradable and do not contain heavy metals or other toxic compounds. Higher inhibitor concentration and longer exposure of metal in inhibitor solution lead to increase in corrosion prevention efficiency.

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