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Calculation the Corrosion Rate of Carbon Steel in Sulfuric Acid Under Static Condition by Using the Weight Loss Method

A research submitted to the University of Maysan, College of Engineering, Department of Petroleum Engineering, as part of the requirements for obtaining a bachelor's degree.

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بسِيم التَّه ٱلتَّحْمَ ٱلتَّحِب مِ

﴿ قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَاك إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيمُ ﴾

[سورة البقرة، الاية 32]

Supervisor Certification

I certify that the preparation of this project entitled "Calculation the Corrosion Rate of Carbon Steel in Sulfuric Acid Under Static Condition by Using the Weight Loss Meth"

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Date: / / 2025

Dedication

To the Qa'im of the Family of Muhammad, the Imam of the Age and Time, the Awaited Proof (may God hasten his reappearance)

To the one I hold most dear to myself, and why not? She has sacrificed for me and spared no effort in making me happy always...

(My beloved mother).

To the one with the kind face and good deeds, who never withheld anything from me throughout his life... (My dear father).

To those who have illuminated my path of knowledge, my esteemed teachers... To those I have been honored to know, my dear friends.

I dedicate to you the fruits of my humble efforts.

Acknowledgments and Appreciation

Be a scholar. If you cannot, be a teacher. If you cannot, love scholars. If you cannot, do not hate them.

I extend my sincere thanks and appreciation to my dear parents, who have been the light that guides my life and instilled in me sublime values and principles.

I also extend my special thanks to my esteemed teachers, who spared no effort in teaching and guiding us. They are, after God, responsible for what we have achieved.

I will not forget my dear colleagues, who have been the best companions on this journey. Through cooperation and participation, this accomplishment was achieved.

May God grant us success and guidance.

Abstract

This study investigates the corrosion behavior of **carbon steel** when immersed in **sulfuric acid (H₂SO₄)** under **constant environmental conditions**, employing the **weight loss method**—a widely accepted, direct technique for quantifying corrosion.

Objectives:

- To quantify the corrosion rate (in mm/year or mils per year, mpy) of carbon steel.

- To assess the influence of exposure time and acid concentration under stable temperature and agitation conditions.

- To correlate weight loss data with surface degradation mechanisms.

Significance:

Understanding the corrosion dynamics of carbon steel in acidic environments is essential for industries like **chemical processing**, **infrastructure maintenance**, and **pipeline integrity**. This research contributes to optimizing material selection and predicting service life in corrosive environments.

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1.1 Introduction

The most accepted definition for corrosion is the destruction of material due to a chemical reaction of the material with its environment. Generally, this destruction takes place on its surface in the form of material dissolution or redeposit ion in some other forms. Metallic systems are the predominant materials of construction, and as a class, are generally susceptible to corrosion. Consequently, the bulk of corrosion science focuses upon metals and alloys (Guthrie and Gretchen, 2002).

Corrosion usually begins at the surface of material and occurs because of the spontaneous tendency of the materials to return to their thermodynamic stable state or to one of the forms in which they were originally found. Metals are generally prone to corrosion because most of them occur naturally as ores, which is the most stable state of low energy and there is a net decrease in free energy ΔG from metallic to oxidized state (Ogunleye et. al., 2011).

Carbon steel, the most widely used engineering material, accounts for approximately 85% of the annual steel production worldwide. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment (Fouda et.al, 2011). Sulphate corrosion is one of the most ordinary and widest kinds of chemical corrosion. There are plenty of sulphate ions in coastal areas which can cause great damages to concrete structures (Liang et. al., 2011).

There are many investigations for corrosion of carbon steel in neutral aerated salt solutions, especially in sodium chloride (NaCl) solution. Little investigation has been found for corrosion of carbon steel in Na2SO4 salt solution. Generally, corrosion of turbine caused by a thin film deposit of fused salt (sodium sulphate)

on alloy surface (carbon steel) is an example of corrosion in sodium sulphate (Bornstein and Decrescente, 1971; Goebel et. al., 1973). During combustion in the gas turbine, sulfur from the fuel reacts with sodium chloride from ingested air at elevated temperatures to form sodium sulphate. The sodium sulphate then deposits on the hot-section components, such as nozzle guide vanes and rotor blades, resulting in accelerated oxidation attack. This is commonly referred to as "hot corrosion" (Stringer, 2007).

Sodium sulphate also cusses corrosion in boiler that used sodium sulfite (Na2SO3) as oxygen scavenger when Na2SO3 reacted with oxygen at low temperature and pressure it forms sodium sulphate that causes serious attack to the tubes of the boiler (Huijbregts, 2007).

Sodium sulphate is also present in considerable amount in the water accompanying petroleum drawn from underground. Salts dissolved in water have a marked influence on the corrosivity of water. At extremely low concentrations of dissolved salts, different anions and cations show varying degrees of influence on the corrosivity of the water. The anions most commonly found in water are chloride, sulphate and bicarbonate. The sulphate ion has a greater effect on the corrosivity of the water than the chloride ion, and the bicarbonate ion shows inhibitive tendencies. Generally, the corrosivity of waters containing dissolved salts increases with increasing salt concentration until a maximum is reached, and then the corrosivity decreases. This may be attributed to increased electro-conductivity because of the increased salt content, until the salt concentration is great enough to cause an appreciable decrease in the oxygen solubility, resulting in a decreased rate of depolarization (Revie and Uhlig 2008).The following reactions occur as the result of the corrosion of carbon steel in

 $Fe_{(s)} \leftrightarrow Fe^{+2} + 2e^{-1}$

$SO_4^{-2} + Fe_{(s)} \leftrightarrow Fe SO_{4(aq)} + 2e^{-1}$

The morphology of the corrosion attack occurring on the surface of mild steel after a certain exposure can be regarded as partially uniform. This attack started in isolated locations and then spread laterally without developing any pits. The effect of SO on the rate of oxidation of iron in mildly alkaline solutions results from its ability to form soluble complexes with Fe or Fe ions.

Also, it was found that sulphate ions accelerate the active dissolution of iron and the films formed in sulphate solutions result from supersaturated solutions of iron salts, most probably iron hydroxysulphate. This implies that iron dissolves in sulphate solutions at a high rate, creating a supersaturated solution and allowing precipitation of a non-protective film (Peralta et. al. 2002).

Corrosion of mild steel is a fundamental academic and industrial concern that has received considerable amount of attention. However, most equipment in industries is usually corroded owing to the general aggression of acid solutions. Some of the important fields of application of acid solutions in industries being acid pickling of iron and steel, chemical cleaning, ore production and oil well acidification (Obi-Egbedi et. al. 2011).

Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys. Metals are exposed to the action of acids in many different ways and for many different reasons. One of the most commonly used acids intoday"s industrialized world is hydrochloric acid HCl. The wide use of this acid has led to

the concentration on the corrosive effects of this acid on carbon steel, which is a versatile component in many industrial structures (Khadom et. al., 2009).

In order to prevent or minimize corrosion rates of metallic materials corrosion, inhibitors are usually used in the industry. Organic, inorganic, or a mixture of both inhibitors can inhibit corrosion by either chemisorptions on the metal surface or reacting with metal ions and forming a barrier-type precipitate on its surface (Al-Sehaibani 2000). Because of the toxic nature and/or high cost of some chemicals currently in use as inhibitors, it is necessary to develop environmentally acceptable and inexpensive ones (Nahl'e et. al., 2010). The corrosion of carbon steel in neutral environments is of practical importance, therefore it is considered by many studies. It is widely recognized that the corrosion of carbon steel may be accounted for by the anodic reaction as in equation 1.1 and cathodic reaction in presence of oxygen,

 $\frac{1}{2}O2 + H2O + 2e \rightarrow 2OH \rightarrow$

the cathodic process requires high activation energy, temperature will have the most significant effect. The effects of concentration, velocity and temperature are complex and it will become evident that these factors can frequently outweigh the thermodynamic and kinetic considerations (Shreir et. al., 2000).

1.2 The Scope of Present Work

The aim of this work is to study the influence of velocity, temperature, time, presence of air bubbles, and using of different corrosion inhibitors on corrosion rate of commercial carbon steel pipe in different concentrations of sodium sulphate (Na2SO4) and hydrochloric acid (HCl) solutions for rotating cylinder electrode (RCE) using both weight loss method and electrochemical polarization technique.



2.1 Corrosion Basic

Most people are familiar with corrosion in some form or another, and almost everyone has seen the rusting of iron fence, spots in car bodies, corroded iron nail, etc. The economic cost of corrosion is enormous, and has been estimated to be in the range of 2-4% of an industrialised country's gross national product [1, 2]. In addition there are also indirect costs associated with plant shutdown, lower efficiency of equipment, contamination and overdesign. Much of this loss is due to the corrosion of iron and steel; although many other metals are susceptible to corrosion process as well. Corrosion is a natural process and defined as the deterioration of metal by electrochemical reactions with its environment. When metallic surface exposed to an aqueous electrolyte usually possesses sites for an oxidation (anodic reaction) that produces electrons in the metal at less stable sites (e.g., where there are dislocation, imperfections), and a reduction (cathodic reaction) that consumes the electrons produced by the anodic reaction. The anodic and cathodic "sites" together make up a corrosion cell. The anodic reaction is the dissolution of the metal atoms to the metal ions. These ions form either soluble ionic products or an insoluble compound of the metal, usually an oxide and can be explained by a simplified equation:

A typical anodic oxidation for metal is:

$$M \Rightarrow M^{2+} + 2e^{-}$$

The common corresponding cathodic reactions involved in corrosion process, at the cathodic sites at the metal/solution interface are:

(1) (neutral and alkaline environments) $O_2 + 2H_2O + 4e^- \Rightarrow 4OH^-$

(2) (acidic in the presence of oxygen environments) $O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$ (3) (acidic environments) $2H^+ + 2e^- \Rightarrow H_2$

2.2 Thermodynamics of Corrosion

Thermodynamics is concerned with energy states. The original metallic ores are said to be in a state of low energy. External energy is applied in the conversion of the ores to usable metals and alloys, transforming them to a higher energy state. The driving force that causes metal to corrode is the thermodynamic instability of metal in its surrounding environment, which is a natural consequence of their temporary existence in metallic form. Pourbaix [3] used thermodynamic data (Nernst equations) to identify regions of active corrosion, immunity when corrosion is thermodynamically not favoured, and regions of passivity, throughout construction of diagrams, which presents the relationship between potential and the solution pH. Pourbaix diagrams are useful as a reference for the selection of a corrosion protection method, e.g., by installing cathodic protection system where the potential is shifted to more negative value and the region is changed from active to immunity, or by applying a neutralizer to adjust the solution pH and reach the passivity region. While thermodynamics can predict whether a corrosion reaction will take place, it does not provide an indication of the rate of corrosion reactions. The rate of reactions is described by kinetic theory.



Figure (2.1): Corrosion of Carbon Steel vs. Temperature in Oil Fields

(Nernst equation)

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

Where,

E = electrode potential under non-standard conditions (volts)

 E° = standard electrode potential (volts)

R = universal gas constant (8.314 J/mol K)

- T = temperature in kelvins (K)
- n = number of electrons transferred.
- F = Faraday's constant (96485 C/mol)

Q = reaction quotient (ratio of product and reactant activities)

$$[reactant] \rightarrow [product] + ne^{-1}$$

[reactant] is the concentration (in moles/litter) of reactant chemical species

[product] is the concentration (in moles/litter) of product chemical species.

The simplest type of these diagrams is based on a chemical system consisting of one element and water solution. Fig. 2.1 shows a typical Pourbaix diagram of iron-water system.

2.3 Corrosion Kinetics

The corrosion process is considered to be a heterogeneous phenomenon taking place in three sequential steps, i) transport of oxidizing agents from the electrolyte

solution to the metalsolution interface, ii) electrochemical reaction at the interface and iii) transport of products away from the interface. The schematic representation of corrosion process is illustrated in

Fig.2.2. The overall corrosion rate is controlled by the slowest of the three sequential steps. When the transport phenomena are capable of proceeding at rates higher than the interfacial electrochemical activities, corrosion is governed by electrode-kinetics and said to be under activation polarization. On the contrary when the capability of the electrochemical reaction is relatively high, the overall corrosion rate is controlled by mass transport (concentration polarization).

2.3.1 Activation Polarization

An activation-controlled reaction is one for which the rate of reaction is controlled only by the rate of the electrochemical charge transfer process. The corrosion current density is not directly measurable because a corroding metal does not show any net current flow.

Figure (2.3): Transport and kinetic of corrosion process [4]

However, if the equilibrium potential of an electrode is changed to some other value (e.g. by connecting it to another electrode to form a galvanic cell or to a potentiostat) it is possible to determine the corrosion current density by using the Butler-Volmer equation (2.1).

$$i = i_0 \left[e^{\frac{(1-a)nF\eta}{RT}} - e^{\frac{-anF\eta}{RT}} \right]$$
(2.1)

Where,

- i: current density (A/m^2) 'n is the value we're trying to find
- i_0 : exchange current density
- η: overpotential (V)

a: charge transfer coefficient (usually between 0.3 and 0.7)

n: number of electrons transferred

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F: Faraday's constant (96485 C/mol)
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R: gas constant (8.314 J/mol K)
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T: absolute temperature (K)
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The Butler-Volmer equation relates the net current density to the change in the electrode potential. The potential change is the potential by which the electrode is polarised away from the corrosion potential and its value depends on the reaction rate of electron transfer. The slower the reaction rate of electron transfer the greater is . The transfer coefficient is related to an energy barrier which the reacting species must overcome for electron transfer to occur. Depending on the ranges of potential the Butler-Volmer equation is used in following simplified forms.

a) In case of small over potentials, assuming that the transfer coefficients are equal for both anodic and cathodic, the equation (2.1) can be reduced to (2.2)

$$i = \frac{\eta}{R_{ct}}$$

Hence

$$R_{ct} = \left(\frac{\partial \eta}{\partial i}\right)$$
(2.3)

Where,

 R_{ct} is charge transfer resistance

b) In case of large over potentials, the Tafel equations are obtained

If -50 equation η >mV, (2.1)can be reduced to (2.4)equation If >+50 mV (2.1)be reduced η can to (2.5)

More generally, the Tafel equation is used as follows

 $= a + b \log i$ (2.6)

2.3.2 Concentration Polarization

When the interfacial concentration of reacting chemical species depleted and approach zero due to relatively high rate of electron transfer at interface, concentration polarization occurs and corrosion process is controlled by the transport of chemical species from the bulk to the surface. Generally corrosion rate in this case cannot exceed the limiting current density, which is restricted by the rate of diffusion of chemical species in the solution.

The limiting current density can be calculated from

$$i_l = \frac{DnFC_B}{\delta}$$

 i_l : Limiting current density (A/cm²) - the highest current achievable due to diffusion limitations.

D: Diffusion coefficient (cm^2/s) - indicates how fast the species move in the solution.

n: Number of electrons involved in the electrochemical reaction.

F: Faraday's constant (\approx 96485 C/mol) - relates electric charge to the amount of substance.

 C_B : Bulk concentration of the chemical species (mol/cm³).

 δ : Thickness of the diffusion layer (cm) - the distance over which diffusion occurs

The concentration polarization can be defined as a function of current density as for the corrosion process concentration polarization is significant only for cathodic reduction process namely reduction of dissolved oxygen, for anodic process usually ignored due to the availability of unlimited supply of metal atoms at the interface.

2.4 Iron Dissolution

The mechanism of iron dissolution in neutral solutions is similar to that encountered in alkaline media [5]. In acidic solutions the mechanisms are different

from that in neutral and alkaline solutions, due to the absence of 3-dimension oxide and corrosion products on the metal surface [6-10]. These mechanisms are characterized by the formation of different oxide intermediates $[Fe(OH)n]_{ads}$ depending on the pH and electrode potential [5].

Bessone [11] proposed a mechanism for iron dissolution in acidic media in which iron oxide is formed on the metal surface in acid solutions but whether, or not this oxide is protective and remain on the surface depends, among other factors, such as the solution pH. However there are some doubts on the pH value where the oxide layer provides protective properties and good adhesion to the metal surface. Geana et al. [6] have reported that at low pH (4 to 5.4) the metal surface remain uncovered and at pH \geq 5.5 formation of [Fe(OH)2]_{ads} occurs at a higher rate and lead to reduces the iron dissolution. In contrasts to Geana et. al. [6], Lorbeer and Lorenz [5] reported that at pH > 4.2 oxide formation on iron surface is timedependent and produces a porous film with sufficient thickness which could be identified visually. A proposed mechanism for the anodic dissolution of iron in alkaline solutions [12,13] said that the adsorption of OH- on the iron surface is the first step to produce Fe(OH)ads and depending on the potential of the electrode, the adsorbed oxygen complex may return into solution or remain on the metal surface and at potential higher than open circuit potential the complex may transfer into an oxide with protection properties which remains on the metal surface. Lorbeer and Lorenz [5] stated that the coverage of iron surface with adsorbed oxide intermediates and oxide reaction products increases strongly with increasing pH. Guzman et. al. suggested that FeOOH and Fe(OH)2 at higher potentials transform into other more stable compounds either through a chemical reaction or via structural rearrangements [14]. Meaning the passivation of iron in alkaline solution is initially due to the formation of Fe2O3 . H2O, which is eventually

transforms to Fe3O4 and hydrated Fe2O3. While iron dissolution is the main anodic reaction at all pH values the cathodic reaction may be either charge-transfer controlled hydrogen evolution or diffusion controlled oxygen reduction depending on the solution pH [15,16]. Lorbeer and Lorenz reported that above pH values of 4.2 in aerated solution, oxygen reduction is the dominant cathodic reaction. It follows from oxygen reduction reactions that the pH increases at the electrode surface due to the consumption of protons and production of hydroxyl ions. Turgoose [17] reported that the pH on a metal surface may be rise up to 10 in unbuffered solutions due to the oxygen reduction this alkaline condition favours formation of three dimensional oxides. Nagayama and Cohen [18] have demonstrated that a linear relationship between passivation potential and pH at constant Fe2+ concentration in alkaline region. The presence of active compounds may affect the mechanism of iron dissolution, for example the iron corrosion inhibitors, the inhibitors used in acid solutions are different from those employed in neutral and alkaline solutions. In acid solutions the inhibitors is due to the adsorption of the inhibitor on to a bare metal surface [8,9]. Where, in neutral and alkaline solutions, the presence of oxide layers and corrosion products on the metal surface play an important role in the mechanism of inhibition. At pH > 4.2 the inhibition may affect the corrosion process via interaction with metal/oxide or the oxide film/solution interphase [19] and through interaction with the metal, as reported [20,21].

2.5 Corrosion Inhibitors

Referring to the electrochemical nature of corrosion process, corrosion inhibitor can be defined as a chemical compound, when added in a small amount to the corrosive environment alters the cathodic and/or anodic reactions, and consequently reduces corrosion rate. Because of this corrosion inhibitors are

classified as anodic, cathodic or mixed type (inhibitors) depending on the inhibited part of the corrosion process [22]. Other proposed classifications have been used such as organic and inorganic [23] with regard to the chemical nature of the inhibitor compound, oxidising or non-oxidising [24] with regard to their redox characteristic, and interface (inhibitors forming two-dimensional adsorption layer) and interphase (inhibitors forming three-dimensional precipitated layer) [25,26] with regard to their retardation mechanism. Over the years many compounds have been tested and efficiently used as corrosion inhibitors for different materials and different environments. However the recently increasing concern toward environmental and health consideration is likely to restrict inhibitor choices. Many effective inhibitors such as chromate and nitrites will eventually abandoned due to the new regulations. Thus there is a need for testing and developing corrosion inhibitors that are effective and in addition being environmentally accepted. Because of the limited range of inorganic compounds, organic ones are most likely to meet those requirements. This review will focus on the organic corrosion inhibitors.

2.5.1 Organic Corrosion Inhibitors

Most organic inhibitors are facilitated by the presence of polar groups in the molecular structure which can strongly adsorb onto the metal surface or react with the corrosion product on the surface to form a protective layer. The most effective polar groups include sulphur, nitrogen, oxygen and phosphorous atoms. Many organic compounds were tested and exhibit inhibitive properties such as carboxylic acids, amines, and other nitrogen containing compounds. Carboxylic acid derivatives as corrosion inhibitor were reviewed and summarized as following. According to Sidgewick [27] monocarboxylic acids with n-alkyl chains of 6-9 carbon atoms are effective corrosion inhibitors and their efficiency increase with

increasing molecular weight. The results obtained by Herschi et.al [28] supported Sidgewick, s results, indicating the octanoic and nonoic acid proved to be more effective than other monocarboxylic acids containing up to 14 carbon atoms under the same conditions. These authors also demonstrated qualitatively that some dicarboxylic acids such as suberic and sebacic acids are effective in the presence of chloride ions. The inhibition of iron corrosion by carboxylic acids has been studied in details by Smialowska et.al [29]. It was reported that the corrosion of iron can be inhibited in sulphuric acid, ammonium nitrate [30] and in sodium sulphate solution [31] in the presence of carboxylic acids containing more than four carbon atoms. The authors have demonstrated that in those solutions the efficiency of carboxylic acids increases with increasing number of carbon in the molecule. Horner [32] employed the concept of hard and soft acid and base (HSAB), proposed by Pearson [33] and explains that carboxylates are hard bases and therefore can be better adsorbed on oxide which is hard acid compared to a bare metal surface which is considered soft acid. In general, carboxylic acids are known as inhibitors which are effective in the presence of dissolved oxygen [34]. Mrowczynski and Smialowska [31,35] attribute the reduction of the corrosion rate of iron in aerated sodium sulphate solution to a synergistic action of these acids and dissolved oxygen. Reinhard et. al. [36] carried out a study on the role of some carboxylates, including straight chain monocarboxylate with one to eight carbons in their molecules on the inhibition of iron and mild steel. They reported that only carboxylate with $C \ge 6$ inhibit iron corrosion. Granata et. al. [37] investigated the inhibition of steel corrosion in mildly corrosive media in the presence of monocarboxalates. Their conclusion was somewhat different from that Reinhard et. al. [36] as they found that carboxylate with $C \ge 2$ inhibits iron corrosion. Granata et, al. [38] proposed a mechanism of carboxylate inhibition. This mechanism is based on the formation of insoluble iron carboxylate at the metal oxide surface. The role of oxygen in this

mechanism is to maintain iron in the ferric state. The presence of oxide layer is considered to be necessary for carboxylate adsorption. The hydrophobic part of the molecule which is oriented towards solution shields the metal surface from water molecules and aggressive ions.

2.5.2 Hydroxamic Acids as Corrosion Inhibitors

In this thesis, organic compounds namely hydroxamic acids were investigated as a promising corrosion inhibitor for carbon steel. A hydroxamic acid is a class of chemical compounds sharing the same functional group in which -NH is inserted into a carboxylic acid. Hydroxamic acids (RCONHOH) were first reported by Lossen in 1869 [39]. They are a class of weak acids and act as ligand, because of their strong affinity toward certain metal ions, the chelating sites being oxygen and nitrogen atoms of the head group [40] Farkas and co-workers conducted intensive research on mono- and di-hydroxamic acids as metal chelators [41-46]. Because of this property hydroxamic acids have been investigated and implemented in the field of medicinal chemistry [47-52], such as antibacterial agent and antiinflammatory. However regarding hydroxamic acids as corrosion inhibitors, only a few studies were carried out testing and evaluating hydroxamic acids corrosion inhibition properties. Shaban et al [53] investigated the inhibition effect of benzohydroxamic acid on copper corrosion in sodium chloride solution. They related the protective effect to the formation of a low solubility complex layer between the inhibitor and copper corrosion product. They used quartz crystal microbalance technique in their work [54] and found that p-chloro-benzo-hydroxamic acid showed excellent protection to copper corrosion. Other data regarding application of hydroxamic acids as self-assembling molecules is presented in the section 2.6.3.

2.5.3 Effect of Cations on the Inhibition of Organic Inhibitors

Felhosi et.al [55] investigated the influence of calcium and zinc ions on the corrosion inhibition of 1-hydroxyethane-1,1-diphosphonic acid (HEDP) on carbon steel. They related the increasing in the inhibition efficiency of HEDP to the formation of different complexes species with the cation additives. They found that the molar ratio play an important role in the formation of protective complexes and reported that zinc ions have a better effect on the inhibition efficiency of HEDP. Turgoose et.al [56] supported the results obtained by Felhozi et.al [55] they studied the effect of calcium and zinc ions on the effectiveness of 1hydroxyethylidene-1,1-diphosphonic acid (HEDP) on the inhibition of mild steel corrosion.

They reported that zinc-HEDP mixture give effective inhibition, at a molar ratio 2:1 of zincHEDP. Addition of calcium showed some inhibition for the corrosion of mild steel, but it is much lower than that for zinc. This is attributed by the authors to the low stability of calcium complexes compared with ferrous complexes, which facilitates the displacement of calcium ions from their complexes by ferrous ions forming soluble un-protective ferrous complexes. Gomma [57] suggested that addition of copper cations to the benzotriazole reduced the corrosion rate of steel in 0.1 M H2SO4, due to the co-adsorption process. Gaur et.al [58] investigated the effect of the cations (Cu2+ As3+ Sb3+ and Sn2+) on the inhibition of steel by hexamine in hydrochloric acid solution. They attributed the positive role of the cations on the inhibitive performance of hexamine to the formation of anion complexes with chloride ions of acid solution. These anions replace the adsorbed chloride ions from the metal-electrolyte interface owing to their higher affinity toward the interface and help the protonized molecules of hexamine to be adsorbed more strongly at the interface. Telegdi et. al. [59] demonstrated that bivalent cations (Ba2+, Sr2+, Ca2+ and Zn2+) synergically improved the inhibition efficiency of amino-phosphoric acid. They found that the addition of zinc ions

influenced both anodic and cathodic process, while the rest of cations hindered the anodic iron dissolution. Pech-caul [60] reported that the N-phosphono-methyl-glycine/Zn2+ mixture inhibited steel corrosion in neutral chloride solutions by retardation of both the anodic dissolution and oxygen reduction reactions. Venkatachari [61] related the enhanced inhibition performance of polyaniline in the presence of cerium ions to the formation of metal-amine complexes, with more quinoid moiety which facilitate strong adsorption and higher coverage on iron surface. Gomma et.al [62] attributed the corrosion inhibition of oxalic to the adsorption of a stable Fe/oxalate complex having the formula FeL2, where L is an acid ligand.

2.6 Self-assembled Monolayers

2.6.1 Concept and Application of Self-Assembled Monolayers

Self-assembled monolayers (SAMs), generally defined as well-ordered and oriented molecular films, which are formed spontaneously, upon immersion of a substrate (solid surface) into a solution containing an active organic molecule. These molecules organize themselves in a two-dimensional (2-D) arrangement on the surface of the substrate. The structure of these respective molecules consists of three parts: a surface-active head group which binds strongly to the substrate, a long chain that connects the head and tail groups and specific tail group that constitutes the outer surface of the film and modifies bulk surface properties (Figure 2.3). Tail groups can also affect the self-assembled monolayers' structure significantly, providing it has a strong polar characteristic or is sufficiently large. The process to prepare self-assembled monolayers is simple only minimum amounts of organic molecules are needed and can be obtained by chemical adsorption from aqueous or organic solutions. Studies on assembled monolayers have

attracted a considerable interest over the last 20 years. Owing to the flexibility to design and prepare SAM with different organic molecule for different substrates. Intensive research activities were carried out to obtain the desired surface properties. In addition to the SAM technique, other common methods were available and used for preparing organic thin films include 1. Langmuir films consist of amphiphilic molecules spread on a liquid surface like water. The hydrophilic head group has an affinity to the water while the hydrophobic end group sticks out on the other side [65,66]. 2. Langmuir-Blodgett (LB) films are prepared by transferring Langmuir films onto a solid substrate [67]. The head group is hydrophilic while the tail group is hydrophobic, so that the direction of the molecules is achieved prior to the transfer step. Multilayers are prepared by repeated (periodic) dipping of the substrate in appropriate solutions. Compared with the LB technique, the self-assembling method has more advantages [68]: (i) the layers are strongly attached to the substrate, throughout the chemisorptions process and electrostatic interactions; (ii) it does not need a specific experimental apparatus. Therefore, the selfassembling method seems to be simpler and more flexible, and for these reasons appears to be very attractive. Self-assembly technique has a number of applications such as chemical and biological sensors [69], efficient electronic and optical devices [71,71], nonlinear optical materials, artificial membrane [72], electron-transfer barriers [73] and high-density memory devices photo patterning methodology [74-79], Also SAMs can be used either to provide model systems of organized functional molecules for studying the interfacial phenomena, such as electron transfer or redox behaviour [80].

Figure (2.4): Formation mechanism of the self-assembled monolayers process [63].

2.6.2 Self-Assembled Monolayers as Corrosion Inhibitors

It is well known that organic coating is one of the important methods used for corrosion protection of different metals, these coating usually consist of a thick multilayer films with thickness ranging from 10 μ m to 100 μ m, and work as barrier between the substrate and environment. However, thin and ultrathin corrosion protecting films provided by SAM with thicknesses less than 10 nm are of considerable interest especially in modern areas of materials research such as microelectronic devices or micromechanics. Felhosi et al. [81] studied the corrosion protection of iron by 1-phosphonic-alkane SAM in aqueous solution. They reported that a significant corrosion protection was observed, due to the formation of SAM with a continuous and dense structure. The mechanism of

inhibition is anodic type, hindering the active dissolution of iron. The formation process of SAM take place in two steps, firstly fast adsorption of molecules on bare iron surface, and secondly ordering in the layer structure is occur during long immersion time. Aramaki et al. [82-84] studied the effect of carboxylate and hexadecanoate self-assembled monolayers on the breakdown of iron passive film. They found that the formation of such SAM on the previously passivated iron electrode, prevent the breakdown of passive film, because of the ordered and densely packed SAM acted as a barrier layer to the diffusion of Cl- through the layer, incorporation of Cl- into the passive film and accumulation of Cl- at defects of the film suppressed by coverage of the film with the SAM. However many other SAM systems have been investigated from the corrosion protection point of view, for iron and other metals, but still the intensive thoroughly investigated system is the organic molecules containing sulphur compound on gold, silver and copper. Sulphur compounds have a strong affinity to transition metal surfaces and coordinate very strongly to the surface of the metal. For example alkanethiol SAM have proven to be excellent inhibitors of oxygen reduction throughout formation of a diffusion barrier to the oxygen transport [85-93].

2.6.3 Surface Modification by Hydroxamic Acids

To the best of our knowledge, only limited studies were carried out for hydroxamic acids as surface modification (SAM and LB). These studies were reviewed below. Using contact angle measurements and XPS analysis Folkers et al. [94] studied the properties of self-assembled monolayer of hydroxamic acids, carboxylic acid and phosphonic acid on the native oxides of copper, iron, silver, aluminium, zirconium and gold. They concluded that hydroxamic acids present an alternative and improvement to other organic acids for the formation of selfassembled monolayers. On the native oxides of aluminium, zirconium and iron, hydroxamic acid, appears

to form more stable monolayer than either carboxylic acid or phosphonic acid. The smaller size of the hydroxamic acid compared to the phosphonic acid, may allow the formation of more coherent and more ordered monolayers. Telegdi et al. [95] studied the deposition of alkyl hydroxamic acid on copper surface as a Langmuir-Blodget (LB) and as a self-assembled molecular layer (SAM). They demonstrated that both LB and SAM were effective as corrosion inhibitors for copper, and the inhibition is influenced by the chain length of the amphiphiles, by increasing carbon atoms in the alkyl chain the corrosion inhibitive effect in acidic environment was enhanced. Rigo et al. [96] investigated the corrosion inhibition effect of hydroxamic acid and phosphonic acid Langmuir-Blodgett films on iron corrosion in sodium per chlorate solutions. They observed that both acids provide high inhibition efficiencies, due to the blocking effect of the applied LB layers. Moreover they found that hydroxamic acid LB is more compact and efficient than that of phosphonic acid.

Chapter Three

3.1 Introduction

Experimental work was carried out to determine the corrosion behavior of carbon steel under static conditions in temperature 30C, 40C and 50C, in acid concentrations (H₂SO₄) range of 0.1 to 0.7 N using weight loss methods. The experimental work is divided into three parts:

- 1. Weight loss in order to determine the average corrosion rates at temperatures of 30 C and acid concentration of 0.1, 0.4, 0.7, and 1N which were performed to assess carbon steel corrosion behavior.
- **2.** Weight loss in order to determine the average corrosion rates at temperatures of 40 C and acid concentration of 0.1, 0.4, 0.7, and 1N which were performed to assess carbon steel corrosion behavior.
- **3.** Weight loss in order to determine the average corrosion rates at temperatures of 50 C and acid concentration of 0.1, 0.4, 0.7, and 1N which were performed to assess carbon steel corrosion behavior.

3.2 Materials

Spacemen carbon steel specimens were made with a surface area exposed of each specimen equal to 4 cm². Each specimen was 2 cm long (L) and 2 cm width. These dimensions were measured accurately using electronic digital caliper.

Figure (3.1): Temperature Measurement

Figure (3.2): Sample Weighing Device

3.2.1 Solutions Used

Three different solutions were prepared by diluting concentrated sulfuric acid 11.5N using distilled water as follows:

a. 0.1N H₂SO₄

b. 0.4 N H₂SO₄

 $c.\ 0.7\ N\ H_2SO_4$

Where the above concentrations prepared according to the principle:

N1V1 = N2V2

3.3 Experimental Procedure

3.3.1 Weight Loss Experiment

1. Before each test run the carbon steel specimens were abraded with glass emery paper of grade numbers; 180, 220, 400 and 2000 respectively, washed continuously with brushing by plastic brush under running tap water, followed by distilled water, dried with a clean tissue, rinsed with acetone and dried with clean tissue, followed by ethanol and dried with clean tissue. The specimens were then stored in a vacuum desiccator over high activity silica gel for 4h before use.

2. The dimensions of each specimen were measured with vernier to the 2nd decimal of millimeter and accurately weighed to the 4th decimal of gram (w1) by using digital balance before being used.

3. After that the specimen was exposed to the corrosion environment for 1h period of immersion at desired concentrations of acid.

4. After each test, the specimen was washed by running tap water with brushing to remove the weakly adherent corrosion products formed on the specimen surface, washed with tap water, followed by distilled water, dried with clean tissue, rinsed with acetone, dried with clean tissue, followed by ethanol, dried with clean tissue, then the specimen was kept in a desiccator for 4 h to dry over silica gel, and accurately weighed to the fourth decimal of gram (w2) to determine corrosion rate(CR) as follows:

(3.2)

$$CR. = \Delta W / A \times t$$

Figure (3.3): Sample

Figure (3.5): Thermometer

 $CR = \Delta W / A \times t$

Where,

A = sample area

t = time required

Temperature = 30 c

concentration = 0.1 N

Wi. = 3.2045 g

Wf = 3.2002 g

 $\Delta W = Wi - Wf$

 $\Delta W = 3.2045 - 3.2002$

 $\Delta W = 0.0043 \text{ g}$

 $CR = \Delta W / A \times t$

1 hr = 1/24 = 0.0417 day

 $A = 2 \text{ cm}^2$

 $= 4 \times 10^{-4} m^2$

 $CR. = \Delta W / A \times t$

 $= 0.0043 / 0.0004 \times 0.0416$

= 258.41. gmd

concentration = 0.4

wi = 3.4437g

wf =
$$3.4355 \text{ g}$$

 $\Delta W = \text{wi} - \text{wf}$
= $3.4437 - 3.4355$
= 0.0082 g
CR = $\Delta W / A \times t$
= $0.0082 / 0.0004 \times 0.0416$
= 492.788 gmd
concentration = 0.7
wi = 3.2253 g
wf = 3.2133 g
 $\Delta W = \text{wi} - \text{wf}$
= $3.2253 - 3.2133$
= 0.012 g
CR = $\Delta W / A \times t$
= $0.012 / 0.0004 \times 0.0416$
= 721.153 gmd

 $CR = \Delta W / A \times t$

Where,

A = sample area

t = time required

Temperature = 40 c

concentration = 0.1 N

Wi. = 3.4868 g

Wf = 3.4771 g

 $\Delta W = Wi - Wf$

 $\Delta W = 3.4868 - 3.4771$

 $\Delta W = 0.0097 g$

 $CR = \Delta W / A \times t$

1 hr = 1/24 = 0.0417 day

 $A = 2 \text{ cm}^2$

 $= 4 \times 10^{-4} m^2$

 $CR = \Delta W / A \times t$

 $= 0.0097 / 0.0004 \times 0.0416$

= 582.93 gmd

concentration = 0.4

wi = 3.5338g

wf = 3.5136 g $\Delta W = wi - wf$ = 3.5338-3.5136 = 0.0202 g $CR = \Delta W / A \times t$ = 0.0202 / 0.0004×0.0416 = 1213.94 gmdconcentration = 0.7wi = 3.6998 wf = 3.6566 $\Delta W = wi - wf$ = 0.0432 $CR = \Delta W / A \times t$ $= 0.0432 / 0.0004 \times 0.0416$ = 2596.15 gmd

 $CR = \Delta W / A \times t$

Where,

A = sample area

t = time required

Temperature = 50 c

concentration = 0.1 N

Wi = 3.3321 g

Wf = 3.2799 g

 $\Delta W = Wi - Wf$

 $\Delta W = 3.3321 - 3.2799$

 $\Delta W = 0.0522 \text{ g}$

 $CR = \Delta W / A \times t$

1 hr = 1/24 = 0.0417 day

 $A = 2 \text{ cm}^2$

 $= 4 \times 10^{-4} m^2$

 $CR. = \Delta W / A \times t$

 $= 0.0522 / 0.0004 \times 0.0416$

= 3137.019 gmd

concentration = 0.4

wi = 3.4520 g

wf = 3.3832 g $\Delta W = wi - wf$ = 3.4520 - 3.3832= 0.0688 g $CR = \Delta W / A \times t$ = 0.0688 / 0.0004 × 0.0416 = 4134.615 gmd concentration = 0.7wi = 3.6889wf = 3.5999 $\Delta W = wi - wf$ = 3.6889 - 3.5999= 0.089 g $CR = \Delta W / A \times t$ $= 0.089 / 0.0004 \times 0.0416$ = 5348.55 gmd

Table (4.1): concentrations, temperature and rate of erosion Weight after and

CR	ΔW	Weight after	Weight before	concentration	Temperature
gmd		g	G	N	С
258.41	0.0043	3.2002	3.2045	0.1	
492.788	0.0082	3.4355	3.4437	0.4	30
721.153	0.012	3.2133	3.2253	0.7	
582.93	0.0097	3.4771	3.4868	0.1	
1213.94	0.0202	3.5136	3.5338	0.4	40
2596.15	0.0432	3.6566	3.6998	0.7	
3137.019	0.0522	3.2799	3.3321	0.1	
4134.615	0.0688	3.3832	3.452	0.4	50
5348.55	0.089	3.5999	3.6889	0.7	

before corrosion

35

Interpretation of curves

Why does corrosion rate increase with concentration?

Higher concentration means:

More chemical activity with the metal surface.

More ions or reactive compounds attacking the metal.

Possibly damaging the protective layer on the metal.

Simple example:

A weak acid causes little corrosion.

A stronger (more concentrated) acid will corrode the metal faster.

Conclusion:

At a constant temperature of 30°C, increasing the concentration leads to an increase in corrosion rate.

This is shown clearly by the straight-line trend in the graphs.

Overall Conclusion from the three graphs:

Based on these three plots, it appears there is a direct relationship between the concentration ("conct") and the rate of corrosion. Higher concentrations lead to higher rates of corrosion, assuming the "x-axis" variable (time/condition) is consistent across the experiments.

- * conct 0.1: Lowest corrosion rates.
- * conct 0.4: Medium corrosion rates.
- * conct 0.7: Highest corrosion rates.

This is a common trend in corrosion studies, where increasing the concentration of a corrosive agent often accelerates the corrosion process

This chapter presents the discussion on experimental results of the whole investigated ranges of acid concentrations; rotational velocities, temperatures, and inhibitor concentrations. The influence of these variables needs to be interpreted, discussed, and understood.

Corrosion behavior of carbon steel in hydrochloric acid solution with and without inhibitor was studied under different conditions of temperature of System consists of HCl solution and iron, such system is made of anodic and cathodic reactions as follows:

• Anodic reaction, which is the dissolution process of iron.

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{5.1}$$

•Since the environment is acidic solution and not deaerated, so one of the cathodic reaction takes place is oxygen reduction expressed as:

$$O_2 + 4H^+ + 4e^- \to 2H_2O$$
 (5.2)

• The other cathodic reaction takes place is hydrogen evolution reaction expressed as:

$$2H^+ + 2e^- \to H_2 \tag{5.3}$$

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This is a common trend in corrosion studies, where increasing the concentration of a corrosive agent often accelerates the corrosion process

Objectives of the Weight Loss Corrosion Test

1. Determine the Corrosion Rate:

Accurately calculate the corrosion rate using the weight difference before and after exposure, helping engineers assess the risk of corrosion on equipment.

2. Evaluate Material Corrosion Resistance:

Compare the performance of different metals (such as iron, carbon steel, stainless steel) under specific operating conditions.

3. Test the Effectiveness of Corrosion Inhibitors:

Assess the efficiency of chemical additives used to reduce corrosion rates.

4. Study the Impact of Operating Environment:

Understand how factors such as temperature, pH level, salinity, and the presence of gases like H₂S and CO₂ affect corrosion behavior.

5. Support Equipment Design:

Use the test results to estimate the service life of pipelines and equipment, and to develop preventive maintenance or replacement plans.

6. Enhance Safety and Economic Efficiency:

Reduce production losses and minimize the risk of sudden equipment failure by selecting appropriate materials

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