The Effect of Temperature and Concentration on Corrosion Inhibition of Mild Steel in Carbon Dioxide Saturated Solution

by

Mohammad Firdaus Bin Muhammad

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

Supervisor: AP Dr Mohamad Azmi Bin Bustam @ Khalil
MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

The Effect of Temperature and Concentration on Corrosion Inhibition of Mild Steel in Carbon Dioxide Saturated Solution

by

Mohammad Firdaus Bin Muhammad

A project dissertation submitted to
Chemical Engineering Program
Universiti Teknologi PETRONAS
in partial fulfillment of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

Approved by:

____
AP Dr Mohamad Azmi Bin Bustam @ Khalil

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
AUGUST 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

____

MOHAMMAD FIRDAUS MUHAMMAD

ABSTRACT

CO2 corrosion is the main threat in oil and gas industry. In order to reduce the corrosion of carbon steel pipelines in CO2 environment, inhibitors are added to control corrosion rate to an acceptable level. However, the successful of the corrosion inhibitor injection depends not only on the good inhibitor formulation used but also operational parameters such as temperature, pH and its concentration. The objective of the project is to investigate the effect of ethanolamine on the corrosion rate for mild steel in CO2 environment. Temperature and corrosion inhibitor's concentration are varied from 25°C to 80°C and 250ppm to 500ppm respectively. The corrosion inhibitor used is ethanolamine and pH is set at 5. The test medium is 3% NaCl solution saturated with carbon dioxide gas at 1 bar. From the experiment, it is found that the efficiency of inhibitor decreased when temperature increases from room temperature 25°C to 80°C. The highest efficiency of inhibitor is at room temperature and inhibitor concentration at 500ppm with the value of 96.4%. However, at temperature 80°C and concentration of ethanolamine at 250ppm, the inhibitor efficiency is the lowest with the value of 72.8%. This is possibly due to the active sites blocking effect and it will discuss later on the Chapter 4. The recommendations are to do further testing to simulate the turbulence flow condition and to investigate the formation of corrosion product film at higher pH that affects the efficiency of the inhibitor.

ACKNOWLEDGEMENT

First and foremost, thanks to God for His blessing and mercy in completing this one year project. It would befit to extend my outstretched gratitude to AP Dr. Mohamad Azmi Bin Bustam @ Khalil, Head of Chemical Engineering Department, Universiti Teknologi PETRONAS. It is a privilege to be under his supervision. Even with his tight schedules as lecturer and high commitment to Universiti Teknlogi PETRONAS, there was no moment where he fails to provide support and guidance. His advices and moral support gave a sense of strength and confidence in conducting the final year project.

Many thanks to our Final Year Project Coordinators, for their unlimited contributions success in providing the students with guidelines and seminars to enlighten hopes of confidence. Not forget to thank all lab executive and technicians as their willingness to provide the facilities and entertain our demand during conducting the project.

Last but not least, thanks to all the Universiti Teknologi PETRONAS involved lecturers and students who have been contributing great efforts and ideas making this final year project a success.

TABLE OF CONTENTS

CHAPTER 1: PROJECT BACKGROUND

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: METHODOLOGY

CHAPTER 4: RESULTS AND DISCUSSION

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

PROJECT BACKGROUND

1.1 Background Study

Mild steels are the most commonly used construction materials for pipelines in the oil and gas industry but they are very susceptible of both a high general corrosion rate and severe localized corrosion. CO_2 corrosion is one of the most significant causes in the oil and gas pipelines failures and occurs at all stages of production from down hole to surface equipment and processing facilities.

It is generally accepted that organic molecules inhibit corrosion via adsorption at the metal-solution interface. Two primary mechanism of adsorption are associated with organic compounds: act by blocking the reaction sites or generating a physical barrier to reduce the diffusion of corrosive species to the metal surface. The mode of adsorption is dependent on the following factors: chemical and electronic structure of the molecule, inhibitor concentration and the temperature of the corrosion reaction.

The corrosion rate was found to depend on the concentration and temperature. Temperature and concentration have great effects on the rate of metal corrosion and their variations are very useful tool for studying and clarifying the adsorption mechanism of an inhibitor.

In this study the inhibition effect of ethanolamine on the corrosion of mild steel in 3 wt. % NaCl aqueous solution saturated with CO2 is discussed. In order to determine the corrosion inhibition efficiency of investigated inhibitor and the optimal concentration and temperature of inhibitor that provides the lowest corrosion of steel, the electrochemical impedance spectroscopy (EIS) had been conducted.

1.2 Problem Statement

With the exploitation of oil and gas well containing carbon dioxide, CO2 corrosion has become one of the universal problems in the oil and gas industries responsible for lost production and expensive repairs. The problems arising from CO2 corrosion have led to the development of various method of corrosion control which includes the injection of corrosion inhibitors that has proven to be a practical and economical method to control CO2 corrosion. Ethanolamine acts as a corrosion inhibitor have been used successfully in combating CO2 corrosion (R. T. Vashi, 2010). Even though the investigation had been done regarding this inhibitor, but less studies have been performed on the effects of concentration and temperature of the inhibitor into the corrosion rate of steel in the CO_2 saturated solution.

1.3 Objective

The objective of this research is to investigate the effect of corrosion rate in different of concentration and temperature of ethanolamine which is acts as corrosion inhibitor in CO_2 saturated solution.

1.4 Scope of study

The scopes of study based on the objectives can be simplified as follow:

i) To investigate the effect of temperature of ethanolamine in the range of 25-80°C to the corrosion rate of mild steel (EN 24)

ii) To investigate the effect of concentration of ethanolamine in the range of 250-500ppm to the corrosion rate of mild steel (EN 24)

1.5 Relevancy of Project

By doing this research, there are few advantages that noticeably will help for future enhancement especially for pipeline system. By getting the result from this experimental project, we can identify which condition of corrosion inhibitor and the thermal stability that is suitable for reducing the corrosion rate therefore can reduce the possibility of the pipeline system from being exposed to more severe CO2 corrosion.

1.6 Feasibility of Project

The project is initiated by collecting materials such as books, journals and technical papers specifically on CO_2 corrosion of mild steel and corrosion inhibitors. Research will be conducted by stages to ensure better understanding is captured. This project will then focus on conducting laboratory experiments on mild steel in CO_2 environment. Study and analysis will be emphasized more on the behavior of corrode formation and the effect of temperature and concentration of corrosion inhibitor on corrosion rate.

It is assumed that the project is feasible within the scope and time frame regardless of no issues with regard to equipment function and material availability and the project should be successfully done. The proposed Gantt chart with the milestone and expected due date is shown in Chapter 3.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Corrosion

Corrosion is a general term for a reaction between a metal and its environment that causes the metal to breakdown. While there are many types of corrosion, they all involve either a chemical reaction or an electrochemical reaction. In chemical reactions, chemicals in the environment react with the metal to create different chemicals. Thus, atoms or molecules of the metal combine with other atoms or molecules that contact the metal to form different, generally weaker materials. Rust is an example of this type of corrosion.

In electrochemical corrosion, the environment around the metal results in the creation of an electrical current, which is simply a flow of electrons. The metal corrodes by giving up electrons to create the electrical flow.

The oil field environment is filled with metal pipes and other components that often exposed to chemicals that can cause corrosion, especially when the metal and chemicals are in a solution such as downhole fluids. The pumper must understand how to reduce corrosive damage to the metal in wells, flow lines, tank batteries, and equipment.

There are three general types of corrosion of concern in the oil field. These involve three chemicals of concern and electrochemical corrosion. The types of corrosion include:

I. Carbon dioxide (sweet corrosion)
II. Hydrogen dioxide (sour corrosion)
III. Oxygen corrosion (oxidation)

2.2 Overview CO_2 Corrosion

Carbon dioxide (CO_2) corrosion is one the most studied form of corrosion in oil and gas industry. This is generally due to the fact that the crude oil and natural gas from the oil reservoir / gas well usually contains some level of CO_2 (and H_2S – hydrogen sulfide). The major concern with CO_2 corrosion in oil and gas industry is that CO_2 corrosion can cause failure on the equipment especially the main down hole tubing and transmission pipelines and thus can disrupt the oil/gas production (H.M Abd Lateef et al, 2012). Figure 2.1 shows the model of CO_2 corrosion of a crude oil pipeline made of mild steel.

The study of CO_2 corrosion rate and $FeCO_3$ film formation are essential to enhance the understanding and modeling the kinetics of $FeCO_3$ precipitation process (H.M Abd Lateef et al, 2012). The presence of CO_2 in solution would initiate the CO_2 corrosion process. It would produce a weak carbonic acid (H_2CO_3) which is corrosive to carbon steel or low alloy steel and it is presented by equation 2.1 below: (H.M Abd Lateef et al, 2012)

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad \text{(Carbonic Acid)} \qquad (2.1)$$

The reaction process will continue with three cathodic reactions (reduction) and one anodic reaction (oxidation). The cathodic reactions in CO_2 solutions are:

1. Reduction of carbonate acid into bicarbonate ions.

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^- \qquad (2.2)$$

2. Reduction of bicarbonate ions into carbonate ions.

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3 \qquad (2.3)$$

3. Reduction of hydrogen ions.

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2.4)$$

There are some main factors that can affect the severity of CO_2 Corrosion Rate (CR). The first factor is CO_2 partial pressure: higher partial pressure of CO_2, CR will be higher. The second is temperature: higher temperature, higher CR while the third is pH will result in higher CR. Flow velocity also can affect the severity of CO_2 corrosion: consequence higher velocity is higher CR (Huey J. Chen, 2000).

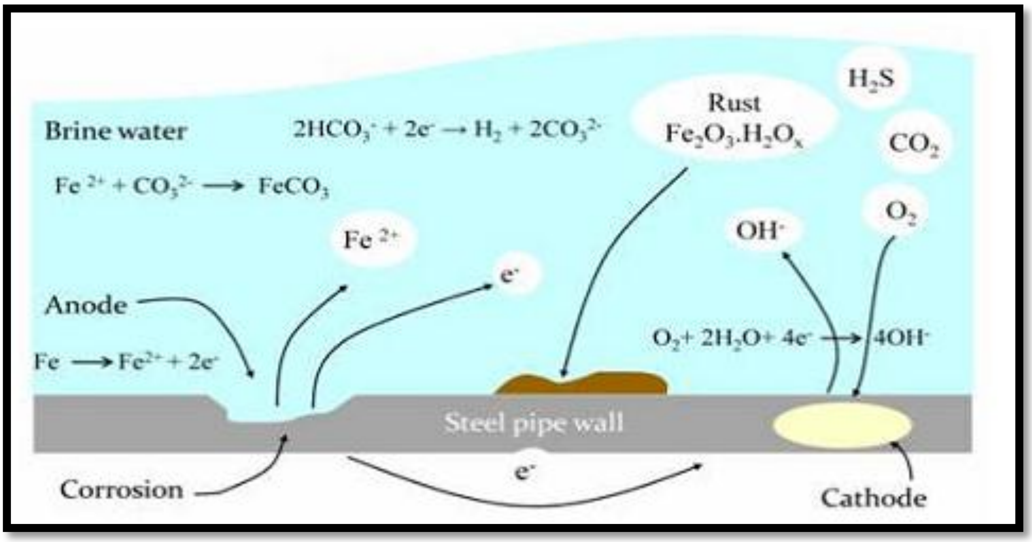


FIGURE 2.1. Model CO_2 corrosion of crude oil pipeline made of a mild steel.

2.3 Corrosion attack in oil and gas pipeline

The presence of carbon dioxide (CO_2), hydrogen sulphide (H_2S) and free water can cause severe corrosion problems in oil and gas pipelines. Internal corrosion in wells and pipelines is influenced by temperature, CO_2 and H_2S content, water chemistry, flow velocity, oil or water wetting and composition and surface condition of the steel. A small change in one of these parameters can change the corrosion rate considerably, due to changes in the properties of the thin layer of corrosion products that accumulates on the steel surface (Rolf Nyborg, 2004).

When corrosion products are not deposited on the steel surface, very high corrosion rates of several millimeters per year can occur. The corrosion rate can be reduced substantially under conditions where iron carbonate ($FeCO_3$) can precipitate on the steel surface and form a dense and protective corrosion product film (Mythili Koteeswaran, 2010). This occurs more easily at high temperature or high pH in the water phase. When H_2S is present in addition to CO_2, iron sulphide (FeS) films are formed rather than $FeCO_3$, and protective films can be formed at lower temperature, since FeS precipitates much easier than $FeCO_3$ (Mythili Koteeswaran, 2010).

Localised corrosion with very high corrosion rates can occur when the corrosion product film does not give sufficient protection, and this is the most feared type of corrosion attack in oil and gas pipelines (Mythili Koteeswaran, 2010). The line had been in operation for several years without problems, but changes in the well composition over time led to more aggressive conditions, resulting in unacceptably high corrosion rates. In order to control the corrosion in pipelines, it is important to understand the underlying corrosion mechanisms and be able to predict whether localised corrosion will be initiated and how it can be prevented.

2.4 Corrosion inhibitors

Most corrosion inhibitors used in oilfields are organic compounds, containing nitrogen or sulfur functionalities. They belong to the surfactant category of molecules (surface-active agents), which preferentially adsorb onto any surface or interface in a system and alter the surface and interfacial free energies, even at low concentration (Hernandez et al, 2003). The surface-active properties come from their amphipathic, lipid like, molecular structure, which contains a polar head group having strong attraction to water, referred to as a hydrophilic head and a non-polar hydrocarbon chain having little attraction to water, called a hydrophobic tail.

The way organic corrosion inhibitors inhibiting CO_2 corrosion of carbon steel is related to their surface active properties can be described in three parts (Hernandez et al, 2003);

I. Adsorption onto the steel surface (diffusion or protective layer),
II. Changing the wettability of the steel surface (so it is not wetted with water),
III. Accumulation at the oil-water interfaces (changing the oil-water interfacial tension and making it easier for the oil to entrain the water).

It is accepted that organic corrosion inhibitors adsorb onto the steel surface to inhibit corrosion processes. The types of adsorption can be distinguished by the mechanisms: physical (electrostatic) adsorption involves an electrostatic attractive force between ionic charges on inhibitor molecules and electric charged steel surface; chemisorption results from sharing free electron pairs or charge transfer to form strong chemical bonds between nonionic inhibitor molecules and steel (Papavinasam et al, 2007).

2.5 Corrosion control by organic corrosion inhibitors

The corrosion of metals cannot be stopped completely, but it can be controlled by decreasing the rate of corrosion. Corrosion control functions by eliminating or reducing the effectiveness of one or more of the corrosion cell components. Corrosion control methods in oilfield systems include cathodic protection, protective coatings, chemical inhibitors, plastic or cement liners, use of special alloys, solids removal and removal of corrosive gases.

In general, cathodic protection is an approach where the metal surface to be protected is made into the cathode of a corrosion cell. Since corrosion and material loss occurs at the anode, this approach protects the metal. Protective coatings can be used to protect tubing, downhole equipment, wellhead components and pressure vessels. Coatings work by reducing the cathodic area available for the corrosion reaction. The use of organic corrosion inhibitors is the most effective way of protecting internal corrosion of carbon steel pipelines for oil product transportation.

Inhibition is used internally with carbon steel pipes and vessels as an economic corrosion control alternative to stainless steels, coatings and non-metallic composites. A particular advantage of the corrosion inhibitor is that it can be introduced insitu without disrupting the transportation process and it adsorbs into the hard-to-reach surfaces inside the pipes. The major industries using corrosion inhibitors are oil and gas exploration and production, petroleum refining, chemical manufacturing, heavy manufacturing, water treatment and the product additive industries (S. Ramachandran et al, 1999).

2.6 Mechanism of corrosion inhibitors

The corrosion inhibitors used in oilfield applications are organic or ionic compounds that are employed in small concentrations (less than 0.1 wt.%). They are often categorized as mixed inhibitors as they adsorb on the steel surface and inhibit both anodic and cathodic reactions. Almost all organic molecules used in oilfield corrosion inhibitor packages are strongly polar, with many being based on nitrogen, such as the amines, amides, imidazolines or quaternary ammonium salts and compounds containing P, S and O elements. Molecular structures for some of the most commonly used organic corrosion inhibitors in the oilfield system are given in Figure 2.2. The organic corrosion inhibitors are typical surface-active agents due to the presence of hydrophilic and hydrophobic moieties within the same molecule.

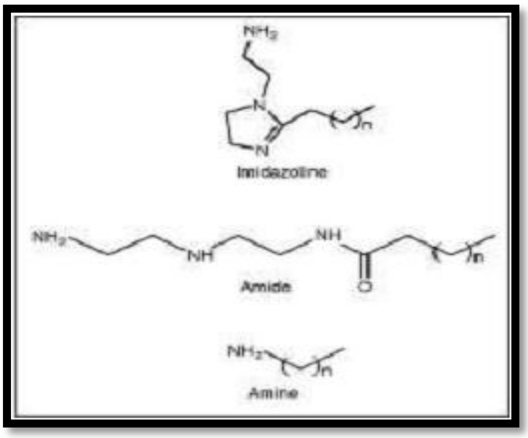


FIGURE 2.2. Basic molecular structure of oil field corrosion inhibitors

Typically, the molecules have a hydrocarbon chain attached to the polar group, the length of which varies. The mechanism by which the organic corrosion inhibitor used to reduce the corrosion is not fully understood so far. The polar group of the molecule provides the functionality that displaces the water molecules from the surface (Figure 2.3). The adsorption of the corrosion inhibitor from aqueous solution onto the metal surface is driven by both of the polar head group and the hydrocarbon tail group. The concentration of inhibitor has a profound effect upon corrosion inhibition.

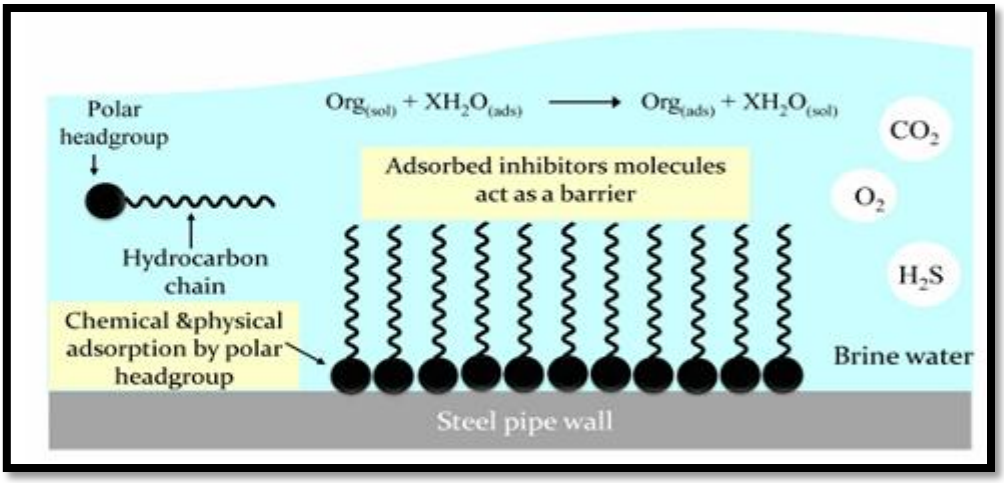


FIGURE 2.3. Schematics diagram of action of oilfield corrosion inhibitor

At low concentration, the inhibitor adsorbs parallel or titled onto the steel surface. As the bulk concentration increases, the hydrophobic tail groups begin to protrude into the aqueous phase to accommodate more surfactant molecules, which increases the surface coverage. At the critical micelle concentration (cmc), monolayer coverage is achieved and the tail groups are parallel to each other and perpendicular to the metal surface (B.P.Binks *et.al*, 2005) which becomes hydrophobic. Therefore, the adsorbed corrosion inhibitor molecules are believed to act as a waterproof barrier between the corrosive aqueous phase and steel pipe.

An investigation into the inhibition of iron corrosion by a series of imidazoline derivatives by Ramachandran *et al.* in 1996 suggests a self-assembled monolayer mechanism for corrosion inhibition. The model suggests the following criteria for an efficient corrosion inhibitor:

I. Adequate solubility and rate of transport of the inhibitor from solution to the surface.
II. Strong binding of the surfactant head groups to the metal surface.
III. Self-assembly of head groups to form a dense and ordered layer.
IV. Self-assembly of hydrocarbon tails to form a hydrophobic barrier.

2.7 The inhibitive effect of ethanolamine on corrosion behavior

Carbon dioxide gas when dissolved in water forms carbonic acid which is corrosive to metals. Injection of film forming inhibitors has been the common method for prevention of CO_2 corrosion. Different groups of organic compounds have been reported to exert inhibitive effects on the corrosion of metals. Most of the inhibitors are organic heterocyclic compounds with N, S, or O atoms (S.A. Ali, 2003). The sites of these elements have higher electron density, making them the reaction centers (S. Patel & S. Jauhari, 2009). The addition of corrosion inhibitors effectively secures the metal against an acid attack. It has been found that most of the organic inhibitors act by competitive adsorption on the metal surface with the aggressive ion and by blocking the active corrosion sites (B. Wang et.al, 2011).

The adsorption on the metal surface is influenced by the nature and surface charge of metal, by the type of aggressive electrolyte, and by the chemical structure of inhibitors (R.A. Prabu et.al, 2008). Corrosion inhibitors based on organic compounds like alkanolamine influence the corrosion process by forming an adsorptive film on the metal surface (U. Maeder, B. Marazzani,2004). The amino-alcohols are common inhibitors and they are widely applied since they are non-toxic and cost attractive (L. BE. Mechmeche et.al, 2008).

Ethanolamine, commonly called monoethanolamine (MEA) is an organic chemical compound that is both a primary amine and a primary alcohol and acts as a weak base (V. Sivertz, 1994). The main functional groups are hydroxyl and nitrogen atom. All amines have a lone pairs of electrons. However, the readiness with which the lone pair of electrons is available for co-ordination with a proton determines the basic strength of amines (C. Jeyaprabha, S. Sathiyanarayanan, G Venkatachari, 2005). The inhibitive effect of ethanolamine is achieved by donating unshared pair of electrons from nitrogen atom, followed by surface complex forming (R.T Vashi et.al, 2010).

CHAPTER 3

METHODOLOGY

3.1 Laboratory Simulation Test

Laboratory test is conducted to determine the effect of corrosion inhibitor to the corrosion rate of mild steel. In this laboratory test corrosion inhibitor dosage used is 500 ppm that affects the corrosion rate. Concentration of corrosion inhibitor will be injected into the testing environment solution and the corrosion rate of each test will be recorded down to determine the effect of the corrosion inhibitor dosage on the corrosion rate. The variables such as temperature and concentration of corrosion inhibitor will be varied for each different laboratory tests.. Methodology of the experiment is as describe in the flow chart shown in the Figure 3.1.

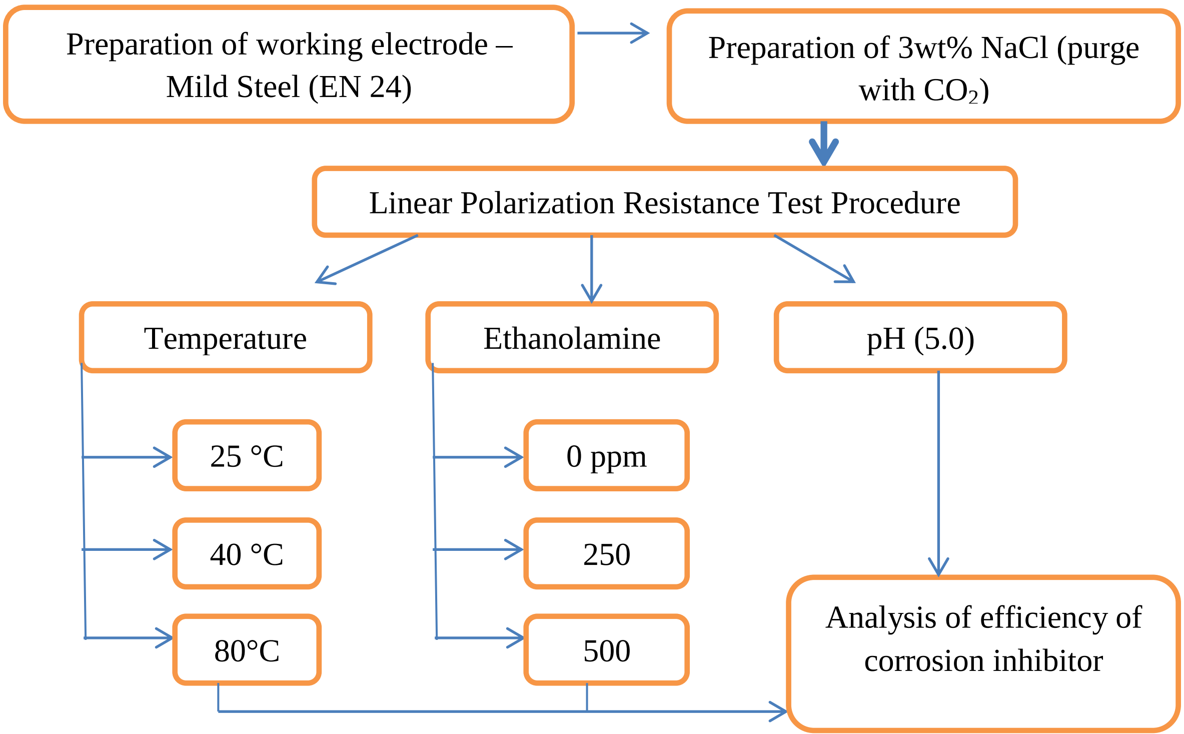


FIGURE 3.1. Flowchart methodology of the corrosion test

3.1.1 Test Matrix

Table 3.1 indicates that fifteen tests are carried out. The operational parameters of pH and NaCl concentration are kept constant at 5.0 pH and 3wt% respectively. For 3wt% NaCl percentage concentration, corrosion inhibitor of dosages 0ppm, 250ppm and 500ppm is injected to the solution at different temperature which are 25 °C, 40 °C and 80 °C

TABLE 3.1. Test matrix for the laboratory works for Corrosion Inhibitor study

Concentration of Ethanolamine (ppm)	Temperature (°C)			pH[26]
	25	40	80	
0	Test 1	Test 2	Test 3	5.0
250	Test 4	Test 5	Test 6	
500	Test 7	Test 8	Test 9	

.

3.1.2 Laboratory Set-up

The set-up for the laboratory test using electrochemical measurement method of Linear Polarization Resistance experiments is showed in Figure 3.2. The test assembly consists of one-liter glass cell bubbled with CO_2 gas. The required test temperature is set through the hot plate. The electrochemical measurements are based on a three-electrode system, using a commercially available potentiostat with a computer control system. The reference electrode used is a saturated calomel electrode (SCE) and the auxiliary electrode is a platinum electrode.

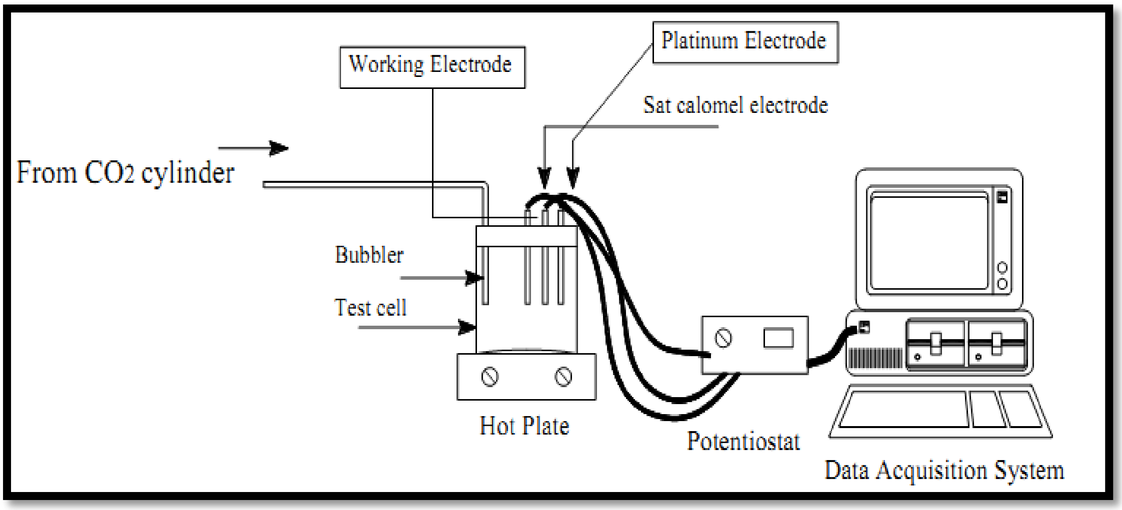


FIGURE 3.2. Schematic diagram for static experimental set-up

3.2 Materials

The working electrode or the sample in this experiment is mild steel (EN 24). The composition of the mild steel (EN 24) as shown below: [21]

TABLE 3.1a. Properties of Mild Steel (EN 24)

Sample	Mild Steel (EN 24)	
Composition	Min (%)	Max (%)
Carbon	0.35	0.45
Silicon	0.1	0.35
Manganese	0.45	0.7
Nickel	1.3	1.8
Chromium	0.9	1.4
Moly	0.2	0.35
Sulphur	-	0.05
Phosphorous	-	0.05

The working electrode for electrochemical measurements was prepared from a cylindrical copper rod (99.9%) sealed with epoxy resin so that only the circular cross section (0.5 cm2) of the rod was exposed. The working electrode was polished with silicon carbide (SiC) emery papers (400, 800, 1200 grit), rinsed with double-distilled water, and degreased ultrasonically in acetone (CH3COCH3), dried at room temperature, and stored in a moisture-free desiccator.

3.3 Preparation of Solution

Testing solution was deaerated by purging CO_2 (99.95%) for 2 h prior to the experiments. The oxygen concentration of the solution was measured with a Fi-box 3-trace v6 (PreSens GmbH) instrument with an accuracy of 1 μmol dm^{-3}, and it was kept below 40 μmol dm^{-3} during the experiments. Test solution was 3 wt. % NaCl (analytical-reagent grade) saturated with deoxygenated CO_2. A positive pressure of deoxygenated CO_2 was maintained throughout the experiments to avoid air ingress.

3.4 Experiment Environment

The environment for the laboratory test is set according to the determined operational parameters. The test solution used is NaCl solution of concentration 3% and the pH value is adjusted to 5.0 and kept constant (Hassan Malik, 2000). For the first of readings, corrosion inhibitor is not injected to the solution. Then, the tests are repeated for dosages of ethanolamine of 25ppm and 50ppm with various temperatures which are 25 °C, 40 °C and 80 °C. The solution is purged with CO_2 at 1 bar to provide the environment of CO_2 corrosion.

3.5 Addition of ethanolamine as corrosion inhibitor

Corrosion inhibitor dosage of 250ppm and 500ppm is injected into the solution. Micropipette is used to measure the accurate volume of the corrosion inhibitor into the solution. The volume of corrosion inhibitor added into the solution is based on parts per million (ppm) according to the volume of solution used in the experiment. For this experiment, the volume of the 3% NaCl used is 1 liter. Thus 1ppm of corrosion inhibitor in this experiment is equivalent to 1μ L.

3.6 Experiment Procedure

In this study, there are several laboratory tests which have to be conducted by varying the temperature and the concentration of corrosion inhibitor. The procedures of the each experiment are nearly the same. Experiments procedures are as per described below:

Firstly, prepare the solution medium of Sodium Chloride 3%; 30g of sodium chloride is mixed into the distilled water of 1 Liter. Then, prepare the working electrodes as per describe in the section 3.2 and setting up the equipment for the laboratory test as per described in section 3.1.

Before the experiment is start, purging the carbon dioxide gas and continuous purging for half an hour until the carbon dioxide is saturated in the solution. The indication of the cell is saturated with carbon dioxide can be tested with the pH meter when it indicate the reading of pH nearly 3.8.

The first experiment consists of temperature at room temperature which is 25°C and sodium bicarbonate is added into the solution to increase the pH of the solution to 5.

For the first section of laboratory test, use constant of pH value, which is 5.0 and at room temperature, which is 25°C and corrosion inhibitor is not added into the solution. The experiment was running for 8 hours. The second and third experiments will running at the same conditions, which are pH value of 5.0 and absent of corrosion inhibitor but at different temperature which are at 40°C and 80°C, respectively.

For the second section of laboratory test using constant of pH value, which is 5.0, run the experiment at room temperature, which is 25°C and the corrosion inhibitor will be added into the solution in the concentration of 250ppm. The experiment was running for 8 hours. The fifth and sixth experiments will running at the same conditions, which are pH value of 5.0 and the concentration of corrosion inhibitor is 250ppm but at different temperature which are at 40°C and 80°C, respectively.

For the third section of laboratory test using constant of pH value, which is 5.0, run the experiment at room temperature, which is 25°C, and the corrosion inhibitor will be added into the solution in the concentration of 500ppm. The experiment was running for 8 hours. The eighth and ninth experiments will running at the same conditions, which are pH value of 5.0 and the concentration of corrosion inhibitor is 500ppm but at different temperature which are at 40°C and 80°C, respectively.

Once the chemicals and electrodes added into the solution, access the data acquisition system, in this laboratory, the computer connected to the ACM Instruments Version 5, run Gill 12 Weld Tester Serial No. 1350 –Sequencer and the Core Running software. Then, key in all the parameters that set for the measurement of the experiment into the Sequencer software. After that, run the ACM Instruments and data is gathered automatically into the ACM Analysis Version 4, where they record down the Linear Polarization Resistances and calculate the corrosion rate.

To calculate the corrosion rate, use the linear polarization resistance test. From linear polarization resistance test, determine the corrosion rate of the sample. The theory of the calculation for linear polarization is as shown below:

The corrosion current density is related to polarization resistance by Stern Geary coefficient, B. The Stern-Geary Constant, B, is approximated as 25 mV for all pH.

$$\mathbf{i_{corr} = B/Rp}$$

The dimension of Rp is ohm-cm^2, icorr is mA/cm^2, and B is in V.

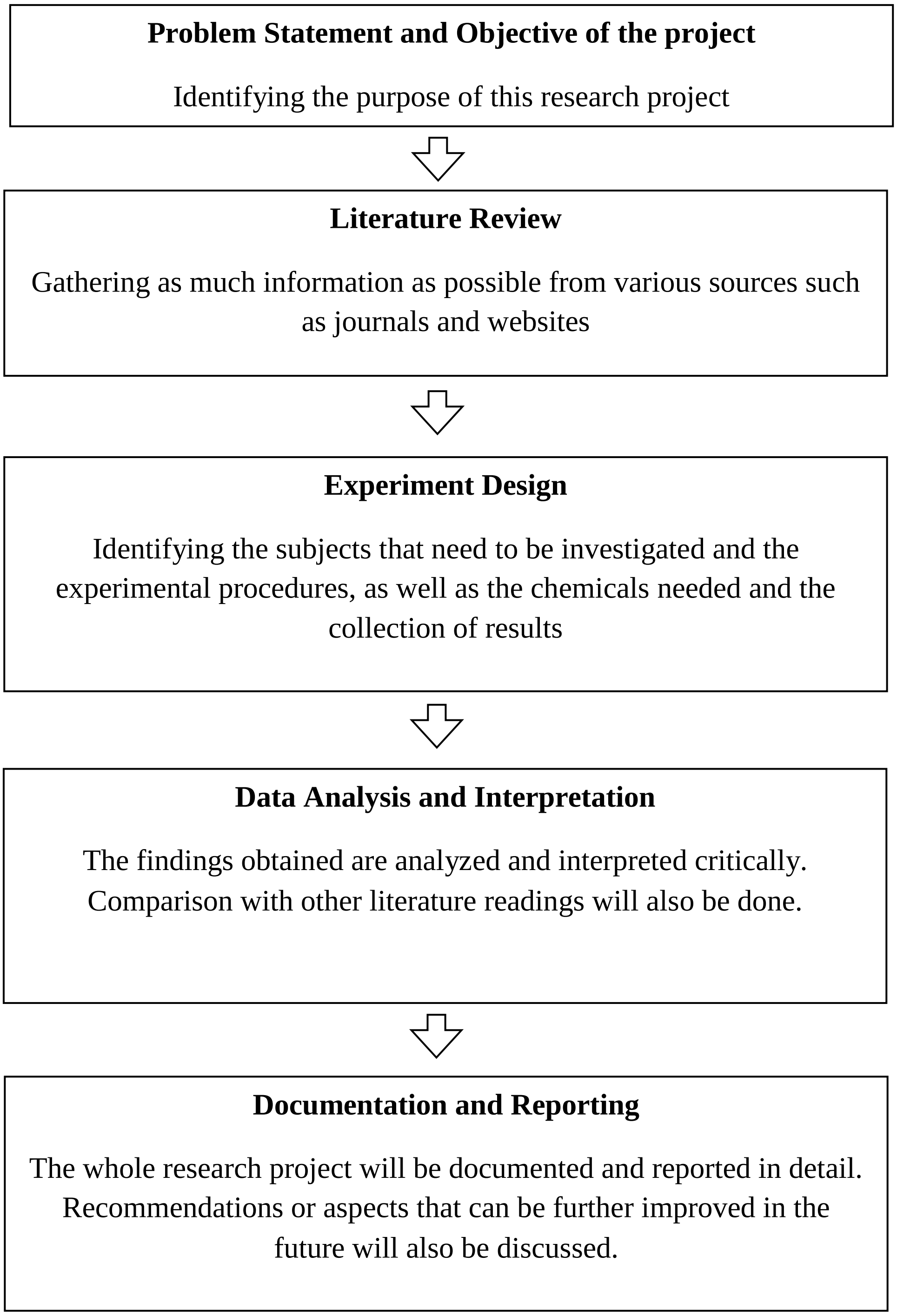
B also can be written as;

$$B = \frac{b_a \ b_c}{2.303(b_a + b_c)}$$

Where b_a, b_c is the Tafel slope for cathodic and anodic reaction.

3.7 Key Milestones

Several key milestones for this research project must be achieved in order to meet the objective of this project:



Problem Statement and Objective of the project

Identifying the purpose of this research project

Literature Review

Gathering as much information as possible from various sources such as journals and websites

Experiment Design

Identifying the subjects that need to be investigated and the experimental procedures, as well as the chemicals needed and the collection of results

Data Analysis and Interpretation

The findings obtained are analyzed and interpreted critically. Comparison with other literature readings will also be done.

Documentation and Reporting

The whole research project will be documented and reported in detail. Recommendations or aspects that can be further improved in the future will also be discussed.

3.8 Gantt Chart

NO	DETAIL WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Simulation Process on The Project Continues	🟩	🟩	🟩	🟩	🟩	🟩	🟩	MID – SEM								
2	Submission of Progress Report							●									
3	Simulation Work on The Project Continues									🟩	🟩	🟩	🟩	🟩	🟩		
4	Pre-Sedex											●					
5	Submission of Draft Report												●				
6	Submission of Dissertation (soft bound)													●			
7	Submission of Technical Paper													●			
8	Oral Presentation														●		
9	Submission of Project Dissertation (hard bound)																●

● Suggested milestone

🟩 Process

CHAPTER 4

RESULTS AND DISCUSSION

4. 1 Potentiodynamic Polarization Measurements

Potentiodynamic Polarization measurements results consist of the result for the system of 3% NaCl with 25°C and pH 5, 3% NaCl with 40°C and pH 5 and last the system of 3% NaCl with 60°C and pH 5. The result for each experiment can be seen from all the figures below.

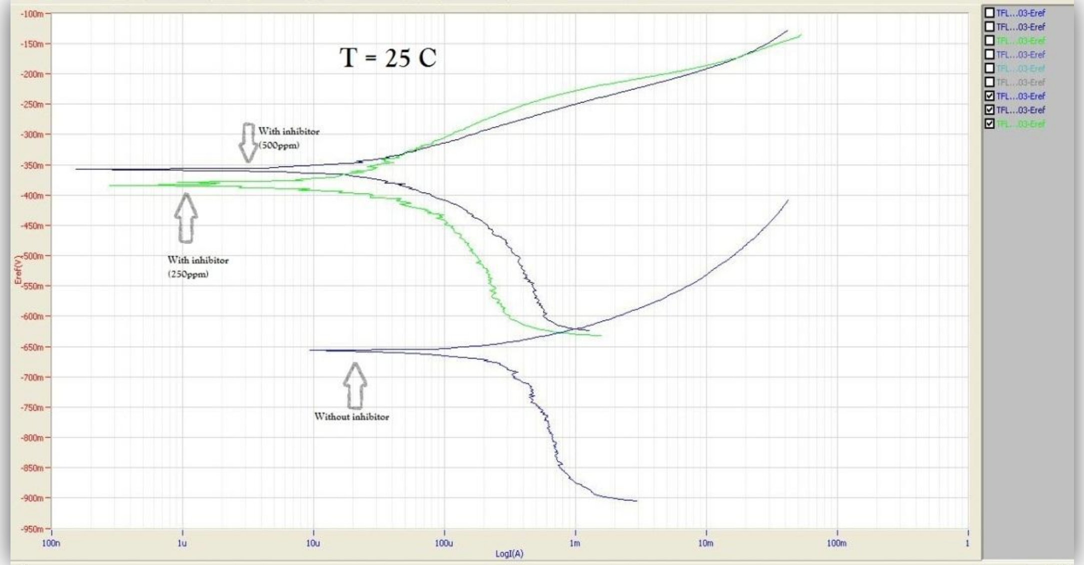


FIGURE 4.0a. The polarization curve for mild steel electrode in uninhibited and inhibited 3% NaCl carbon dioxide saturated solutions at temperature 25°C

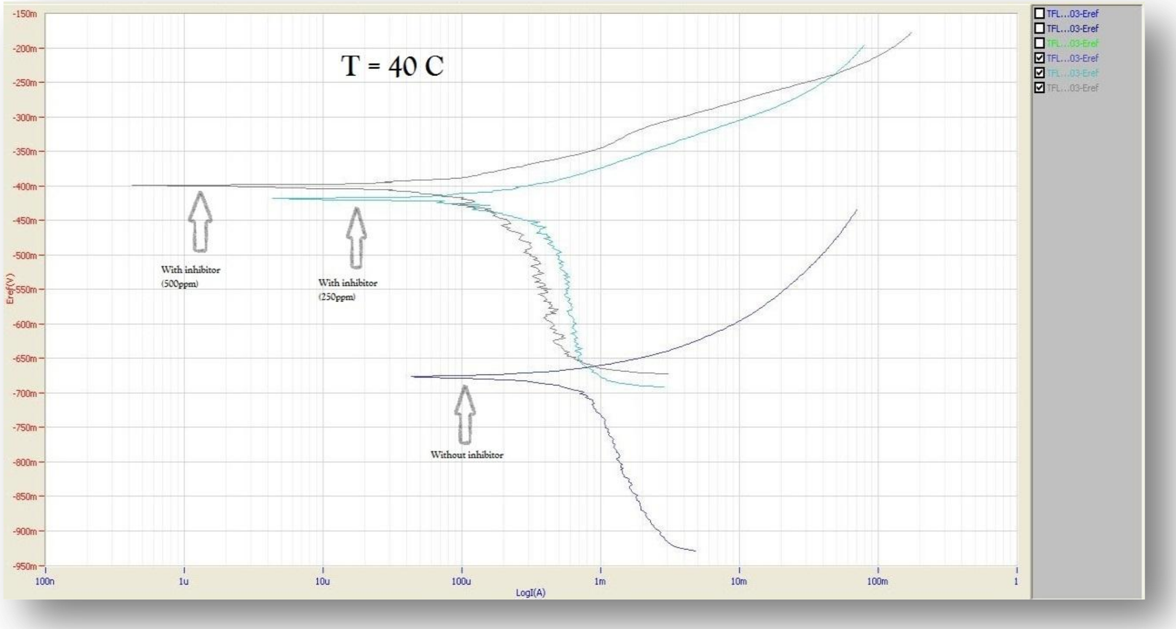


FIGURE 4.0b. The polarization curve for mild steel electrode in uninhibited and inhibited 3% NaCl carbon dioxide saturated solutions at temperature 40°C

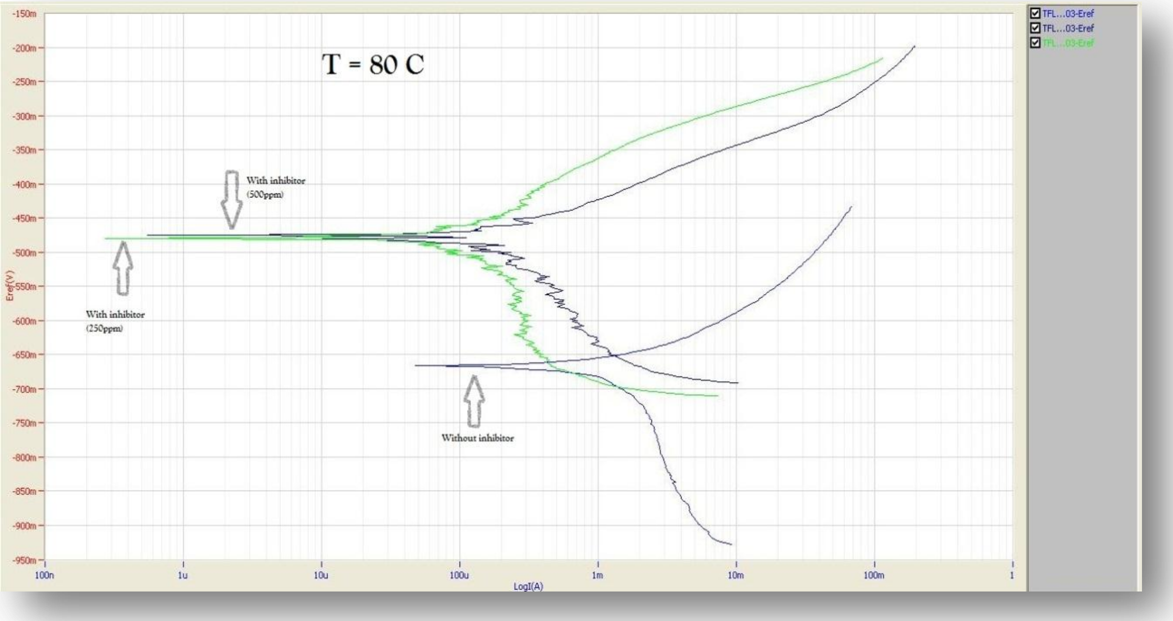


FIGURE 4.0c. The polarization curve for mild steel electrode in uninhibited and inhibited 3% NaCl carbon dioxide saturated solutions at temperature 80°C

The influence of temperature and concentration on the performance of ethanolamine (250ppm and 500ppm) in 3% NaCl solution was investigated within the temperature of 25°, 40°C and 80°C. The cathodic and anodic polarization curves for mild steel in the medium with and without inhibitor at three temperatures (i.e. 25, 40 and 80°C) are shown in Figure 4.0a, Figure 4.0b and Figure 4.0c.

From all the figures above we can observe that the kinetic parameters at these different temperatures deduced from polarization curves. There are really obvious when the ethanolamine is injected into the solution. All of these discussions will be further discuss at the next sub-sections.

4.1.1 The system of 3% NaCl solution with 25°C and pH 5

From Figure 4.1 and Figure 4.2, there is biggest decrement between the first readings until the reading of 8. All the experiments had been done in 8 hours with one reading had been taken in one hour.

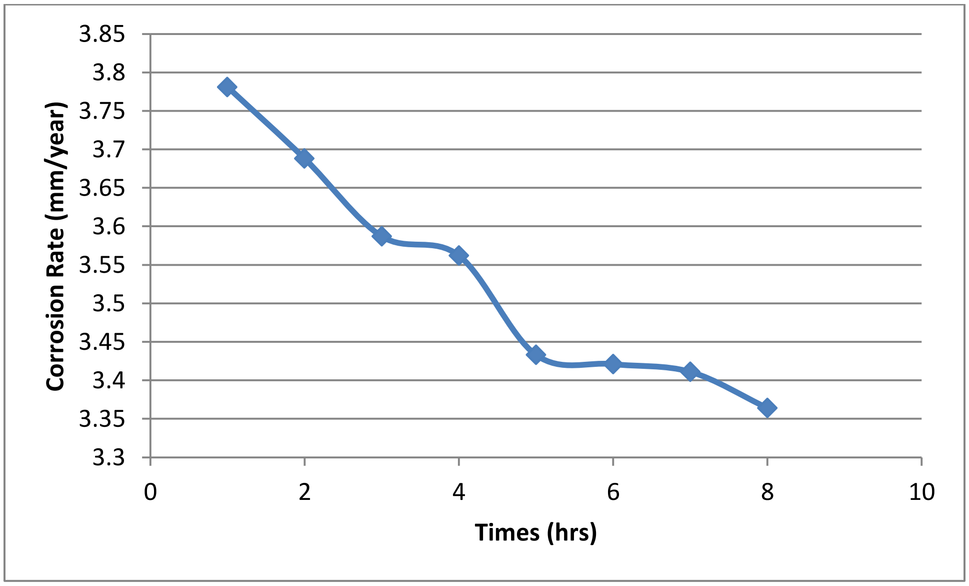


FIGURE 4.1. The trend of uninhibited corrosion rate for the system of 3% NaCl at 25°C with pH 5

From Figure 4.1, the uninhibited mean corrosion rate for 3% NaCl with temperature 25°C and pH 5 is 3.531 mm/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

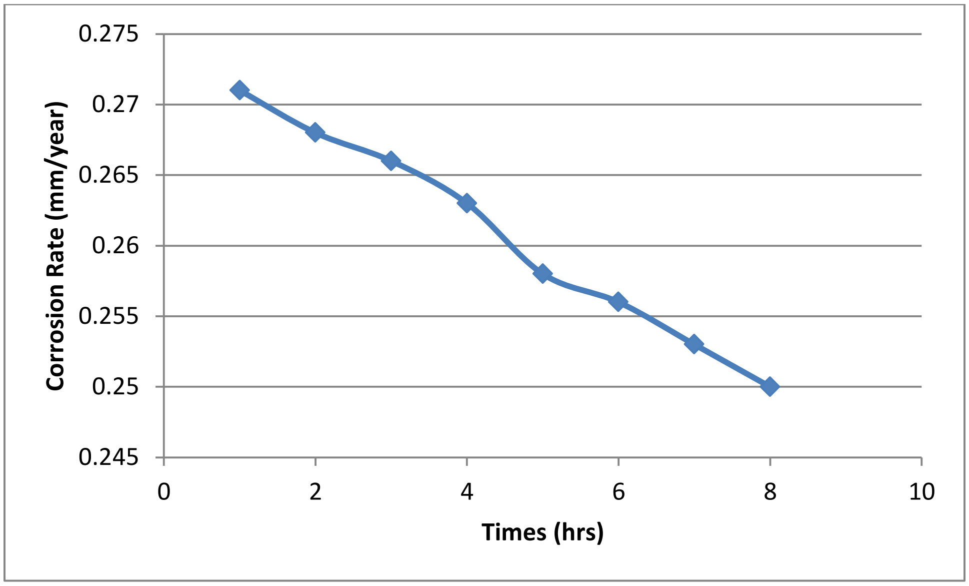


FIGURE 4.2. The trend of inhibited of Corrosion Rate with 250 ppm of ethanolamine for the system of 3%NaCl at 25°C with pH 5

From Figure 4.2, the mean corrosion rate with 250 ppm corrosion inhibitor for 3% NaCl with temperature 25°C and pH 5 is 0.261 m/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

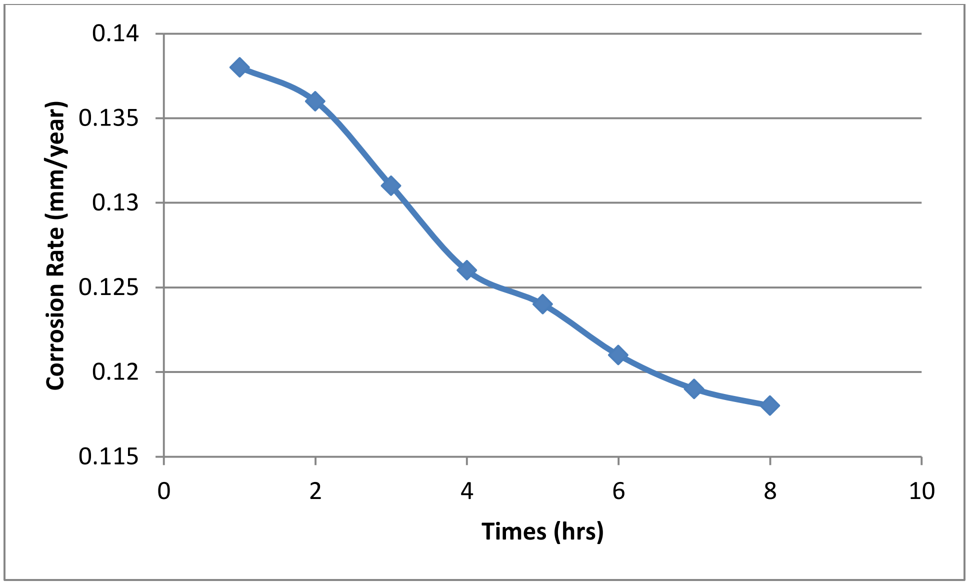


FIGURE 4.3. The trend of inhibited of Corrosion Rate with 500 ppm of ethanolamine for the system of 3%NaCl at 25°C with pH 5

From Figure 4.3, the mean corrosion rate with 500 ppm corrosion inhibitor for 3% NaCl with temperature 25°C and pH 5 is 0.127 m/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

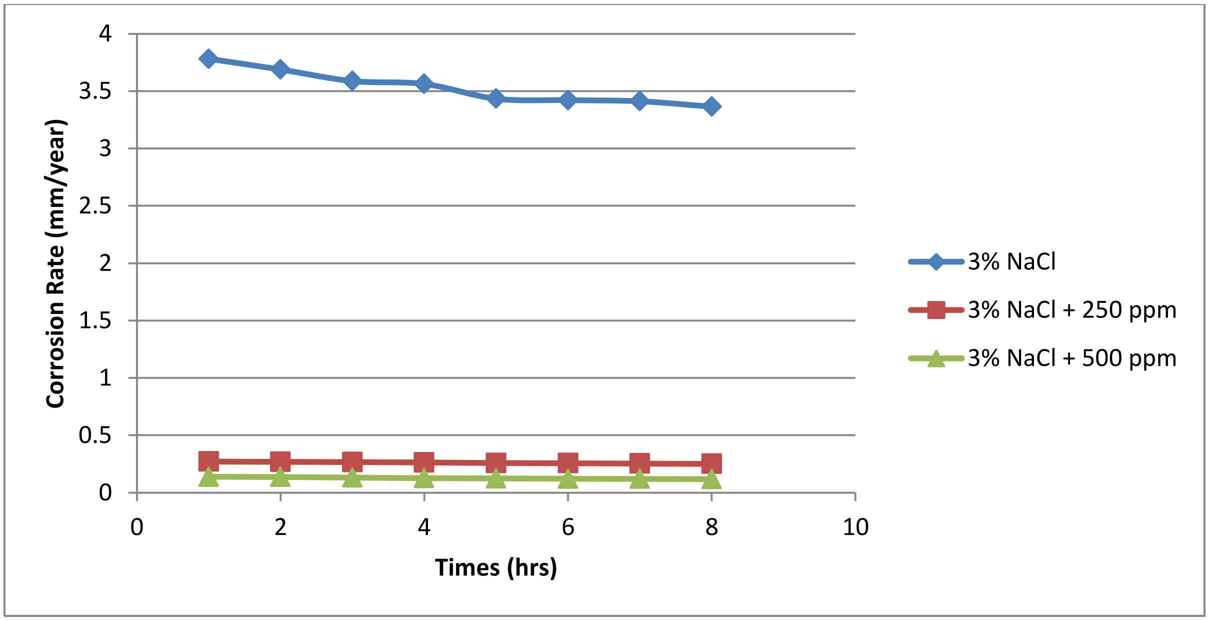


FIGURE 4.4. The trend of uninhibited CR and CR with 250 ppm and 500 ppm of ethanolamine versus Time for 25°C

From the Figure 4.4 above, there are three plots of lines which are uninhibited corrosion rate and corrosion rate with 250 ppm and 500 ppm corrosion inhibitor for temperature 25°C. There are huge decrements when the concentration of inhibitor is added. The mean corrosion rate decrease from 3.531 mm/year to 0.261 mm/year when 250 ppm of ethanolamine was injected and decrease to 0.127 mm/year when 500ppm was injected. The efficiencies of corrosion inhibitor for these systems are 92.6% and 96.4% respectively.

4.1.2 The system of 3% NaCl solution with 40°C and pH 5

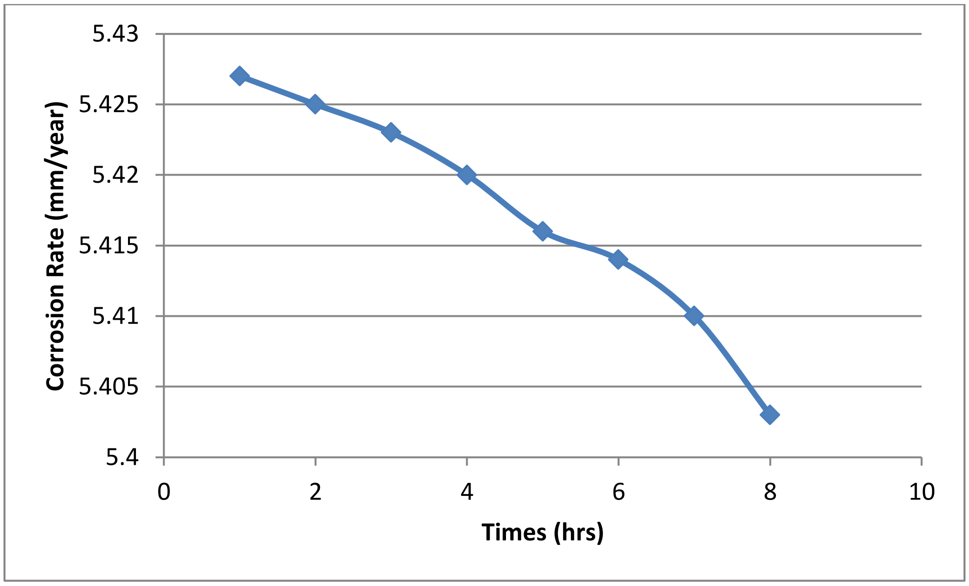


FIGURE 4.5: The trend of uninhibited corrosion rate for the system of 3% NaCl at 40°C with pH 5

From Figure 4.5, the uninhibited mean corrosion rate for 3% NaCl with temperature 40°C and pH 5 is 5.416 mm/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

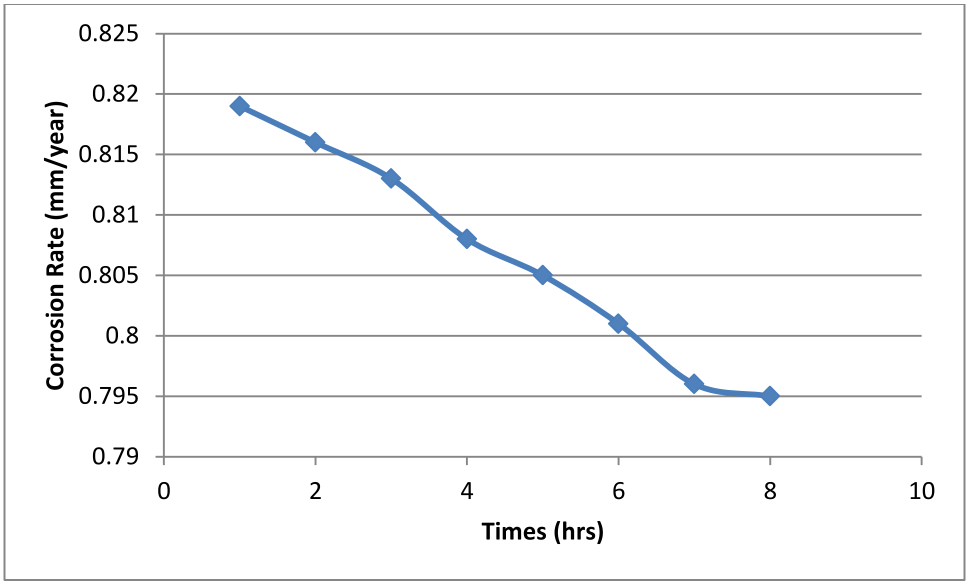


FIGURE 4.6. The trend of inhibited of Corrosion Rate with 250 ppm of ethanolamine for the system of 3%NaCl at 40°C with pH 5

From Figure 4.6 above, the mean corrosion rate with 250 ppm corrosion inhibitor for 3% NaCl with temperature 40°C and pH 5 is 0.807 mm/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

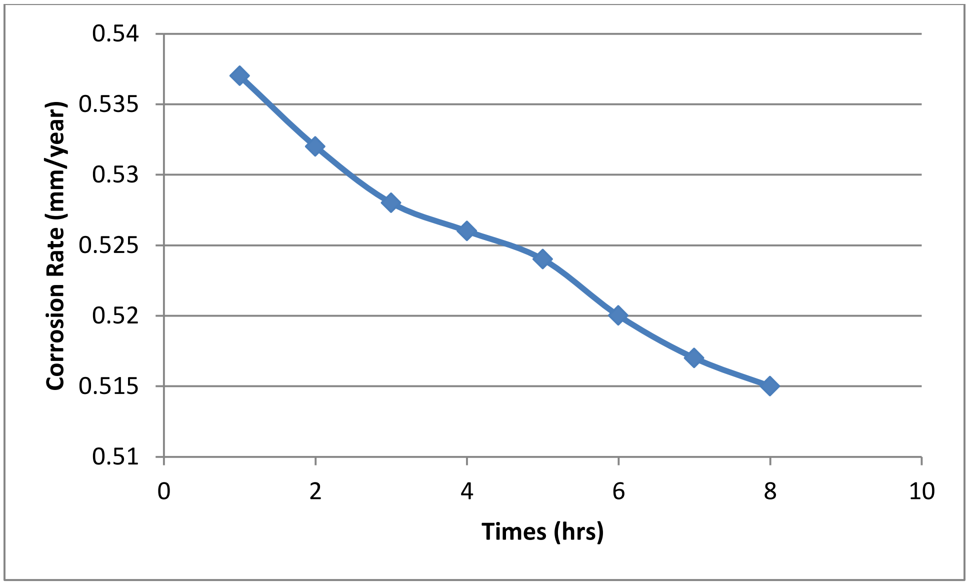


FIGURE 4.7. The trend of inhibited of Corrosion Rate with 500 ppm of ethanolamine for the system of 3%NaCl at 40°C with pH 5

From Figure 4.7 above, the mean corrosion rate with 500 ppm corrosion inhibitor for 3% NaCl with temperature 40°C and pH 5 is 0.525 mm/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

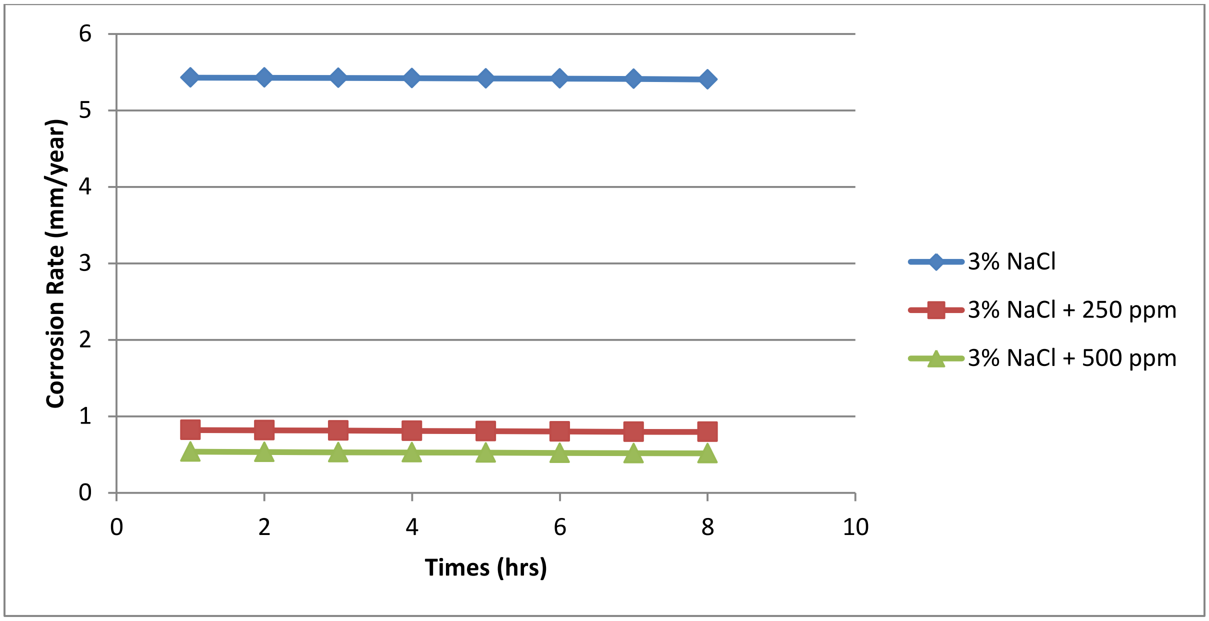


FIGURE 4.8. The trend of uninhibited CR and CR with 250 ppm and 500 ppm of ethanolamine versus Time for 40°C

From Figure 4.8 above, there are three plots of lines which are uninhibited corrosion rate and corrosion rate with 250 ppm and 500 ppm corrosion inhibitor for temperature of 40°C and pH 5. There are really huge decrements when the concentration of inhibitor is added. The mean corrosion rate decrease from 5.416 mm/year to 0.807 mm/year when 250 ppm of ethanolamine was injected and decrease to 0.525 mm/year when 500ppm was injected. The efficiencies of corrosion inhibitor for these systems are 85.1% and 90.3% respectively.

4.1.3 The system of 3% NaCl solution with 80°C and pH 5

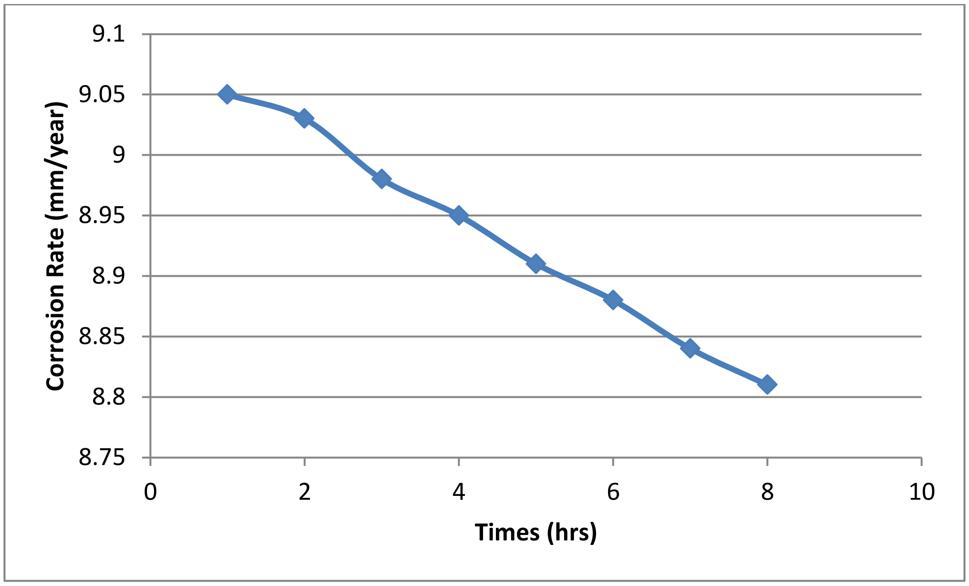


FIGURE 4.9. The trend of uninhibited corrosion rate for the system of 3% NaCl at 80°C with pH 5

From Figure 4.5, the uninhibited mean corrosion rate for 3% NaCl with temperature 80°C and pH 5 is 8.93 mm/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

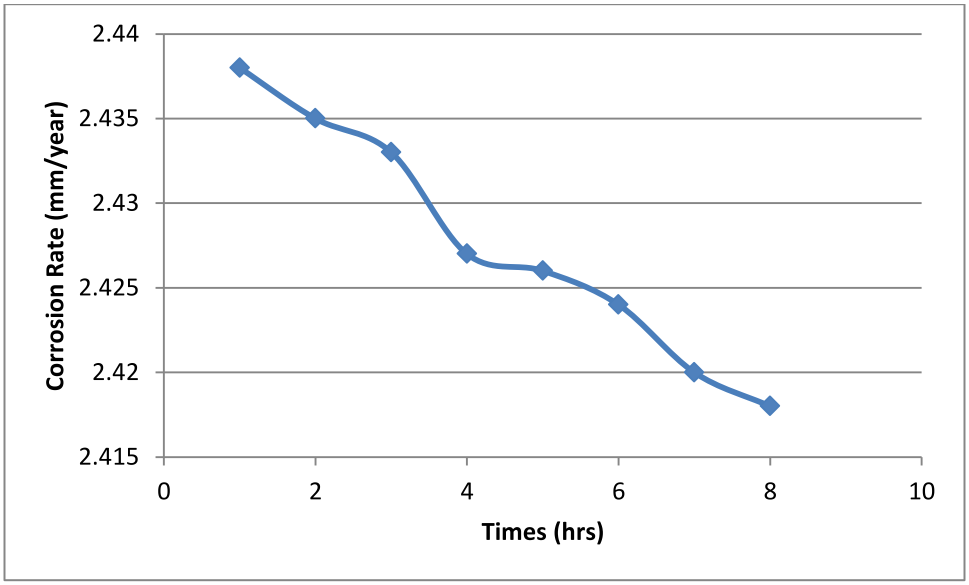


FIGURE 4.10. The trend of inhibited of Corrosion Rate with 250 ppm of ethanolamine for the system of 3%NaCl at 80°C with pH 5

From Figure 4.10 above, the mean corrosion rate with 250 ppm corrosion inhibitor for 3% NaCl with temperature 80°C and pH 5 is 2.429 mm/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

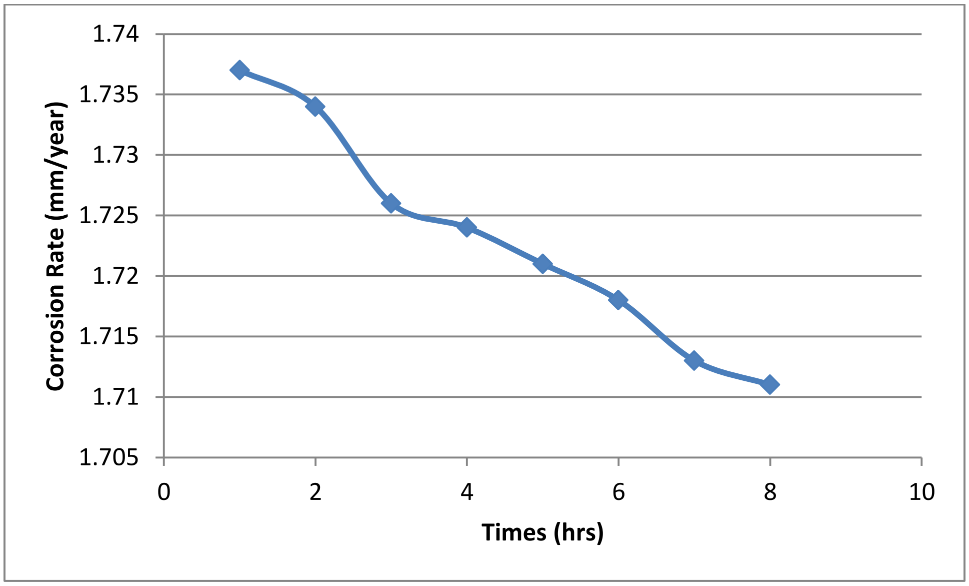


FIGURE 4.11. The trend of inhibited of Corrosion Rate with 500 ppm of ethanolamine for the system of 3%NaCl at 25°C with pH 5

From Figure 4.11 above, the mean corrosion rate with 500 ppm corrosion inhibitor for 3% NaCl with temperature 80°C and pH 5 is 1.723 mm/year. The mean corrosion rate is the average from 8 readings of corrosion rates after immersion of 8 hours.

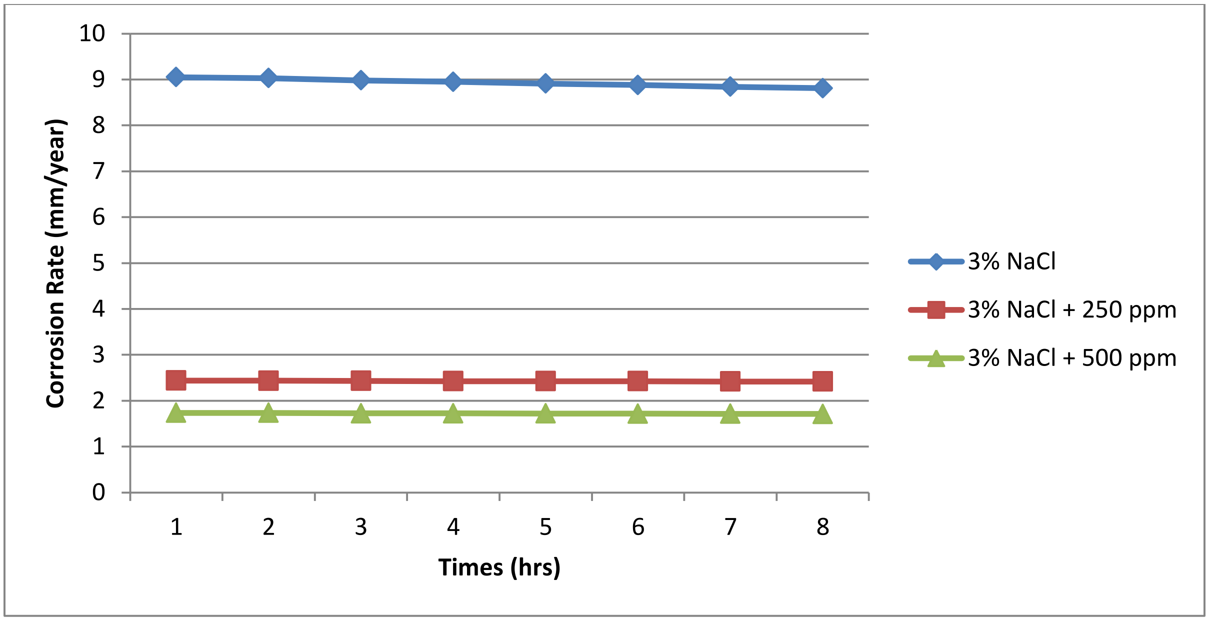


FIGURE 4.12. The trend of uninhibited CR and CR with 250 ppm and 500 ppm of ethanolamine versus Time for 80°C

From Figure 4.12 above, there are three plots of lines which are uninhibited corrosion rate and corrosion rate with 250 ppm and 500 ppm corrosion inhibitor for temperature of 80°C and pH 5. There are really huge decrements when the concentration of inhibitor is added. The mean corrosion rate decrease from 8.93 mm/year to 2.429 mm/year when 250 ppm of ethanolamine was injected and decrease to 1.723 mm/year when 500ppm was injected. The efficiencies of corrosion inhibitor for these systems are 72.8% and 80.7% respectively.

4.1.4 The result of the Efficiencies for each system with the current densities, Icorr, corrosion potential, Ecorr and corrosion rate.

From Table 4.1 below, the efficiency for the inhibitor is highest at system of 3% NaCl with temperature of 25°C and pH 5. Noted here also that each of the result in the Table 4.1 is the result for the last readings for each experiment after 8 hours or running the experiments. The efficiency of the inhibitor can be calculated with the formula below:-

$$CR = \frac{CR_{\text{uninhibited}} - CR_{\text{inhibited}}}{CR_{\text{uninhibited}}}$$

For each system consist of 0 ppm inhibitor and inhibited conditions which are 250 ppm and 500 ppm of inhibitors, the highest efficiency is 96.4% and the lowest is 72.8%.

TABLE 4.1. Efficiencies and the Potentiodynamic polarization parameters for EN 24 mild steel in 3% NaCl solutions saturated with $C0_2$ at pH 5 for uninhibited and inhibited conditions.

Temperature (°C)	pH	System	Polarization		Corrosion rate (mm/year)	Efficiency (ή)
			Ecorr (mV)	Icorr (mA/cm2)		
25	5	3% NaCl	-725.52	0.26	3.531	Uninhibited
		3% NaCl + 250ppm	-713.86	0.05	0.261	92.60%
		3% NaCl + 500ppm	-701.31	0.04	0.127	96.40%
40	5	3% NaCl	-524.91	0.67	5.416	Uninhibited
		3% NaCl + 250ppm	-501.76	0.11	0.807	85.10%
		3% NaCl + 500ppm	-498.23	0.06	0.525	90.30%
80	5	3% NaCl	-231.77	0.85	8.93	Uninhibited
		3% NaCl + 250ppm	-220.94	0.04	2.429	72.80%
		3% NaCl + 500ppm	-203.55	0.02	1.723	80.70%

At pH 5, with the temperature of 25°C, the efficiency is the highest which is 96.4%. While at the highest temperature, which is has concentration of ethanolamine at 250 ppm, the efficiency is the lowest which is 72.8%. Below are the discussion of the parameters that affecting the efficiency of the inhibitor. The parameters are temperature and concentration of inhibitor that had been used to run the experiments. All these parameters give impact to the efficiency of the inhibitor. The mechanism of the inhibitor can also be discussed according to the polarization measurements parameters above.

4. 2 The discussion of the Temperature effect on the inhibitor efficiency

The corrosion parameters obtained by conducting corrosion rate measurements for mild steel in the absence and presence of different concentration of ethanolamine in 3% NaCl at different temperature are tabulated in Table 4.1. It can be clearly seen that the corrosion rate values decreased and inhibition efficiency increased with the increase in the concentration of ethanolamine. This might be due to the fact that the adsorption coverage of the inhibitor on mild steel surface increases with the concentration of the ethanolamine.

It is noted that the inhibition efficiency depends on temperature and decreases with the rise of temperature, indicating that at higher temperature, dissolution of mild steel predominates on the surface. This effect can be explained by the decrease of the strength of the adsorption process at high temperature, suggesting physical adsorption [H. Zarok et.al, 2012].

The increase in temperature might stimulate larger metal surface kinetic energy, which has an adverse effect on the adsorption process where it weakens the adsorption process and encourage desorption process, hence the equilibrium shift towards desorption as follows [M.M. Fares et. al, 2012].

$$\text{adsorption} \leftrightarrow \text{desorption}$$

4. 3 The discussion of the ethanolamine Concentration effect on the inhibitor efficiency

From the Table 4.1, the introduction of ethanolamine inhibitor to the system at 25°C, 40°C and lastly 80°C, three distinct features can be observed. The presence of inhibitor greatly increased the corrosion potential, Ecorr to a mere positive region. This can be seen through the Table 4.1 above. The large shift in the corrosion potential indicates that the inhibitor for the system is probably due to the active sites blocking effect. From the Table 4.1, it can be clearly seen that the corrosion rate values decreased and inhibition efficiency increased with the increase in the concentration of inhibitor. This might be due to the fact that the adsorption coverage of the inhibitor on mild steel surface increases with the concentration of the inhibitor (Nurul Izni, 2013).

Results confirm that the most effective corrosion inhibitor intermediates-based commercial products (ethanolamine) do not have high temperature performance. An inhibitor product which gives high inhibition performance at a normal treatment concentration of 250 ppm would give a reduced inhibition performance at higher operation temperature and wouldn't provide the protection needed. As shown in Table 4.1, increasing inhibitor treatment concentration significantly by a factor of 2 times (from 250 ppm to 500 ppm) can improve the inhibition performance, but with a limited and lower efficiency. Thus, it is not a viable way for corrosion control. Besides, high treating dosages can create chemical compatibility problems with other production chemicals or oil/water emulsion problems which affect the oil/water separation and water quality. Consequently, the need for developing inhibitor intermediates for high temperature corrosion inhibition is obvious and certain.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion the objective of the this study is achieved that is to investigate the effect of corrosion inhibitor to the corrosion rate of the mild steel (EN24) at different operating temperature and inhibitor's concentrations. The variables that are used as constraints for this study are corrosion inhibitor, pH level and NaCl concentrations. From the experiment, it can conclude that the efficiency of the corrosion inhibitor depends on parameters such as temperature and its concentration. The efficiency of ethanolamine inhibitor decreased when temperature increases from room temperature 25°C to 80°C. The highest efficiency of inhibitor is at room temperature and inhibitor concentration at 500ppm with the value of 96.4%. However, at temperature 80°C and concentration of ethanolamine at 250ppm, the inhibitor efficiency is the lowest with the value of 72.8%. These results are possibly due to the active sites blocking effect that occurred on that mild steel. This tendency also suggests that the adsorption of this particular inhibitor is preferred at lower temperature and that desorption rate of inhibitor is increased as the temperature increases. All of these results and discussion are showed the objective of this project has been achieved.

5.2 Recommendation

The recommendation is to further investigate the effect of flow condition to the inhibitor efficiency. Flow condition is one of the factors influenced the efficiency of the inhibitor. The rotating cylinder electrode (RCE) can be used to simulate the condition of turbulence flow for the systems. The static bubble test simulates the static flow condition and does not simulate the real situation in the pipeline due to the low shear wall provided by the static bubble test. The speed of the rotation can be varied in order to determine the effect of turbulence flow condition to the efficiency of the corrosion inhibitor.

Other recommendation is to investigate the formation of corrosion product film on the steel surface at higher temperature of corrosion inhibitor or at high temperature surrounding. More useful tools and equipment can be used such as Fourier Transfer Infrared Spectroscopy (FTIR), Liquid Chromatography"Mass Spectroscopy (LC"MS) and X"Ray Photoelectron Spectroscopy (XPS) for further analyzing the corrosion inhibition and chemistry of the system. Optical Microscope (OM) or Scanning Electron Microscope (SEM) may be used to capture the micrographs of the particles at high magnification and evaluation of the microstructures can be done.

REFERENCES

[1] Nyborg, R. (2004). Internal Corrosion and Protection of it in oil and Gas Pipeline. Retrieved from www.touchoilandgas.com.

[2] Ikeda, A., Ueda, M., and Mukai, S. (1983) CO2 Corrosion Behavior and Mechanism of Carbon Steel and Alloy Steel. Proceedings of CORROSION/83, NACE International, Houston, Taxes, paper No. 45.

[3] Crolet, J.L. (1994) Predicting CO2 Corrosion in the Oil and Gas Industry. Working Party Report, Institute of Materials, London, p. 1.

[4] “Corrosion Inhibitors in the oilfield”, Retrieved December 26, 2011 from http://knol.google.com/k/corrosion"inhibitors"in"the"oilfield#

[5] B.P. Binks, P.D.I. Fletcher, J.T. Hicks, D.I. Horsup and W.H. Durnie, Proceedings of 5ACE Corrosion/2005, Paper No. 05307, NACE International, Houston (2005).

[6] Dayalan, E., Vani, G., Shadley, J.R., Shirazi, S.A., and Rybicki, E.F. (1995) Modeling CO2 Corrosion of Carbon Steels in Pipe Flow. Proceedings of CORROSION/95, NACE International, Houston, Taxes, paper No. 118.

[7] De-Waard, C., and Milliams, D.E. (1975) Carbonic Acid Corrosion of Steel. Corrosion, 31(5), pp. 177-181.

[8] S. Ramachandran, B. L. Tsai, M. Blanco, H. Chen, Y. C. Tang and W. A.Goddard, Langmuir, 12, 6419 (1996).

[9] V. Jovancicevic, S. Ramachandran and P. Prince, Corrosion, 55, 449 (1999).

[10] Hausler, R.H., and Stegmann, D.W. (1988) CO2 Corrosion and its Prevention by Chemical Inhibition in Oil and Gas Production. Proceedings of CORROSION/88, NACE International, Houston, Taxes, paper No. 863.

[11] Dugstad, A. (1992) The Importance of FeCO3 Supersaturation on the CO2 Corrosion of Carbon Steel. Proceedings of CORROSION/92, NACE International, Houston, Taxes, paper No. 14.

[12] López, D.A., Simison, N., and de Sánchez, S.R. (2005) Inhibitors performance in CO2 corrosion: EIS studies on the interaction between their molecular structure and steel microstructure. Corro. Sci., 47(3), pp. 735-755.

[13] Rosenfeld, I.L., Bogomolov, D.B., Gorodetskii, A.E., Kazanskii, L.P., Frolova, L.V., and Shamova, L.I. (1982) Zasch. Met., 18, pp. 163-168.

[14] M. Stern and A.L. Geary, “Electrochemical Polarization”, Journal of the Electrochemical Society, Vol. 104, No.1, January 1957, p.56

[15] H.M. Abd El-Lateef et al / Chemistry Journal (2012), Vol. 02, Issue 02, pp. 52-63

[16] S. A. Ali, M.T. Saeed, S.U. Rahman, Corros. Sci. 45 (2003) 253–266

[17] N. S. Patel, S. Jauhari, G. N. Mehta, Arab. J. Sci. Eng., 34(2009), 61-69

[18] B. Wang, M. Du, J. Zhang, C.J. Gao, Corros. Sci. 53 (2011) 353–361

[19] R.A. Prabhu, T.V. Venkatesha, A.V. Shanbhag, G.M. Kulkarni, R.G. Kalkhambkar, Corros. Sci. 50 (2008) 3356–3362

[20] U. Maeder, B. Marazzani, Cement Concrete Comp. 26 (2004) 209–216

[21] L. Be. Mechmeche, L. Dhouibi, M. B. Ouezdou, E. Triki, F. Zucchi, Cement Concrete Comp.30 (2008) 167–173

[22] R. E. Reitmeier, V. Sivertz, H. V. Tartar, J. Amer. Chem. Soc.62 (1940) 1943–1944

[23] C. Jeyaprabha, S. Sathiyanarayanan, G. Venkatachari, Appl. Surf. Sci. 246 (2005) 108–116

[24] R. T. Vashi, H. M. Bhajivala, S .A. Desai, E-J. Chem. 7 (2010), 665-668

[25] Huey J. Chen, Tao Hong and W. Paul Jepson, "High Temperature Corrosion Inhibition Performance of Imidazoline and Amide", Paper No. 00035, NACE International Conference & Expo (2000)

[26] Koteeswaran, M. (2010). CO2 and H2S corrosion in oil pipeline. Pg.79. Uiversity of Stavenger.

[27] Hassan Malik, (2000),"Effect of pH on the corrosion inhibition of mild steel in CO saturated brine solution", Anti-Corrosion Methods and Materials, Vol. 47 Iss: 2 pp. 88 – 93

[28] Khairi, Nurul Izni (2013). “ The Effect of Temperature on the Corrosion Inhibition of Mild Steel in 1M HCL Solution”. University Sains Malaysia, Malaysia.

[29] Riggs OL jr and Hurd RM. (1967). “Temperature coefficient of corrosion inhibition; *Corrosion*. 23(8): pp.252-258.

[30] H. Zarrok, A. Zarrouk, B. Hammouti, R. Salghi, C. Jama and F. Bentiss, Corros. Sci. 64 (2012) 643

[31] M.M. Fares, A.K. Maayta and M.M. Al-Qudah, Corros. Sci. 60 (2012) 112