Performance Study of Corrosion Inhibitors for CO_2 Corrosion on Pre-Corroded Carbon Steel

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Mechanical Engineering Programme
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In partial fulfilment of the requirement for the
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(MECHANICAL ENGINEERING)

Approved by,

Dr. Kee Kok Eng

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 acknowledgments and that the work contained herein have not been undertaken or done by unspecified sources or persons.

Hazeem Bin Mahayadin

ABSTRACT

CO_2 corrosion is one of the major problems in the oil and gas industry specifically the effect it gives to the integrity of onshore and offshore equipment. Therefore, several methods have been developed to prevent this type of corrosion and this particular work will be focusing on the application of corrosion inhibitors on the operation of pipelines which exposed to high concentrations of carbon dioxide. However, corrosion inhibitor is usually injected when corrosion already occur on the pipelines and it is believed that the pre-corrosion condition will affect the performance of inhibitors. Thus, the objective of this project is to measure the performance of inhibitors on the pre-corroded carbon steel. Additionally, this project also will find out the effect on environment specifically the pH value to the performance of corrosion inhibitors. So, several test studies have been developed to achieve the targeted objective and all experiments were conducted by using Linear Polarization Resistance (LPR), Electron Impedance Spectroscopy (EIS) and Custom Sweep techniques. Additionally, the amount of injected corrosion inhibitors were increased to 100ppm to know the effect in reducing the corrosion rate. The result from this research indicated the 25ppm corrosion inhibitors managed to reduce the corrosion rate at the first five hours after the injection. However, the corrosion rate increased back since the amount is not enough to provide full protection for 48 hours period of time. In contrast, 100ppm of corrosion inhibitors resulted in efficient corrosion rate reduction which implied that the amount of injected CI affect the corrosion rate very much.

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CHAPTER 1

INTRODUCTION

1.1 Background

The impact of corrosion in oil and gas industry is often discussed by engineers due to high costs especially when it is viewed in terms of capital and operational expenditure (CAPEX and OPEX) and health, safety and environment (HSE). Corrosion usually represents a tremendous economic loss and much can be done to reduce it. Fontana [1] described corrosion as the destruction or deterioration of a material because of reaction with its environment. Even though some may insist that corrosion should only be restricted to metal only but corrosion engineers still have to provide the solution for both metal and non-metal since both of them deteriorating towards environment. Corrosion can seriously affect equipment integrity and its serviceability as it may raises the risk of leaks and discharges of flammable gas.

It is highly important to know that there are several types of corrosion that usually occur in the surface of the pipelines. Kermani and Harrop [2] mentioned that corrosion related failures constitute over 25% of failure experienced in the oil and gas industry. Most of them are associated with CO_2 (carbon dioxide) and H_2S (hydrogen sulfide) producing fluid and they are also known as sweet and sour corrosion. Carbon dioxide gas usually presents in the well containing crude oil and natural gas. It can cause danger to the main downhole tubing and transmission pipelines which consequently disrupt the production as mentioned by El-Lateef et al. [3]. Therefore, few methods have been classified to control or reduce the corrosion rate particularly on the equipment used in industry. The most common method is the selection of suitable metal or alloy for corrosive environment and usually conducted during the design. Cathodic protection is applied in most of the oil and gas platform due to its simplicity by maintaining direct current circuit. As for this research, it will be concentrating on the application of chemical inhibitors along the pipelines by looking at the performance of two types of inhibitors to study the efficiency in reducing the corrosion rate.

In oil and gas industry, carbon steel is often become the major material that being selected for pipeline and tubing. Gandy [4] in his report on carbon steel stated that they are used widely throughout the world for the same reason: their cost, properties, ease of fabrication, availability and weldability.

Pipelines are required to transport oil and gas from and to the well, sometimes over long distances. Thus, products that contain water and carbon dioxide are likely to cause corrosion on the pipelines. It is believed that corrosion inhibitors can be very effective in reducing the corrosion rate especially on clear carbon steel that are yet to be corroded. However, it is not the case for corroded carbon steel as mentioned by Gulbrandsen, et al. [5] since the metal surface has been growth by cementite film that will significantly affect the performance of the inhibitor. Additionally, Kowata and Takahashi [6] observed the difficulty in getting a clean surface steel practically which reacts with neutral aqueous solution. The evidences found have directed the main objective of this research work to find out the efficiency of inhibitors on pre-corroded carbon steel in order to be more relevant with the real situation in oilfield.

1.2 Problem Statement

CO_2 corrosion (sweet corrosion) on carbon steel pipelines is the most common problem that faced in oil and gas industry especially in maintaining the integrity of the equipment. Therefore, several methods have been developed and one of them is by injecting corrosion inhibitors through the pipelines with the intention to reduce the corrosion rate.

However, corrosion inhibitor is often injected once the corrosion takes place. A study has shown that the performance and efficiency of the inhibitor will be discounted by severity of pre-corroded steel metal [5]. This is because localized corrosion attack might occur due to the poor adsorption of the inhibitor on the rusted surface. This research is hopefully addressing the problem by looking at the performance of two type of inhibitors known as fatty amine and Quaternary ammonium compound (QAC) experimentally.

1.3 Objectives

There are several specific objectives identified in this research and targeted to be achieved at the end of the work.

- To measure the performance of different types of inhibitors; fatty amine and QAC in reducing the corrosion rate.
- To evaluate the effect of different inhibitor's concentrations and pH value on the corrosion rate of carbon steel.
- To investigate the carbon steel morphology and relate to the form of corrosion attack.

1.4 Scope of Study

It is highly important to state the scope of this research which included the limitations that will be gone through during the project time frame. The following showed in simple point form on the scope of this particular work.

- The experiment will be conducted to only CO_2 corrosion condition even though H_2S corrosion is also observed in the oil and gas industry.
- Even though varies methods were developed to reduce the corrosion rate, this research will be focusing on the usage of corrosion inhibitors that being injected through the pipelines.
- The specimen that will be reacted with the inhibitors in this research is carbon steel since they are used widely in the construction of oil and gas pipelines. Plus, the carbon steel will be left to be corroded before being reacted with inhibitors so that the performance of inhibitors can be assessed accordingly.

CHAPTER 2

LITERATURE REVIEW

2.1 Pre-Corroded Carbon Steel

Steels are known as the composition of different alloys of iron and they usually contain some amounts of manganese and carbon. There are several types of steels existed such as stainless steel, alloyed steel, tool steel and carbon steel. Gandy et al. [4] mentioned that properties of carbon steel depend mostly on the amount of carbon in the composition and usually will have less than 2% carbon content. It is understood from metallurgical point of view that the strength and hardness of steel increase with the increment of carbon in the composition. However, it is only applicable until 1.5% carbon because there will be reduction in the malleability and ductility as stated by Gandy et al. in their book.

Callister and Rethwisch [7] in "Material Science and Engineering" book classified carbon steel into three different stages. Low carbon steel is known as metal that has less than 0.25% carbon content and consist of ferrite and pearlite constituents through microstructure point of view. Carbon steel that has carbon concentrations between 0.25% and 0.60% is called as medium-carbon steel and they are usually being heat-treated by austenitizing, quenching and tempering in order to improve its mechanical properties. High carbon steel normally compose with the carbon concentrations between 0.60% and 1.4% which make it to be very strong but yet less ductile.

One may argue why carbon steel is chosen to be the testing object in the CO_2 corrosion environment. The answer is simply that carbon steel was used in the most of the construction of pressure vessels especially in the oil and gas industry. Paolinelli et al. [8] confirmed that carbon steel has been used widely in the petroleum industry due to economic reasons. Besides, its wide range of mechanical properties and ease of weldability are the main reasons why carbon steel was chosen by most of oil and gas companies.

Interestingly enough, this research was primarily focusing on the CO_2 corrosion in oil and gas pipelines due to its significant effect when there were failures on the materials structure. Anything related with engineering realm often associated with standard or code of practice. As for the transportation pipelines, API 5L or ISO 3183 is the standard used by engineers as the main reference especially when there were problems found. Narrowing down the scope, API 5L X65 is the carbon steel grade that often used for the pipelines manufacturing in oil and gas transportation. The ‘X’ symbol followed by two or three digits after indicated the minimum yield strength in 1000 psi and thus, number ‘65’ vividly showed that this pipeline has 65,000 psi of minimum yield strength as stated by Arcelo Mittal [9] (steel and mining company) in their pipelines product specifications. In order to have better understanding, the following table showed the details of material composition for this grade of carbon steel.

Table 2.1: Material composition for carbon steel API 5L X65 (>0.1%)

Element	**Percentage of Composition (%)**
C	0.16
Si	0.50
Mn	1.10 - 1.60
Cr	0.50
Ni	0.20
Cu	0.20

(Source: Arcelo Mittal product specification)

The understanding on the term “pre-corroded” carbon steel is very important in order to get this research at the right track. Kowata and Takahashi [6] mentioned in their work that the interaction of corrosion inhibitors with clean steel surfaces is well known to be very effective. However, in real situation, it is never like that because the difficulty in getting a clean steel surface in a practical plant system or pipelines. Pre-corroded carbon steel can be defined as metal that has undergone corrosion for certain period of times as can be seen from the experiment conducted by Paolinelli et al. [8].

In addition, Gulbrandsen, et al. [5] founded that the inhibitors performance were less effective on pre-corroded carbon steel compared to the clean one. They further explained that the inhibitor acted slower with increasing in the pre-corrosion time. The reason behind this phenomena is due to the formation of cementite (Fe_3C) layer which disturb the reaction of inhibitor on the metal surface. They also concluded that the corrosion rate is controlled by the rate of cathodic reaction since cathodic inhibition has great influence on the reaction. In fact, steel microstructure and inhibitor molecule structure play important role in making sure that the pre-corrosion carbon steel has negative effect on the performance of inhibitors.

On the other hand, Farida et al. [10] detected that cementite was formed during the pre-corrosion period which to be necessary in promoting the formation of Iron Carbonate ($FeCO_3$) film. They examined different chemical composition like carbon (C), manganese (Mn) and silicon (Si) can influence the amount of cementite and thus, affected the corrosion rate. In order to make the surface to be pre-corroded, anodic current was applied for 24 hours or 48 hours in the experiments which may produce different amount enriched cementite on the surface.

This research is therefore to be believed to extent the study on the effectiveness of different types of inhibitors when injected on pre-corroded carbon steel.

2.2 Mechanism of CO_2 Corrosion

There are several types of corrosion usually occurs in oil and gas industry both downstream and upstream. Oilfield corrosion engineers divided corrosions due to oxygen (sweet corrosion) and hydrogen sulfide (sour corrosion). Sour service refers to the present of H_2S, hydrogen sulfide and it is one of the most deadly gas after carbon monoxide. In contrast, sweet service indicated that the environment that is free from H_2S gas and the most common sweet service known is CO_2, carbon dioxide. However, both have corrosive characteristic that may damage the equipment used in the industry. This particular work will be concentrating on the effect of CO_2 corrosion on pipelines because the crude oil and gas from oil reservoir generally contains an amount of carbon dioxide.

Kermani and Morshed [11] indicated that dry carbon dioxide gas is not corrosive unless it is dissolved in the aqueous solution forming electrochemical reactions between the contacting surfaces with the liquid itself. There are still arguments among the scientist in this subject since various CO_2 mechanism has been illustrated. Generally all agreed that the first step of this mechanism is carbon dioxide will dissolve in water to form carbonic acid (H_2CO_3) which will be corrosive to the contacting surface.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \quad (1)$$

According to George and Nesic [12], carbonic acid is then partially dissociates to form bicarbonate ion and further dissociates to form carbonate ion. They also mentioned that the solutions containing H_2CO_3 are more corrosive when compared with other strong acids at the same pH level. However, this postulation was debated and speculated in the past decades until De waard and Milliams [13] suggested this is due the reduction of un-dissociated of H_2CO_3 after the adsorption on the surface of metal.

Schwenk [14] simply proposed that H_2CO_3 provides source of H^+ when it dissociates to bicarbonate ion and carbonate ion.

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \qquad (2)$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^- \qquad (3)$$

From this argument, it is evident that the CO_2 concentration dissolve in solution do affect the reaction by transporting toward and from the steel surface which will increase the corrosion rate. However, there were two possible cathodic reactions that may occur in this reaction.

$$H_2CO_3 + e^- \longleftrightarrow H + HCO_3^- \qquad (4)$$

$$H^+ + e^- \longleftrightarrow H^+ \qquad (5)$$

From the above chemical equations, the rate of the former equation is depending on the amount of CO_2 dissociated and the latter equation is the main source for the pH of the system. As for the anodic reaction, iron, Fe composed in the carbon steel ionized to keep the process going by distributing two electrons to the cathodic reactions.

$$Fe \longleftrightarrow Fe^{2+} + 2e^- \qquad (6)$$

Another interesting aspect for this type of corrosion is regarding the formation film which will affect the corrosion rate during the corrosion process. Gao et al. [15] illustrated that CO_2 corrosion will form films due to many factors such as pressure, flow rate, pH value and temperature. This argument is one of the reasons why the study was conducted on pre-corroded carbon steel. The iron carbonate, $FeCO_3$ precipitate may form a protective film on the surface metal according the factors mentioned by the reaction between ferrous ions with carbonate ions.

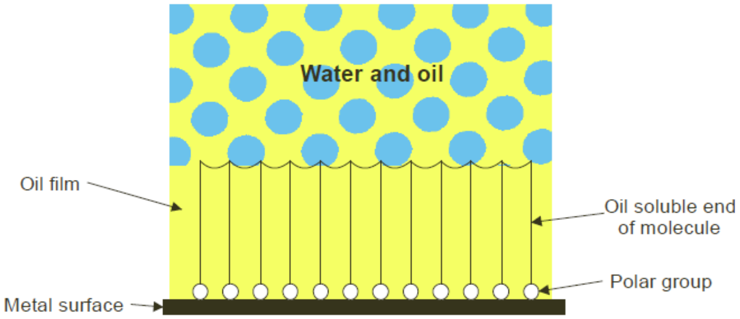
$$Fe^{2+} + CO_3^{2-} \longleftrightarrow FeCO_3 \qquad (7)$$

They further explained that the presence of microstructure also affect the corrosion rate which in this case are cementite (Fe_3C) and ferrite (α-Fe) [15]. The study of CO_2 corrosion mechanism is very vital because it will help to understand on the mitigation step that should be taken to reduce the corrosion rate especially in the pipelines environment.

2.3 Corrosion Inhibitors

Fontana [1] defined inhibitor as a substance that decrease the corrosion rate when added in small concentrations to an environment. The main objective of this corrosion inhibitor is to reduce the anodic oxidation and cathodic reduction reaction in corrosive environment. In other words, it will helps to control the environment to be at a condition which corrosion is not prior to happen. Hobbs [16] in his report indicated that corrosion inhibitors work by forming a protective film on the metal and thus, preventing corrosive elements from contacting with the surface metal as shown in Figure 1.

Figure 2.1: Protective inhibitor film adsorped on metal surface



(Source: Reliable corrosion inhibition in the oil and gas industry, Health and Safety Executive Report 2014 by James Hobbs)

Inhibitors help to reduce the corrosion rate by adsorbing onto the metal surface either through physical or chemical adsorption. Schweitzer [17] in his book on “Corrosion of Linings and Coatings” mentioned that physical adsorption occur when there are electrostatic attractive forces between the organic ions and the electrically charged metal surface. Whilst, chemosorption is known as the transfer of inhibitor molecule’s charge to the metal surface.

He further explained on the classification of inhibitors through electrochemical basis where it can react in anodic, cathodic and even both [17]. Through chemical nature perspective, inhibitors can be classified into two groups; organic and inorganic substances. Whilst, Dietsche et al, [18] classified corrosion inhibitors into three main groups known as; cathodic and anodic inhibitors, inorganic and organic, filming and non-filming. Other than that, it is highly important to determine the efficiency of inhibitors so that the comparison study between them can be done. The efficiency can be calculated through following formula stated by Schweitzer in his book [17]:

$$I_{eff} = \frac{R_o - R_i}{R_o} \times 100$$

Where

I_{eff} = efficiency of inhibitor, %

R_o = corrosion rate of metal without inhibitor present

R_i = corrosion rate of metal with inhibitor present.

Organic inhibitors were most likely to form protective layer on the steel surface in order to prevent from the corrosive environment. This is because they are able to act as cathodic, anodic or together through adsorption process. Dariva and Galio [19] indicated that organic inhibitors will build up a protective hydrophobic film on the metal surface which prevent any corrosive elements from reacting with it. It is said that the efficiency of this type of inhibitors depend on the presence of polar functional group with sulfur, oxygen and nitrogen atoms in the molecule. Interestingly enough, they provide some examples of this type of inhibitors like amines, aldehydes, acetylenic compounds, urea and heterocylic nitrogen compounds.

In regards with pipeline operation, corrosion inhibitors were injected either daily or by batch depend on the corrosion magnitude. It was part of the program in oil and gas industry to control the internal corrosion of petroleum pipelines since it can delay or inhibit the corrosion mechanisms. Pigs were usually used to apply the corrosion inhibitor through the pipelines as it can create seal between the pig cups and the pipe wall which make it efficient enough to form a good protective layer on the steel surface.

In this particular research, corrosion inhibitors that were chosen to be tested known as fatty amine and Quaternary Ammonium Compound (QAC). Therefore, it is necessary to understand the structure of these inhibitors in forming layers on the surface of carbon steel to prevent from the corrosive environment. Fatty amine is produced in two-step process starting from fatty acids and the primary amine can be transformed into di-amines by the addition of acrylonitrile [20]. In order to know this inhibitor better, it is very essential to understand the steps in producing the fatty amine.

Step 1:

$$\text{R- COOH} + \text{NH}_3 \longrightarrow \text{RCN} + 2\text{H}_2\text{O}$$

Step 2:

$$\text{R-CN} + 2\text{H}_2 \longrightarrow \text{RCN} - \text{NH}_2$$

Fatty amine helps to protect the surface of metal from corrosive agents by forming protective layers usually explained as ‘sandwich’ theory. The bottom part of the sandwich is the bond between the metal surfaces with the polar of the molecule while the central part of the molecule is the non-polar. In addition, organic amines have been shown to give effect to both anodic and cathodic areas of the metal.

Tezel [21] Quaternary ammonium compounds (QACs) contain four functional group that are attached covalently to a central nitrogen atom (R_4N^+). Interestingly enough, QACs are known as one of the most high production volume chemicals due to current demand. The following figure showed the molecular structural for QAC where R represents as a functional group, X^- as counter ion such as CI^- and Br^-.

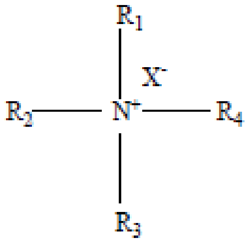


Figure 2.2: General molecule structure of QAC

QAC works like fatty amine by forming protective layers on the surface of metal since it contains hydrophobic and hydrophilic structure which enable it to prevent the corrosive environment from affecting the metal.

CHAPTER 3

METHODOLOGY

3.1 Project Activities

It is highly important to plan and manage the activities required in this research work so that the objective is achieved. Therefore, the research methodology has to be understood in a bigger scope at the first place before knowing the minute details of the work.

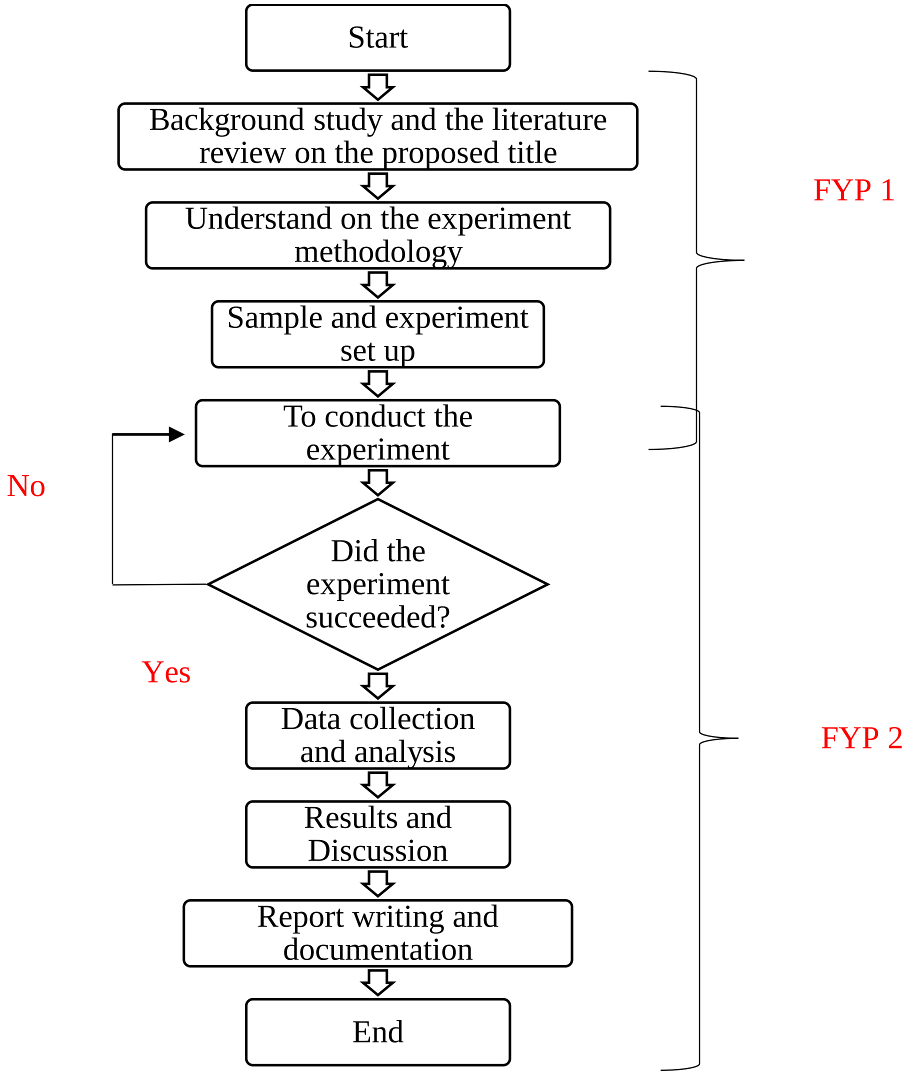


Figure 3.1: Overall work flow for FYP 1 and FYP 2

3.2 Experiment methodology

The laboratory experiment was conducted by using X65 carbon steel with several conditions to achieve the targeted objective. Knowing how to conduct the experiment is definitely the most vital in this research since without them, no conclusion or postulation can be made. For this research, Linear Polarization Resistance (LPR) [23], Electron Impedance Spectroscopy (EIS) and Tafel Plot techniques were conducted to find out the corrosion rates after injected by some of the corrosion inhibitors. However, before proceeding with that, the specimen (X65 carbon steel) has been prepared at the beginning according the American Society for Testing and Materials (ASTM) G1 [22].

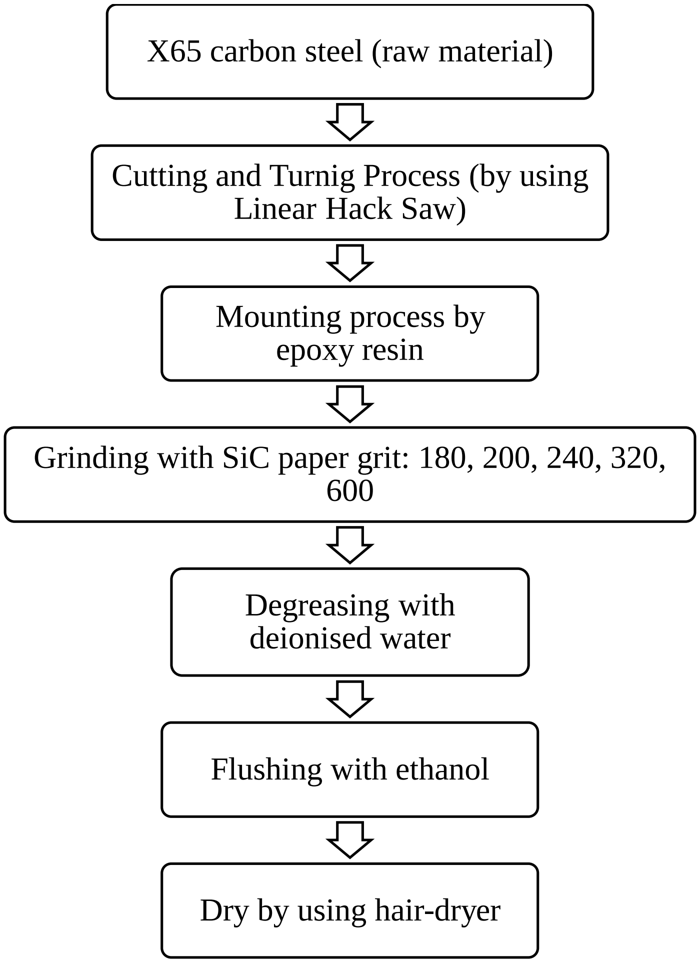


Figure 3.2: Process flow for surface preparation

Before conducting the experiment, it is very important to know the test matrix for this research study so that the experiment will be conducted according to the targeted objective. Therefore, several test matrix was developed based on the general test matrix.

Table 3.1: General Test Matrix for the experiment

Steel Type	API 5L X65
Solution	3 wt% NaCI
De-oxygenated gas	Carbon Dioxide
Temperature (ºC)	25ºC
pH	4.0, 6.6
CO$_2$ Pressure (bar)	1
Rotational velocity (rpm)	0 or stagnant
Type of inhibitors	Amine based, Quaternary Ammonium Solution
Concentration of Inhibitors (ppm)	25, 100
Pre-corrosion Period (h)	24
Inhibition duration (h)	24
Measurement Techniques	Linear Polarization Resistance (LPR), Electron Impedance Spectroscopy (EIS), Tafel Plot, Scanning Electron Microscopy (SEM)

All the experiment will be conducted according to the standard and the details procedure of each activity has been specified for the ease of the execution.

Table 3 below showed the test method that were used in this study and divided into two parts; i) electrochemical analysis, and ii) surface characterization.

Table 3.2: Test method

Test Method	Technique
Electrochemical Analysis	Linear Polarization Resistance (LPR)
	Electrochemical Impedance Spectroscopy (EIS)
	Custom Sweep
Surface Characterization	Scanning Electron Microscopy (SEM)

The following showed the steps that were taken in order to conduct the experiment in general.

1. 3 wt% NaCI was prepared by dissolving 60g of sodium chloride (NaCI) into 2000ml deionized solution in a glass cell and it was stirred by using the electromagnetic stirrer.
2. The solution was purged with carbon dioxide gas for 1 hour and pH value of the solution was keep monitored accordingly.
3. Three electrodes like working electrode, reference electrode and counter electrode were jacketed into glass cell with stainless steel became the counter electrode. Whilst, the Ag/AgCI became the reference electrode. They were connected directly to the ACM Instrument Grill 12 Weld Tester.
4. The solution was then heated to the required temperature by using hot plate.
5. After the solution was deoxygenated, pH value for the solution was regulated according to the targeted pH by adding sodium hydrogen bicarbonate solution or hydrochloric acid.
6. The solution was let for 24 hours for the pre-corrosion period.
7. A commercial amine and Quaternary ammonium solution inhibitors were injected at concentrations of 25ppm after the pre-corrosion period; 24 hours and was let for another 24 hours for inhibition period.

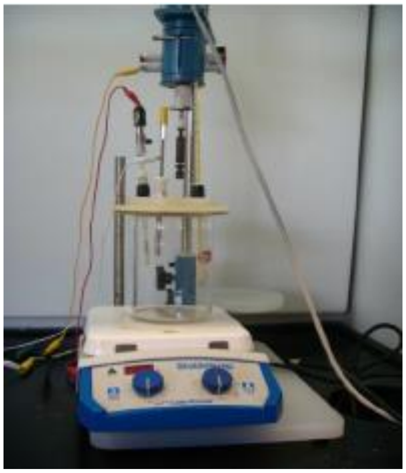


Figure 3.3: A schematic of glass cell arrangemet

The working electrode was prepared to be mounted by epoxy resin and grinded until 600 grit of SiC paper.

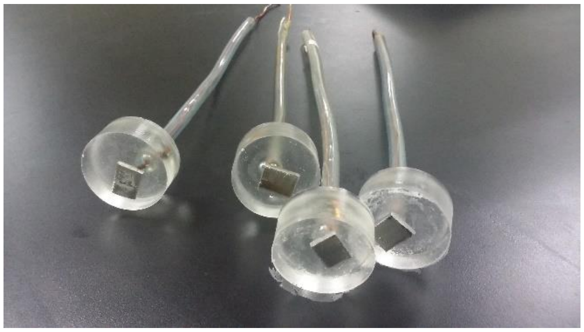


Figure 3.4: Mounted X65 Carbon Steel

The general test matrix was then transformed into specific test matrix according to the condition of field. Each of the test studies differed in several parameters following the targeted objective.

Test Study 1: Baseline study when no corrosion inhibitors were injected into the solution at different pH condition.

Objective: To measure the corrosion rate of carbon steel for baseline at pH 4.0 and 6.6.

Table 3.3: Test Matrix for test study 1

Parameter	**1**	**2**
Type of Corrosion Inhibitors	Baseline	Baseline
Steel Type	API 5L X65	API 5L X65
Solution	3 wt% NaCI	3 wt% NaCI
De-oxygenated gas	1 bar CO2	1 bar CO2
Corrosion Inhibitor concentration (ppm)	0	0
Temperature (degC)	25	25
pH	4.0	6.6
Pre-corrosion Period (h)	24	24
Rotational Velocity (rpm)	0 or stagnant	0 or stagnant

Test Study 2: Performance of different type of corrosion inhibitors by evaluating the effect of different pH value of the solution.

Objective: To measure the different types of inhibitors performance on pre-corroded carbon steel and the effect of pH on them.

Table 3.4: Test Matrix for test study 2

Parameter	**1**	**2**
Type of Corrosion Inhibitors	Amine	Quarternary Ammonium Solution (QAC)
Steel Type	API 5L X65	API 5L X65
Solution	3 wt% NaCI	3 wt% NaCI
De-oxygenated gas	1 bar CO2	1 bar CO2
Corrosion Inhibitor concentration (ppm)	25	25
Temperature (degC)	25	25
pH	4.0, 6.6	4.0, 6.6
Pre-corrosion Period (h)	24	24
Inhibition duration (h)	24	24
Rotational Velocity (rpm)	0 or stagnant	0 or stagnant

Test Study 3: Performance of corrosion inhibitors by increasing the amount of injected inhibitors.

Objective: To measure the effect of inhibitors performance on pre-corroded carbon steel at 100ppm volume.

Table 3.5: Test Matrix for Test Study 3

Parameter	**1**	**2**
Type of Corrosion Inhibitors	Amine	Quarternary Ammonium Solution (QAC)
Steel Type	API 5L X65	API 5L X65
Solution	3 wt% NaCI	3 wt% NaCI
De-oxygenated gas	1 bar CO2	1 bar CO2
Corrosion Inhibitor concentration (ppm)	100	100
Temperature (degC)	25	25
pH	4.0	4.0
Pre-corrosion Period (h)	24	24
Inhibition duration (h)	24	24
Rotational Velocity (rpm)	0 or stagnant	0 or stagnant

Details of test procedure

Interestingly enough, there were four categories of test procedure which designed to achieve the targeted objective.

Blank CO_2 corrosion

All the tests were let with carbon dioxide gas for 24 hours without the presence of corrosion inhibitors and the results will be a baseline for the next 24 hours of inhibition period in the experiment. In fact, it was also acted as the pre-corrosion period for the experiment since the target was to see the performance of inhibitors on pre-corroded carbon steel.

Performance of different type of corrosion inhibitors (Amine and QAC)

The main objective of this research project itself was to investigate the performance of different corrosion inhibitors and thus, Amine and QAC were selected due to their commercialization in the industry. They were injected after 24 hours period at the concentration of 25ppm to see their effectiveness in reducing the corrosion rate of X65 carbon steel.

Different pH value

This type of experiment was to investigate the effect of pH value on the performance of inhibitors. Therefore, the solution was regulated to be at the pH value of 4.0 and 6.6 by adding sodium bicarbonate in the case of increasing the pH value or adding hydrochloric acid to reduce the pH value.

Different temperature

This set of experiment was designed to investigate the effect of temperature on the performance of inhibitors. All the glass cells were placed on the hot plate to heat the solution to be at the temperature of 25ºC and 60ºC. The temperature of the solution was monitored by using thermometer to assure the experiment operated at constant temperature.

Table 3.6: Details test matrix of the experiment

Type of Corrosion Inhibitors	Concentration of inhibitors (ppm)	Temperature (ºC)	pH	Pre-corrosion period (h)	Inhibition Period (h)
Baseline	-	25	4.0	48	-
			6.6		
Amine	25	25	4.0	24	24
		25	6.6		
Quaternary Ammonium Compound (QAC)	25	25	4.0	24	24
		25	6.6		

Electrochemical analysis

The measurement of corrosion rate was conducted by using linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic sweep. All types of analysis were performed and recorded by ACM Instrument Gill 12 Weld Tester as shown below.

Figure 3.5: ACM Instrument Gill 12 Weld Tester

Linear Polarization Resistance (LPR)

This technique was applied to monitor the corrosion rate of X65 carbon steel at the scanning from -10mV to +10mV with a scan rate of 10mV/min. The standard referred was ASTM G102-89 and the calculation was conducted accordingly where the polarization resistance (R_p) was taken from Stern and Geary equation.

Electrochemical Impedance Spectroscopy (EIS)

EIS is a powerful tool to determine corrosion resistance of coatings. It uses alternating current and generating resistance and capacitance data of the experiment. It was carried out in the frequency range from 1mHz to 10kHz with the RMS value of 15mV. The standard referred for this type of experiment is ASTM G106.

Scanning Electron Microscopy (SEM)

SEM was performed for all tested samples at the magnification of 100X. After completed all test study, every specimens were then examined by using SEM to characterize the carbon steel morphology and finally, relate to the form of corrosion.

3.2 Gantt Chart and Key Milestone

Gantt chart plays a very important role in guiding this research to be completed within the time frame which is 28 weeks. Whilst, key milestone helps to stringent the located time to make sure this work is progressing accordingly.

Table 3.7: Gantt chart for FYP 1 and FYP 2

		SEMESTER 1 (FYP I)															SEMESTER 2 (FYP II)														
SUBJECT	**ALLOCATION**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
FYP Topic Selection	1 week	■														Semester Break															
Project Introduction	1 week		■																												
Extended Proposal	4 weeks			■	■	■	■	■																							
Extended Proposal Submission	22-Feb-15								■																						
Proposal Defense Preparation	3 weeks								■	■																					
Proposal Defense Evaluation	2 weeks									■	■																				
Introduction to experimental preparation	3 weeks										■	■	■																		
Submission of Interim Draft Report	1 week													■																	
Submission of Interim Report	1 week														■																
Preparation of LPR test	1 week																■														
LPR experiment	2 weeks																	■	■												
Data Validation of LPR experiment technique	4 weeks																			■	■	■	■								
Progress Report Preparation	5 weeks																			■	■	■	■	■							
Progress Report Submission	1 week																								■						
Critical analysis on the result from LPR test	3 weeks																								■	■	■				
Pre-SEDEX	1 week																											■			
Investigating the Integrity and Reliability of the Technique	2 weeks																										■	■			
Preparation of Final Report	3 weeks																										■	■	■		
Submission of Draft Final Report	1 week																												■		
Submission of Dissertation (Soft Bound)	1 week																													■	
Submission of Technical Paper	1 week																													■	
Viva	1 week																													■	
Submission of Dissertation (Hard Bound)	1 week																														■

As for the key milestone, it is really important to make sure the project is in the progress by constraining the dates. This point can be signaled in the form of project start and end date. However, the key milestone can only be projected until the submission of progress report due to limitation of information from the management.

Table 3.8: Key Milestone

No	**Key Milestone**	**Date**
1	Preparation for LPR test	22/04/2015- 30/04/ 2015
2	Conduct LPR test for all test study	18/05/2015- 02/06/2015
3	Validation and analysis of data obtained	03/06/2015- 17/06/2015
4	Preparation and Submission of progress report	03/06/2015- 01/07/2015

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter will finally presents the results and some discussions on the performance of corrosion inhibitors on pre-corroded carbon steel plus with the effect of pH value on the corrosion rate. The results from the electrochemical analysis will be presented mostly by plotted graph and the analysis will be conducted by investigating the behavior of the graph. Three electrochemical techniques known as LPR, EIS and custom sweep were employed while SEM was conducted to relate the surface structure of tested samples.

4.1 Test Study 1: Baseline study (no CI) at different pH condition of 4.0 and 6.6

4.1.1 Linear Polarization Resistance (LPR)

At the beginning of the experiment, X65 carbon steels were left to be corroded for 24 hours before being injected by corrosion inhibitors. The baseline experiment was conducted in the first place in order to provide basic structure for this research. Two experiments were conducted with different pH condition and no inhibitors were injected to see the behavior of corrosion rate on the carbon steel. The initial corrosion rate estimated was 1.41 mm/year and the final corrosion rate was 2.44 mm/year. From this result, obvious increment can be seen since there was no protective layers formed to prevent or hinder the corrosive agents. Both baseline have been conducted at different pH value; one at pH 4 and the other at pH 6.6.

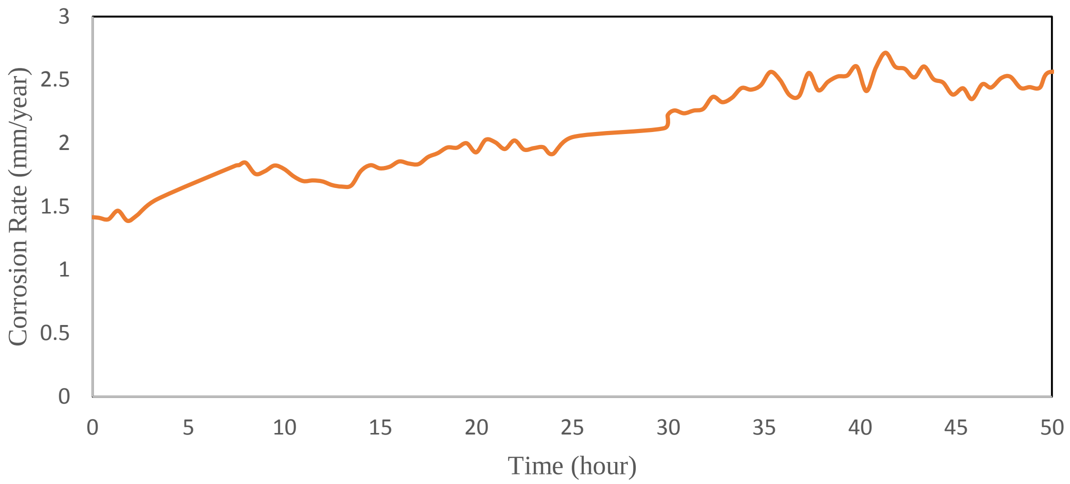


Figure 4.1: Corrosion rate for baseline at pH 4.0

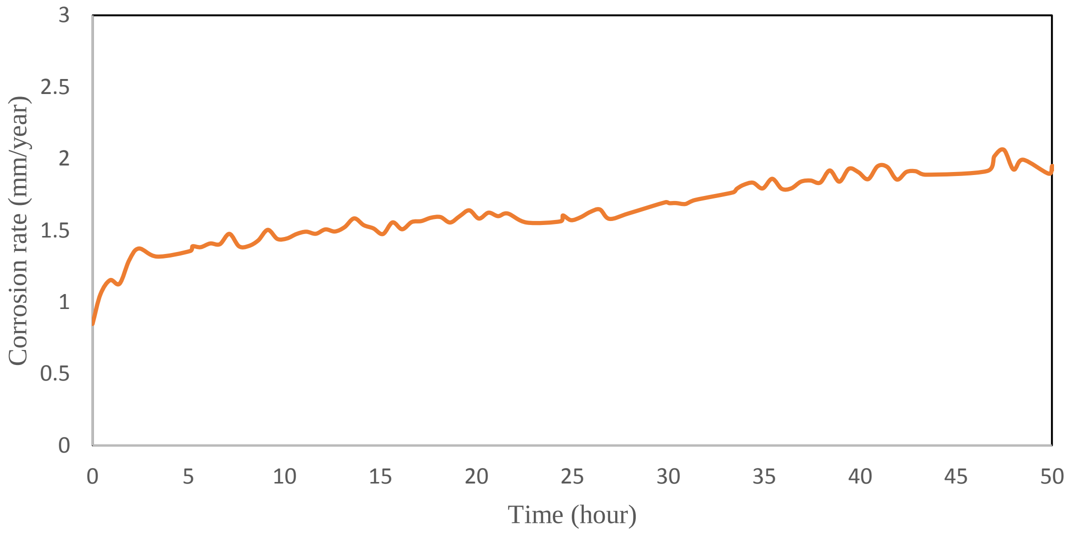


Figure 4.2: Corrosion rate for baseline at pH 6.6

As for the baseline at pH 6.6, the initial corrosion rate estimated was 0.85 mm/year and the final corrosion rate was 1.95 mm/year. It was obvious that the corrosion rate at high pH was lower than the one in lower pH due to significant formation of bicarbonate and carbonate ions. These ions were then reacted with the Iron (Fe^{2+}) ions to form Iron Carbonate ($FeCO_3$) by forming protective layers on the surface of metal. Thus, reducing the corrosion rate as it was seen in the graph at the period of 47 hours.

Table 4.1: Baseline data at pH 4.0

Pre-Corrosion Period (hour)	**E_{corr} (mV)**	**R_p (ohm.cm2)**	**CR (mm/year)**
2	-674.84	211.03	1.43
24	-669.97	157.84	1.92
30	-670.74	133.84	2.26
48	-666.72	124.08	2.44

Table 4.2: Baseline data at pH 6.6

Pre-Corrosion Period (hour)	**E_{corr} (mV)**	**R_p (ohm.cm2)**	**CR (mm/year)**
2	-691.38	234.09	1.29
24	-687.42	193.39	1.56
30	-686.12	178.92	1.69
48	-682.25	157.66	1.93

Both of the table above represent the E_{corr}, R_p and corrosion rate value for 48 hours period since they will be compared with the test study on corrosion inhibitors.

4.1.2 Electron Impedance Spectroscopy (EIS)

Another analysis made was by using EIS technique and it can be presented in the form of Nyquist plot as shown in the figure below. EIS has been conducted for three times; during the third hour, at 21 hour and finally 45 hour for the baseline test at pH4.0 and 6.6. The size of semicircle diameter indicates the magnitude of resistance which can be relate to the measurement of corrosion rate. The following showed the nyquist plot for the baseline at pH condition of 4.0 and 6.6.

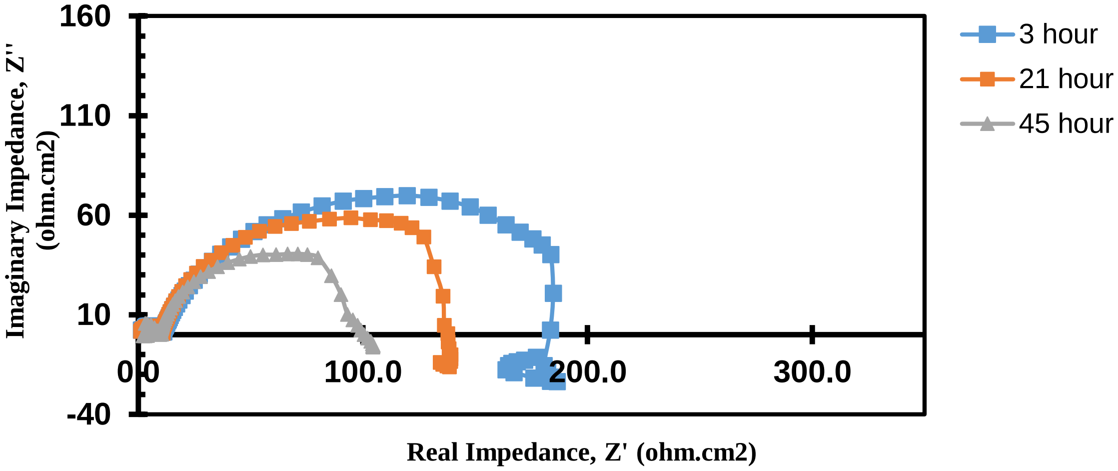


Figure 4.3: Nyquist plot for baseline at 48 hours of test and pH condition 4.0

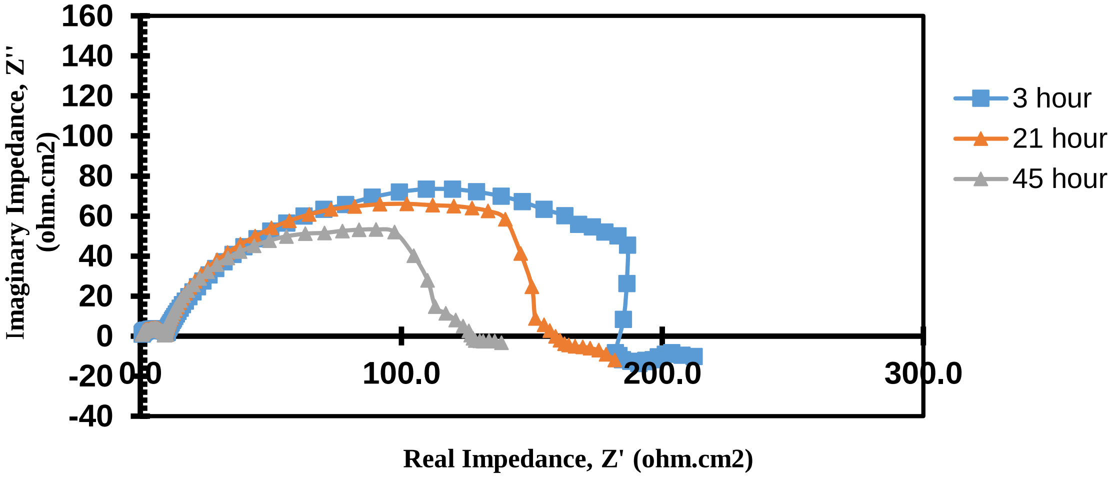
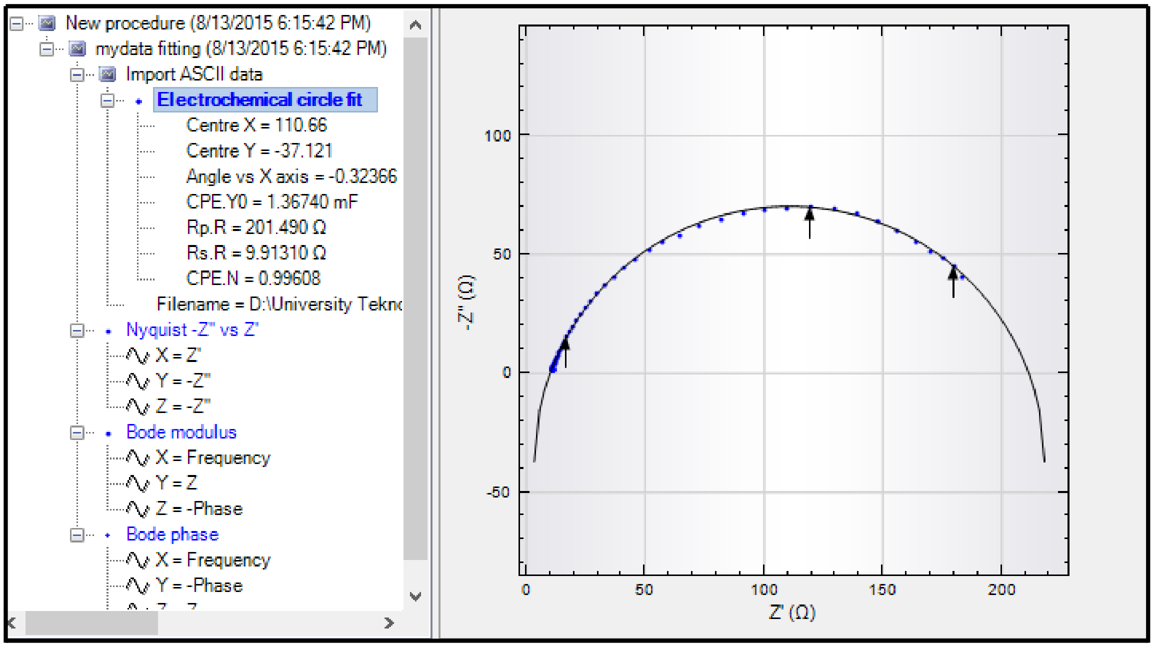


Figure 4.4: Nyquist plot for baseline at 48 hours of test and pH condition 6.

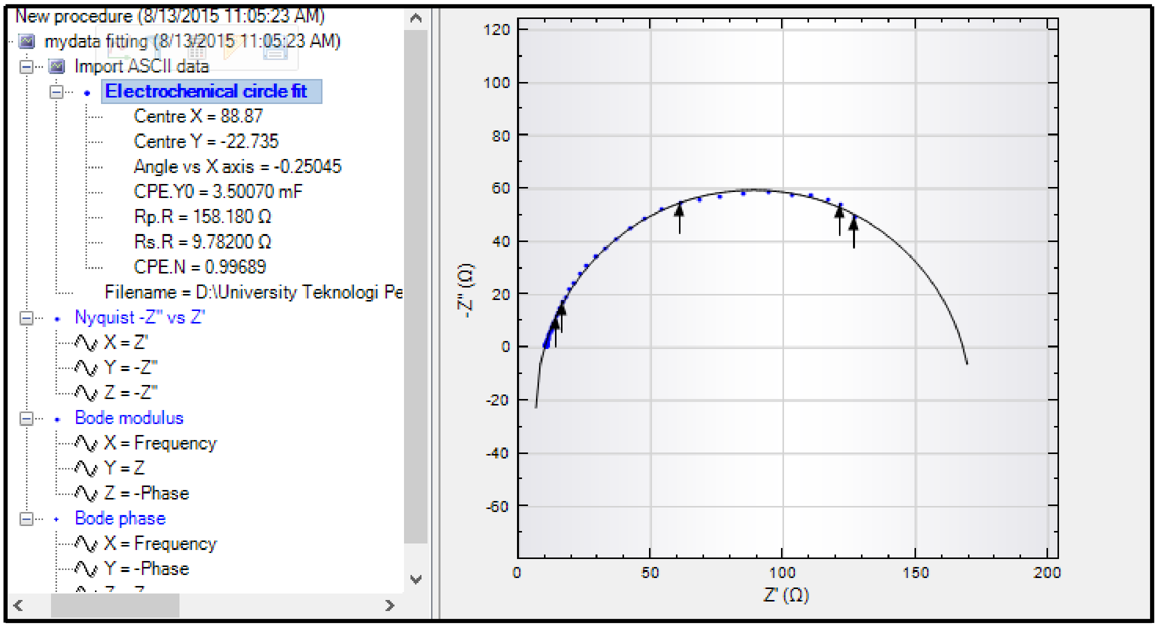
In order to conduct the analysis on EIS data, a software known as Nova 1.11 has to be used to obtain the value of polarization resistance, R_p. This is because the graph need to be fit properly to get the right value of R_p. The following showed the electrochemical fitting conducted on the baseline graph at pH 4.0.



New procedure (8/13/2015 6:15:42 PM)
mydata fitting (8/13/2015 6:15:42 PM)
Import ASCII data
Electrochemical circle fit
Centre X = 110.66
Centre Y = -37.121
Angle vs X axis = -0.32366
CPE.Y0 = 1.36740 mF
Rp.R = 201.490 Ω
Rs.R = 9.91310 Ω
CPE.N = 0.99608
Filename = D:\University Tekn
Nyquist -Z'' vs Z'
X = Z'
Y = -Z''
Z = -Z''
Bode modulus
X = Frequency
Y = Z
Z = -Phase
Bode phase
X = Frequency
Y = -Phase

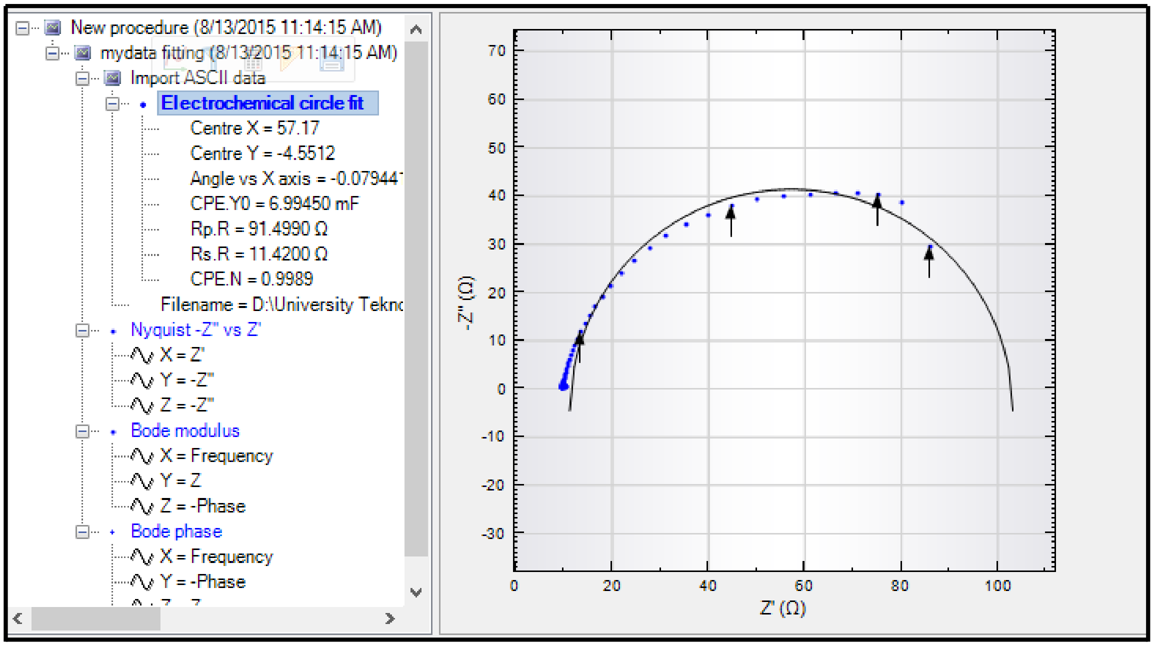
Figure 4.5: EIS analyzer on Nova 1.11 for baseline at the period of 3 hour for pH 4.0

Interestingly enough, the electrochemical circle fit function in Nova 1.11 will give the result for R_p which will speed up the analysis on all EIS graphs and the above R_p obtained was 201.5Ω.



```
New procedure (8/13/2015 11:05:23 AM)
  mydata fitting (8/13/2015 11:05:23 AM)
    Import ASCII data
      Electrochemical circle fit
          Centre X = 88.87
          Centre Y = -22.735
          Angle vs X axis = -0.25045
          CPE.Y0 = 3.50070 mF
          Rp.R = 158.180 Ω
          Rs.R = 9.78200 Ω
          CPE.N = 0.99689
        Filename = D:\University Teknologi Pe
    Nyquist -Z" vs Z'
      X = Z'
      Y = -Z"
      Z = -Z"
    Bode modulus
      X = Frequency
      Y = Z
      Z = -Phase
    Bode phase
      X = Frequency
      Y = -Phase
```

Figure 4.6: EIS analyzer on Nova 1.11 for baseline at the period of 21 hour for pH 4.0



```
New procedure (8/13/2015 11:14:15 AM)
  mydata fitting (8/13/2015 11:14:15 AM)
    Import ASCII data
      Electrochemical circle fit
          Centre X = 57.17
          Centre Y = -4.5512
          Angle vs X axis = -0.07944
          CPE.Y0 = 6.99450 mF
          Rp.R = 91.4990 Ω
          Rs.R = 11.4200 Ω
          CPE.N = 0.9989
        Filename = D:\University Tekno
    Nyquist -Z" vs Z'
      X = Z'
      Y = -Z"
      Z = -Z"
    Bode modulus
      X = Frequency
      Y = Z
      Z = -Phase
    Bode phase
      X = Frequency
      Y = -Phase
```

Figure 4.7: EIS analyzer on Nova 1.11 for baseline at the period of 45 hour for pH 4.0

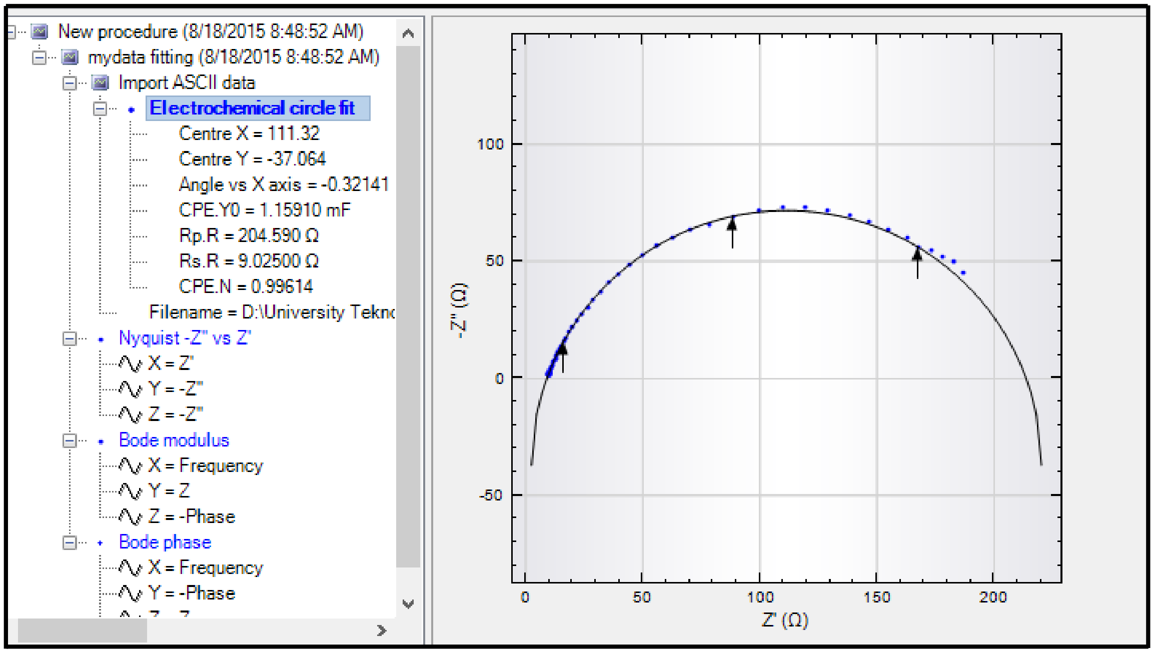

New procedure (8/18/2015 8:48:52 AM)
mydata fitting (8/18/2015 8:48:52 AM)
Import ASCII data
Electrochemical circle fit
Centre X = 111.32
Centre Y = -37.064
Angle vs X axis = -0.32141
CPE.Y0 = 1.15910 mF
Rp.R = 204.590 Ω
Rs.R = 9.02500 Ω
CPE.N = 0.99614
Filename = D:\University Tekn
Nyquist -Z'' vs Z'
X = Z'
Y = -Z''
Z = -Z''
Bode modulus
X = Frequency
Y = Z
Z = -Phase
Bode phase
X = Frequency
Y = -Phase

Figure 4.8: EIS analyzer on Nova 1.11 for baseline at the period of 3 hour for pH 6.6

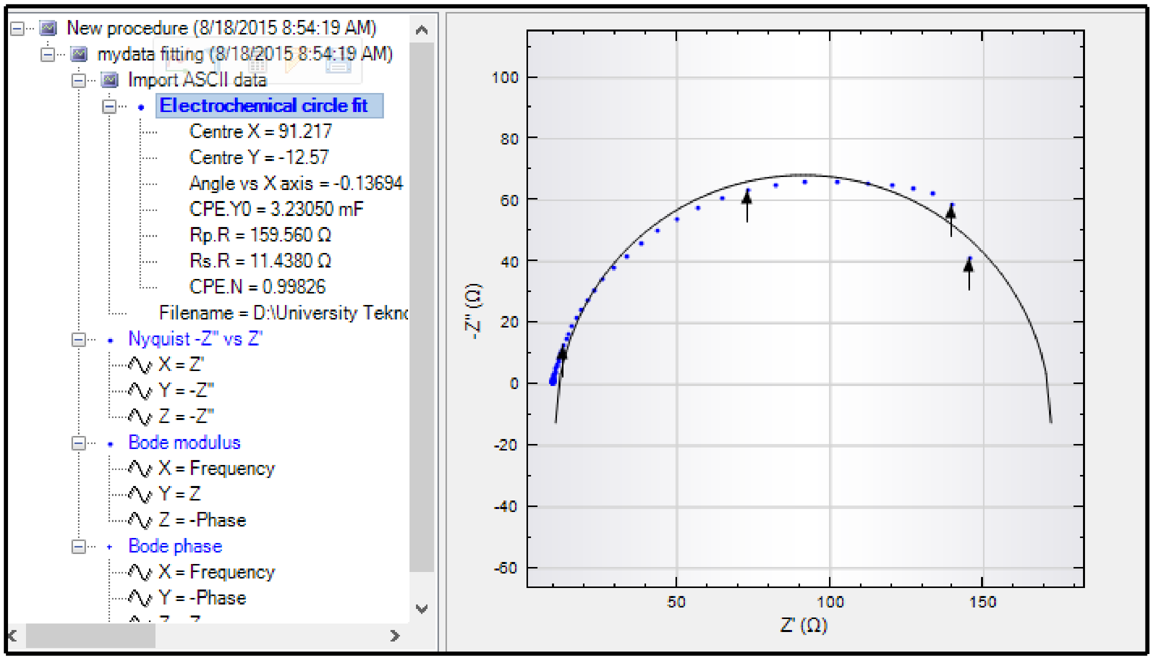
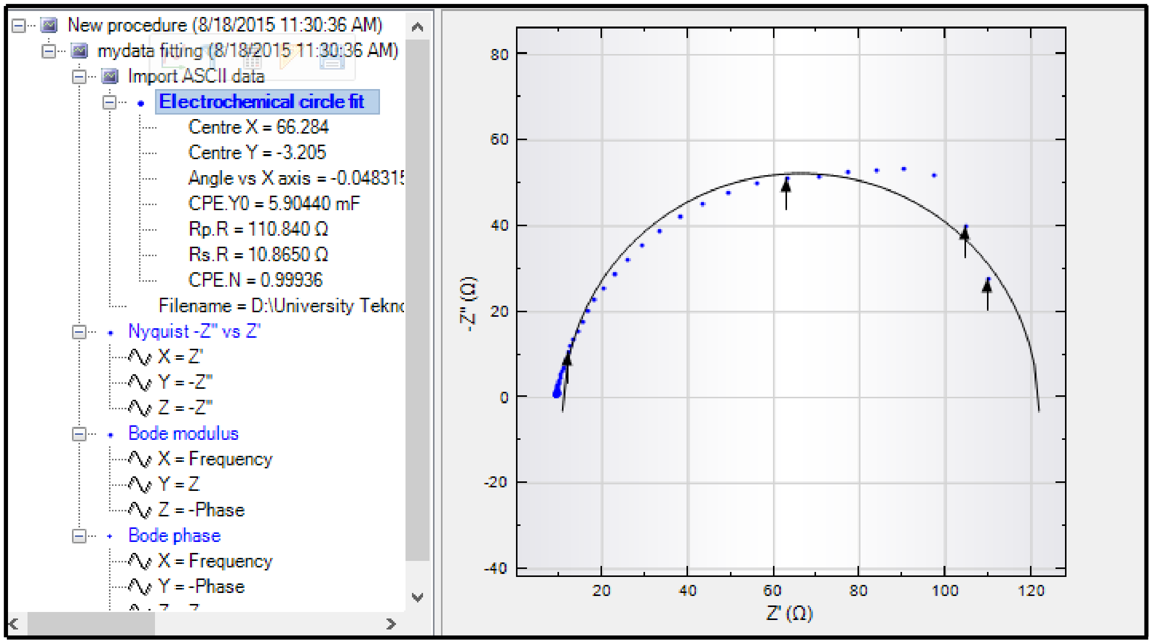

New procedure (8/18/2015 8:54:19 AM)
mydata fitting (8/18/2015 8:54:19 AM)
Import ASCII data
Electrochemical circle fit
Centre X = 91.217
Centre Y = -12.57
Angle vs X axis = -0.13694
CPE.Y0 = 3.23050 mF
Rp.R = 159.560 Ω
Rs.R = 11.4380 Ω
CPE.N = 0.99826
Filename = D:\University Tekn
Nyquist -Z'' vs Z'
X = Z'
Y = -Z''
Z = -Z''
Bode modulus
X = Frequency
Y = Z
Z = -Phase
Bode phase
X = Frequency
Y = -Phase

Figure 4.9: EIS analyzer on Nova 1.11 for baseline at the period of 21 hour for pH 6.6



```
New procedure (8/18/2015 11:30:36 AM)
    mydata fitting (8/18/2015 11:30:36 AM)
        Import ASCII data
            Electrochemical circle fit
                Centre X = 66.284
                Centre Y = -3.205
                Angle vs X axis = -0.04831
                CPE.Y0 = 5.90440 mF
                Rp.R = 110.840 Ω
                Rs.R = 10.8650 Ω
                CPE.N = 0.99936
            Filename = D:\University Tekn
        Nyquist -Z'' vs Z'
            X = Z'
            Y = -Z''
            Z = -Z''
        Bode modulus
            X = Frequency
            Y = Z
            Z = -Phase
        Bode phase
            X = Frequency
            Y = -Phase
```

Figure 4.10: EIS analyzer on Nova 1.11 for baseline at the period of 45 hour for pH 6.6

All of the above graph simulated in the software Nova 1.11 managed to draw fitting on the EIS plotting from Microsoft Excel. Thus, estimating the right value of R_p for the calculation of the corrosion rate.

Table 4.3: R_p value for baseline at pH 4.0 and 6.6

Type of test	**pH**	**Condition**	**Polarization Resistance, Rp (Ohm.cm^2)**
Baseline	4.0	3 hour	201.49
		21 hour	158.18
		45 hour	91.50
	6.6	3 hour	204.59
		21 hour	159.56
		45 hour	110.84

The polarization resistance, R_p values will then be applied to calculate the corrosion current density, i_{corr} and also the corrosion rate. R_p was given by the Stern-Geary equation as shown below.

$$R_p = \frac{\Delta E}{\Delta I} = \frac{B}{i_{corr}} \text{ where, } B = \frac{b_a b_c}{2.303\,(b_a + b_c)} \tag{4.1}$$

The Stern-Geary constant, B is normally taken as 25mV since both of anodic and cathodic reaction are activation controlled. Whilst, b_a and b_c are the tafel slope for anodic and cathodic curves respectively.

After the value of i_{corr} obtained, the calculation on the corrosion rate can be done by using the formula that is directly related from Faraday's Law.

$$CR\ (mm/year) = \frac{315 Z i_{corr}}{\rho n F} \tag{4.2}$$

Where, CR = corrosion rate in mm/year

Z = atomic weight iron, 55.847 g/mole

i_{corr} = corrosion current density, µA/cm^2

p = density of iron, 7.8 g/cm^3

n = number of exchanged electrons

F = Faraday's constant, 96500 C/mole

The table below showed the calculation of corrosion rate done on the baseline at pH condition of 4.0 and 6.6.

Table 4.4: Corrosion rate calculated for baseline at pH 4 and 6.6

Type of test	**pH**	**Condition**	**Polarization Resistance, Rp (Ohm.cm^2)**	**icorr (µA/cm2)**	**Corrosion rate (mm/year)**
Baseline	4.0	3 hour	201.49	124.08	1.45
		21 hour	158.18	158.05	1.85
		45 hour	91.50	273.22	3.19
	6.6	3 hour	204.59	122.20	1.43
		21 hour	159.56	156.68	1.83
		45 hour	110.84	225.55	2.64

When comparison is done on the corrosion rate analyze by LPR and EIS technique, it seems that they were having almost the same corrosion rate which bring us to the understanding that the EIS confirms LPR technique. Furthermore, the corrosion rate calculated was relevant to the literature review as the value keep increasing along the period of time.

The same method as in the baseline will be applied to the other experiment for both pH 4.0 and 6.6. The result on custom sweep and scanning electron microscopy will be presented at the end of this part in order to provide some comparison on the effectiveness of inhibitors in reducing the corrosion rate of carbon steel. Whilst, the following part of this research will discuss the behavior of impedance when corrosion inhibitors were injected into the solution at two different pH condition.

4.2 Test Study 2: Performance of different type of corrosion inhibitors by evaluating the effect of different pH value of the solution.

In this particular study, performance on fatty amine and QAC as corrosion inhibitors will be examined by injecting them with the volume of 25ppm after the pre-corrosion period or at 24 hours. Another 24 hours of inhibition period was observed by using LPR, EIS and custom sweep technique. This study also aimed to know the effect of pH value on the corrosion rate and it was done by regulating the pH at 4.0 and 6.6.

4.2.1 Linear Polarization Resistance (LPR)

The same technique will be applied like test study 1 on the baseline and the graph below showed the behavior of corrosion rate when corrosion inhibitors were injected into the solution at pH 4.

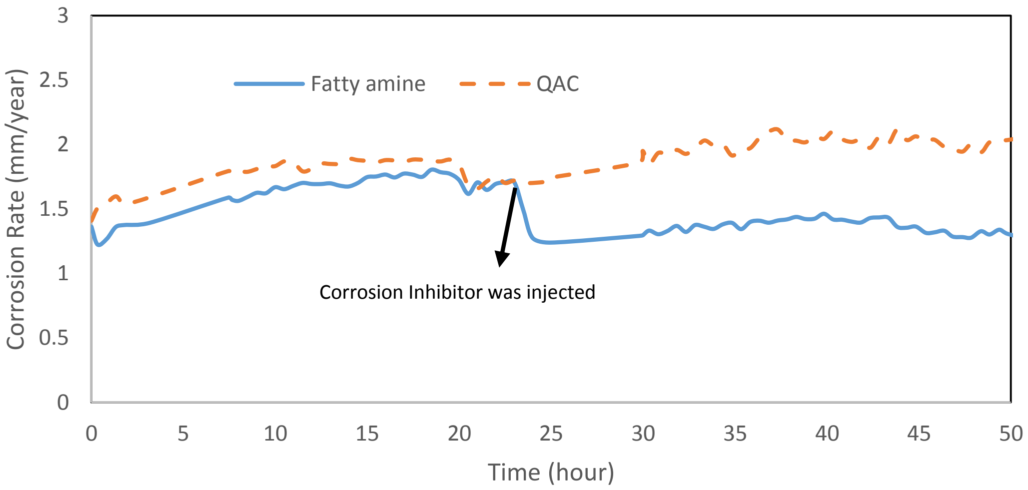


Figure 4.11: Corrosion rate of carbon steel when 25ppm corrosion inhibitors were injected into the solution at pH 4.0

From the above graph, the initial corrosion rate estimated was 1.36 mm/year for fatty amine glass cell and 1.41 mm/year for the other. Since then, the corrosion rate for both solution was gradually increasing until the period of 24 hours. However, the situation changed when corrosion inhibitors were injected into the solution. Obvious decrement can be seen on fatty amine since it had successfully reduced the corrosion rate. As for the QAC, it seems that the corrosion rate still gradually increasing along the time period even though there was a small drop at the period of 21 hour.

At pH value 6.6, the corrosion rate graph showed different behavior by having very low initial corrosion rate compare to the one in pH 4.0. The following graph showed another reaction of fatty amine and QAC at pH 6.6 and Sodium Hydroxide (NaOH) was added into the solution to regulate the pH value.

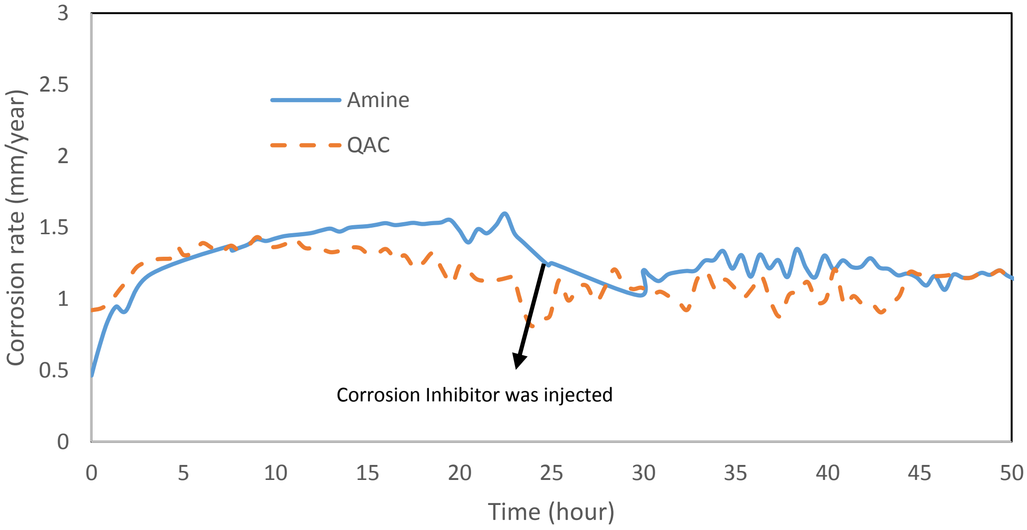


Figure 4.12: Corrosion rate of carbon steel when 25ppm corrosion inhibitors were injected into the solution at pH 6.6

The initial corrosion rate estimated was 0.46 mm/year and 0.92 mm/year and there was increasing along the time period. However, it was clearly that the corrosion rate measured were very small compare to the one in pH 4.0. At higher pH value, the direct reduction of bicarbonate ion can become very significant since the concentration increases with pH which directly promoted the formation of Iron Carbonate ($FeCO_3$) on the surface of carbon steel. After the period of 24 hours, the corrosion rate measurement was not constant as it keeps going up and down even though fatty amine and QAC were injected at that time. This phenomena suggested that the corrosion inhibitors disrupted the potentiometer to measure the resistance efficiently in order to provide better corrosion rate data.

The tables below showed in great details the value of E_{corr} and Polarization Resistance, R_p of the LPR at the period of 2, 24, 30 and 48 hour. The reason behind this analysis was to compare the corrosion rate measurement before and after the corrosion inhibitors were injected.

Table 4.5: Fatty amine glass cell data at pH 4.0

Pre-Corrosion Period (hour)	**E_{corr} (mV)**	**R_p (ohm.cm2)**	**CR (mm/year)**
2	-685.5	219.69	1.38
24	-656.5	237.07	1.28
Inhibition Period (hour)			
30	-658.2	226.9	1.33
48	-658.9	227.72	1.33

Table 4.6: QAC glass cell data at pH 4.0

Pre-Corrosion Period (hour)	**E_{corr} (mV)**	**R_p (ohm.cm2)**	**CR (mm/year)**
2	-681.8	196.39	1.54
24	-677.98	177.88	1.69
Inhibition Period (hour)			
30	-677.88	163.36	1.85
48	-676.26	155.85	1.94

Table 4.7: Fatty amine glass cell data at pH 6.6

Pre-Corrosion Period (hour)	**E_{corr} (mV)**	**R_p (ohm.cm2)**	**CR (mm/year)**
2	-690.71	331.17	0.91
24	-678.53	244.89	1.23
Inhibition Period (hour)			
30	-670.1	259.82	1.16
48	-665	255.72	1.18

Table 4.8: QAC glass cell data at pH 6.6

Pre-Corrosion Period (hour)	**E_{corr} (mV)**	**R_p (ohm.cm2)**	**CR (mm/year)**
2	-698.85	265.63	1.14
24	-702.22	372.46	0.81
Inhibition Period (hour)			
30	-695.56	293.27	1.03
48	-693.17	315.24	0.96

4.2.2 Electron Impedance Spectroscopy (EIS)

EIS was again applied to see the behavior of nyquist plot and corrosion rate calculation from polarization resistance, R_p value by using the software Nova 1.11. The following figures represent nyquist plot for both pH 4.0 and 6.6.

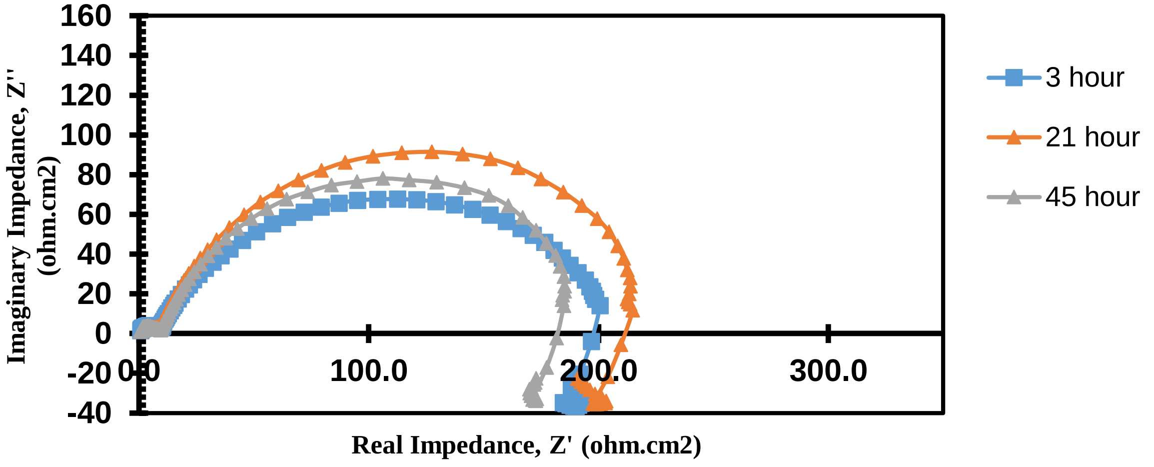


Figure 4.13: Nyquist plot for fatty amine at pH condition 4.0

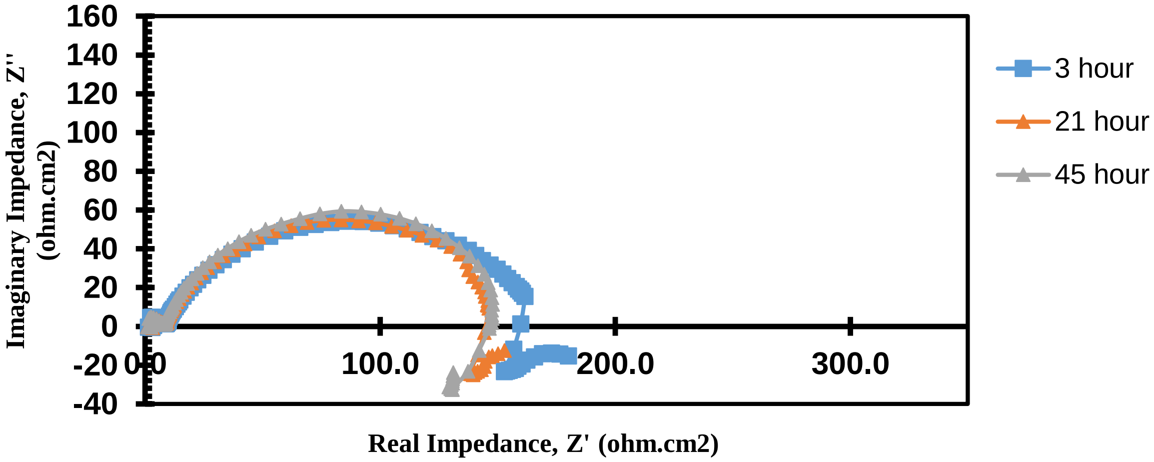


Figure 4.14: Nyquist plot for QAC at pH condition 4.0

Based on the above graph, it aims to indicate the magnitude of polarization resistance, R_p before and after the corrosion inhibitors being injected. Corrosion rate measured in fatty amine glass cell was smaller compare to the QAC since the R_p value was very big. The higher the R_p, the smaller the corrosion rate measured. By looking at both semicircle, fatty amine was founded to be more effective than QAC since the semicircle was larger than the other. Both graph were also being analyzed by using the Nova software to get the correct value of R_p and the following table showed them nicely.

Table 4.9: R_p value for fatty amine and QAC at pH 4.0

Type of Corrosion Inhibitors	**Condition**	**Polarization Resistance, Rp (Ohm.cm^2)**
Fatty amine	3 hour	201.75
	21 hour	215.15
	45 hour	186.21
QAC	3 hour	162.52
	21 hour	143.86
	45 hour	143.94

After getting the R_p value, i_{corr} can now be calculated by using the Stern-Geary equation and finally determine the corrosion rate for both type of corrosion inhibitors.

Table 4.10: Corrosion rate calculated for fatty amine and QAC at pH 4.0

Type of Corrosion Inhibitors	**Condition**	**Polarization Resistance, Rp (Ohm.cm^2)**	**icorr (µA/cm2)**	**Corrosion rate (mm/year)**
Fatty amine	3 hour	201.75	123.92	1.45
	21 hour	215.15	116.20	1.36
	45 hour	186.21	134.26	1.57
QAC	3 hour	162.52	153.83	1.80
	21 hour	143.86	173.78	2.03
	45 hour	143.94	173.68	2.03

It is best to compare the corrosion rate analyzed by LPR and EIS to provide strong proof for this experiment and the following table presented them side by side.

Table 4.11: Corrosion rate calculated for EIS and LPR at pH 4.0

	EIS		**LPR**
Type of Corrosion Inhibitor	**Condition**	**Corrosion Rate, CR (mm/year)**	**Corrosion Rate, CR (mm/year)**
Amine	3 hour	1.45	1.39
	21 hour	1.36	1.71
	45 hour	1.57	1.32
QAC	3 hour	1.80	1.59
	21 hour	2.03	1.66
	45 hour	2.03	2.02

From Table 4.11, it was observed that the corrosion rate increases after the period of 21 hours even though corrosion inhibitors have been injected with the purpose to reduce the corrosion rate. However, it was not the case for fatty amine by looking at the LPR technique where the corrosion rate reduced and proven that it works really well. LPR graph for fatty amine previously showed vividly that it did reduced the corrosion rate especially after its being injected. Most of the results of EIS and LPR showed that they are consistent and matched really well.

This part will now analyze the data at another pH value and the following graph will present the behavior of impedance spectroscopy at pH 6.6 which is at alkaline state. It was expected the corrosion rate for them will be very small since the pH is very high [8].

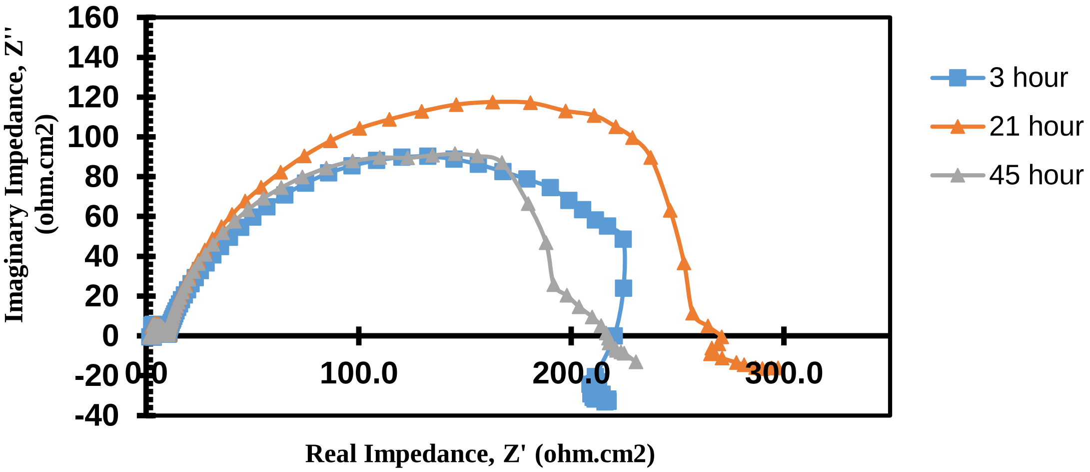


Figure 4.15: Nyquist plot for fatty amine at pH condition 6.6

It was observed that the corrosion rate reduced when compared at the period of 3 hour and 21 hour as the semicircle became bigger. Iron Carbonate ($FeCO_3$) was expected to form a layer on top of the carbon steel surface and thus, making the corrosion rate very small.

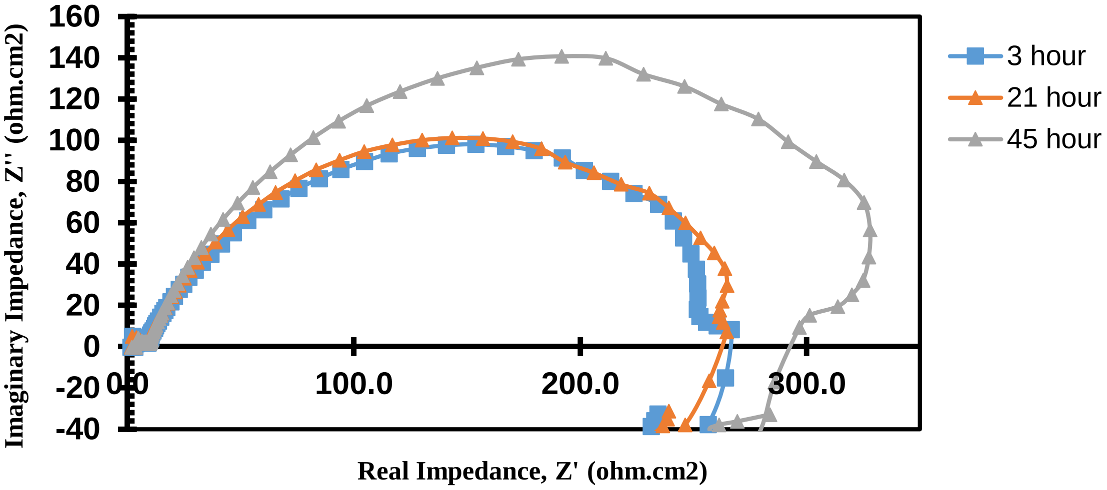


Figure 4.16: Nyquist plot for QAC at pH condition 6.6

However, as for the QAC, the reaction on the reduction of corrosion rate was a bit slower since at only period of 45 hour of the test, the corrosion rate reduced tremendously. In order to get more correct result, this graph was again analyzed by using software Nova 1.11. The following table will show the polarization resistance, R_p obtained from the software.

Table 4.12: R_p value for fatty amine and QAC at pH 6.6

Type of Corrosion Inhibitors	Condition	Polarization Resistance, Rp (Ohm.cm^2)
Fatty amine	3 hour	237.06
	21 hour	262.17
	45 hour	196.11
QAC	3 hour	260.87
	21 hour	272.85
	45 hour	336.61

With the R_p value, i_{corr} value can now be calculated and thus, corrosion rate for carbon steel at pH condition 6.6.

Table 4.13: Corrosion rate calculated for fatty amine and QAC at pH 6.6

Type of Corrosion Inhibitors	**Condition**	**Polarization Resistance, Rp (Ohm.cm^2)**	**icorr (µA/cm2)**	**Corrosion rate (mm/year)**
Fatty amine	3 hour	237.06	105.46	1.23
	21 hour	262.17	95.36	1.11
	45 hour	196.11	127.48	1.49
QAC	3 hour	260.87	95.83	1.12
	21 hour	272.85	91.63	1.07
	45 hour	336.61	74.27	0.87

From the above table, it seems that QAC was able to reduce the corrosion rate from 1.12 mm/year to 0.87 mm/year and it was not the case for fatty amine. However, the corrosion rate at this pH condition for both inhibitors was much lower compared to the pH 4.0 and it goes with the hypothesis really well. The table below will present the comparison between the corrosion rate analyzed by LPR and EIS.

Table 4.14: Corrosion rate calculated for EIS and LPR at pH 6.6

	EIS		**LPR**
Type of Corrosion Inhibitor	**Condition**	**Corrosion Rate, CR (mm/year)**	**Corrosion Rate, CR (mm/year)**
Amine	3 hour	1.23	1.17
	21 hour	1.11	1.49
	45 hour	1.49	1.09
QAC	3 hour	1.12	1.28
	21 hour	1.07	1.13
	45 hour	0.87	0.96

The corrosion rate by both techniques seem to be compatible with each other even though there was slight difference for the fatty amine. This result indicated that the data obtained was very convincing and has confirmed the literature review done in the beginning of the research.

4.2.3 Custom Sweep

Custom sweep was conducted at the end of the experiment at sweep rate of 10mV/min and potential between -250mV and 250mV. This technique will then produce tafel plot which can provide the movement of the plot when corrosion inhibitors were injected into the solution. The plot was compared with the baseline according to the pH condition so that the behavior of current and potential can be observed. In order to watch the effect of inhibitors clearly, the data plotting was done on the baseline and the inhibitors according to the pH value.

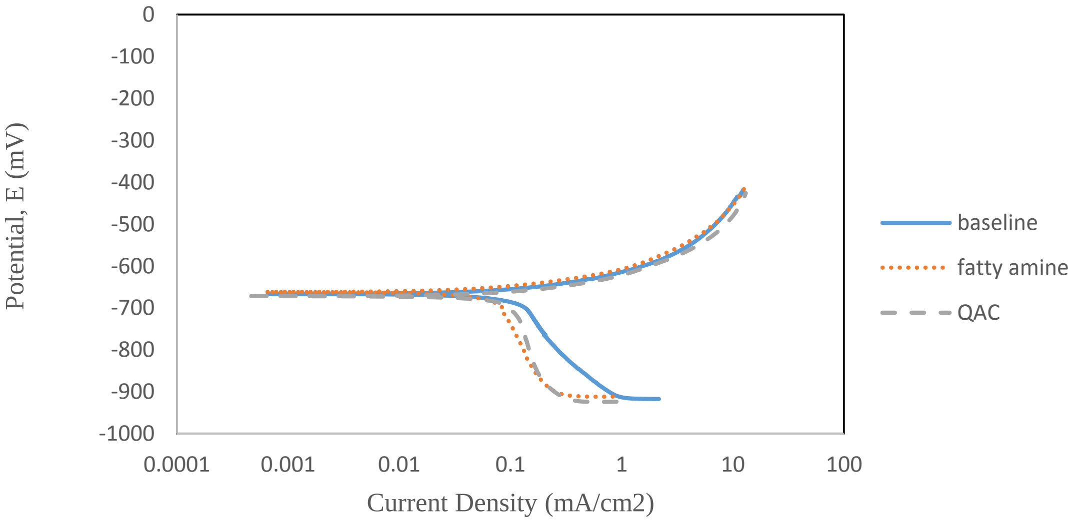


Figure 4.17: Tafel Plot for baseline, fatty amine and QAC at pH 4.0

From the above graph, the anodic reaction was observed to have rigorous reaction which indicatively defined that the corrosion rate increased. Whilst, cathodic reaction seemed to have some limiting current that may implied to the formation of layers on the surface of X65 carbon steels. The E_{corr} value for baseline, fatty amine and QAC was founded to be the same and interestingly enough, corrosion inhibitors did effect the corrosion rate by shifting the i_{corr} to the left.

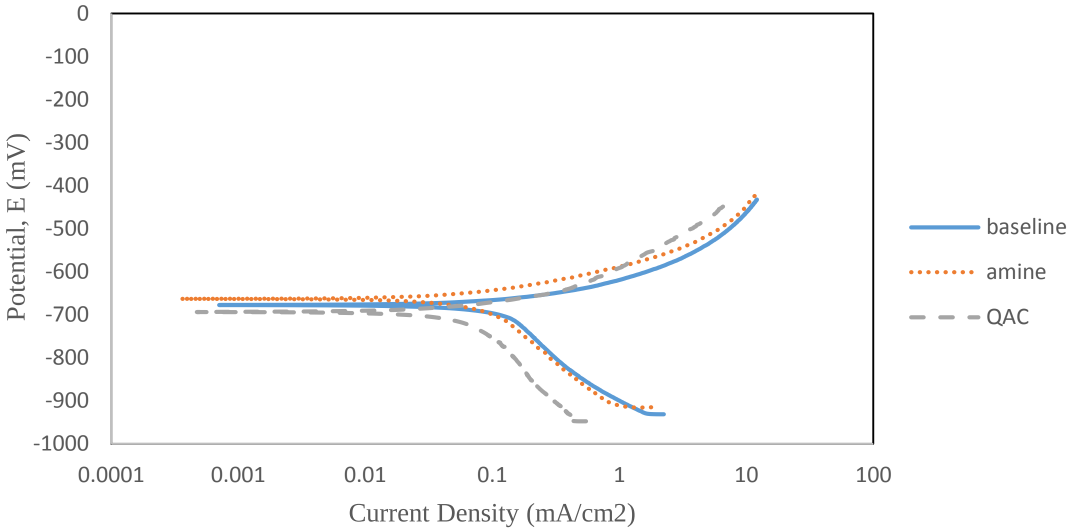


Figure 4.18: Tafel Plot for baseline, fatty amine and QAC at pH 6.6

As for the pH 6.6, the same behavior showed on the cathodic reaction by having the limiting current and rigorous anodic reaction was a sign of more production of hydrogen gas. However, the E_{corr} value was not the same due to the effect of inhibitors and high pH value. The shifting of i_{corr} to the left for pH 6.6 seems to be more rigorous compared to the one in pH 4.0.

4.2.4 Scanning Electron Microscopy (SEM)

This surface analysis testing was conducted to observe the surface morphology or the microstructure of the carbon steel sample after the experiment. This analysis will definitely help this research in terms of relating to the type of corrosion occurred. The picture below showed the surface structure of carbon steel at baseline condition when no corrosion inhibitors were injected into the solution after 48 hours period.

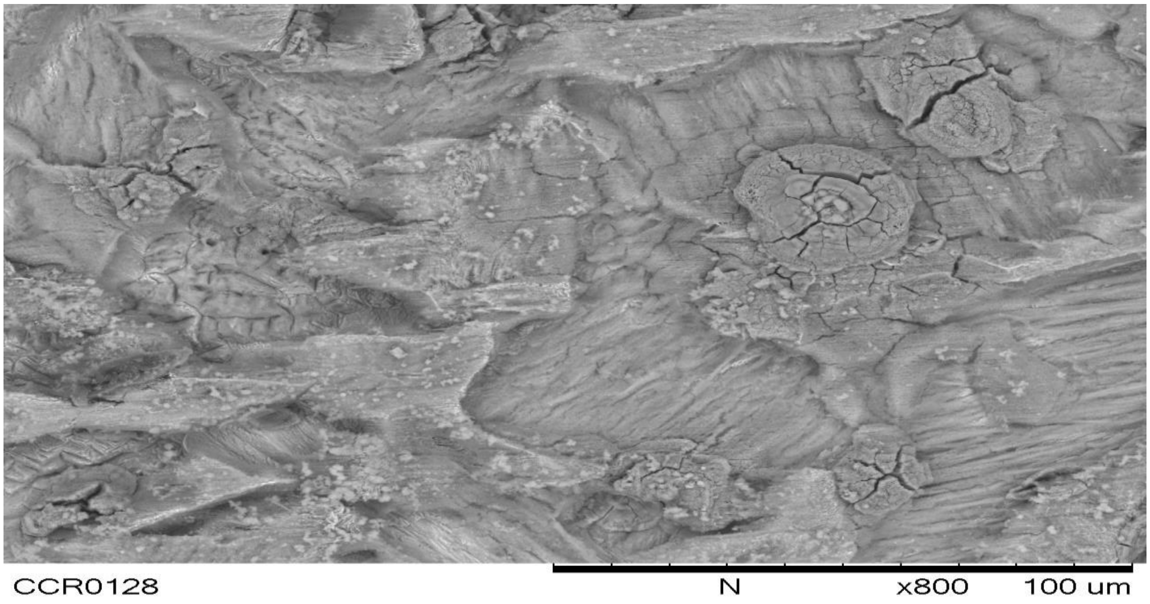


Figure 4.15: SEM images for baseline at pH 4 (800X)

Based on the figure above, cracks were clearly observed due to attack from corrosive agents such as H^+ (hydrogen ions) on the surface of carbon steel. The reason behind this phenomena was due to no protective layers formed on the surface and thus, making it fragile towards the CO_2 corrosive environment. In order to know the effectiveness of the inhibitors, the following figure showed the structure of carbon steel when fatty amine and QAC were injected into the solution.

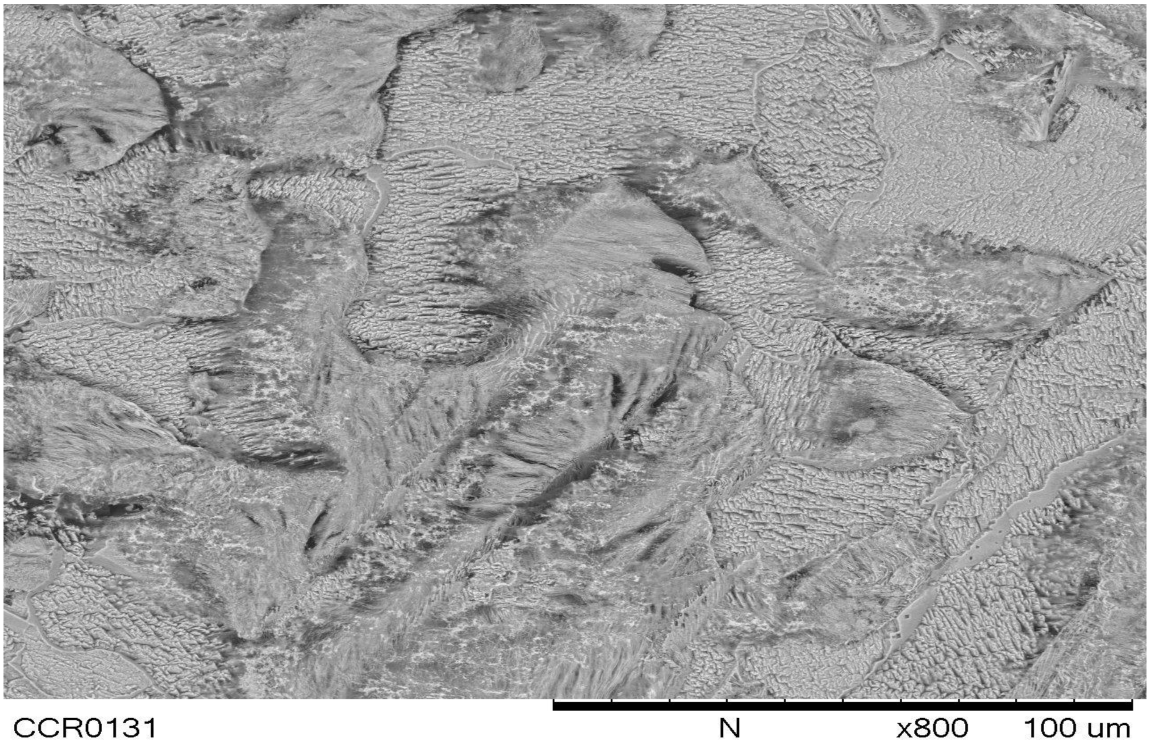


Figure 4.16: SEM images for fatty amine inhibitors at pH 4 (800X)

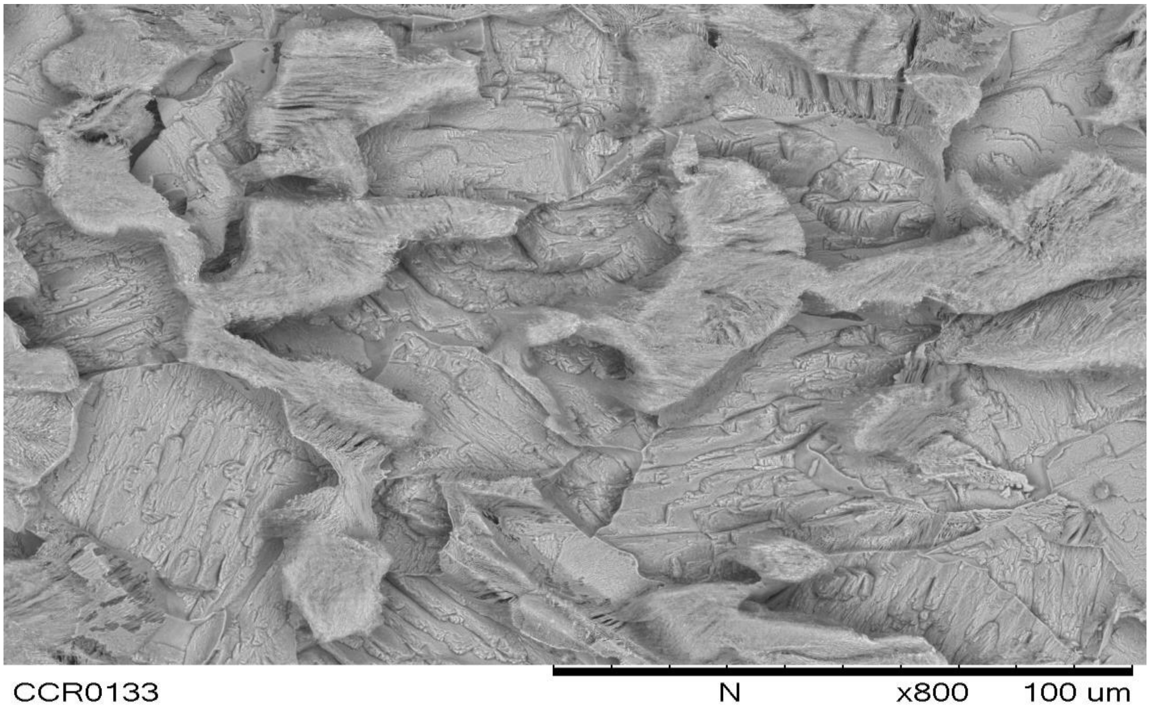


Figure 4.17: SEM images for QAC inhibitors at pH 4 (800X)

Looking at the carbon steel structure above, no cracks were observed on surface but in fact, layers of chemicals were clearly seen on the surface hinder from seeing the microstructure of the carbon steel. Therefore, this analysis provided another proof on the reason of small reduction of corrosion rate when corrosion inhibitors were injected into the solution. The same situation was witnessed on the pH condition of 6.6 and the following showed the surface structure after the period of 48 hours.

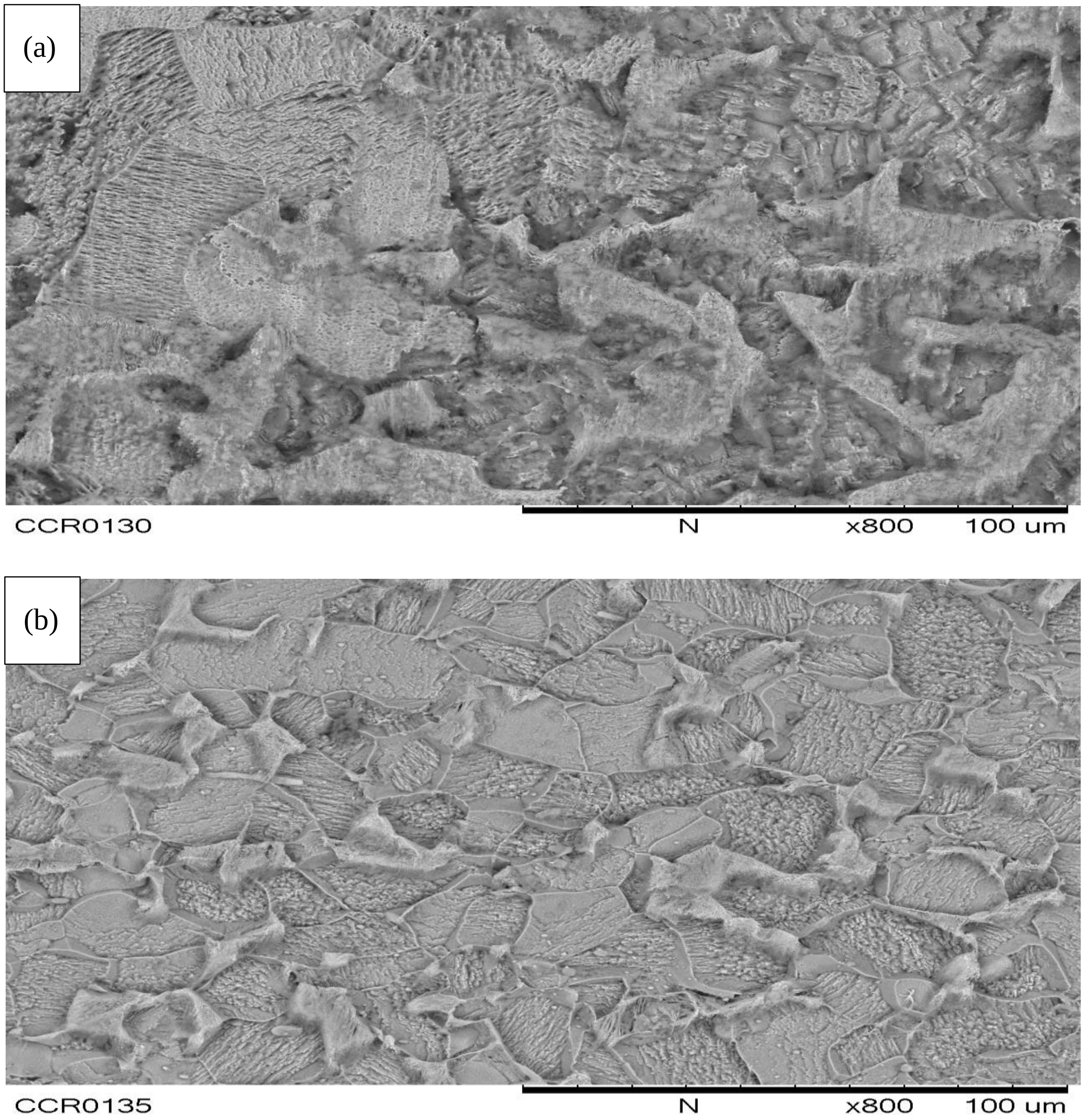


Figure 4.18: SEM images for fatty amine and QAC inhibitors at pH 6.6 (800X)

(a) Fatty amine (b) QAC

4.3 Test Study 3: Performance of corrosion inhibitors by increasing the amount of injected inhibitors.

From the previous results, it seems that 25ppm corrosion inhibitors were not enough to reduce the corrosion rate even though they were managed to drop the corrosion rate right after being injected. Therefore, it was suggested to increase the volume of injected inhibitors by 100ppm and the same method like test study 2 was employed again in this test.

4.3.1 Linear Polarization Resistance (LPR)

The same technique was employed to see the corrosion rate behavior when the volume of injected inhibitors increased. The following graph showed the corrosion rate when 100ppm of fatty amine was injected into the solution.

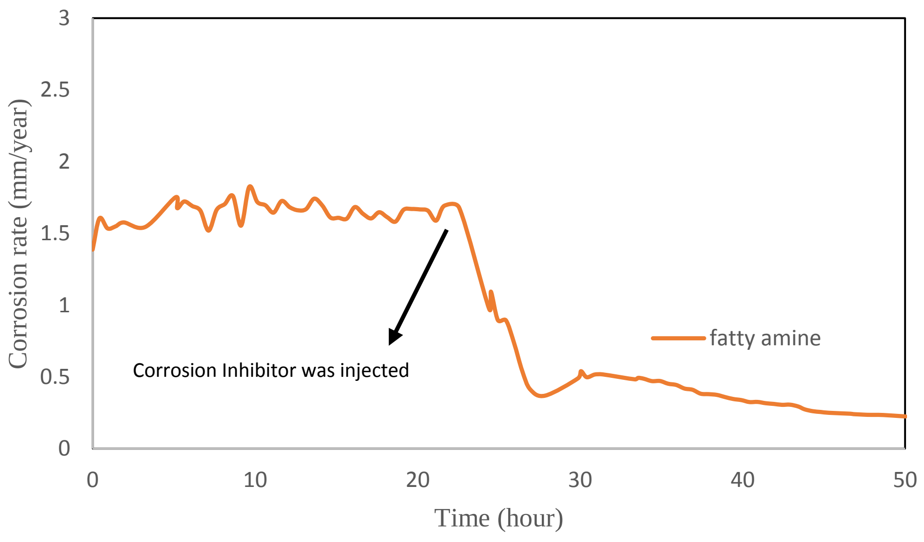


Figure 4.19: Corrosion rate of carbon steel when 100ppm of fatty amine was injected into the solution at pH 4.0

Based on the above graph, the initial corrosion rate estimated was 1.39 mm/year and the final corrosion rate was reduced to 0.23 mm/year. This results simply explained that the 100ppm fatty amine managed to reduce the corrosion rate incredibly even though at pH 4.0. Now, the following graph will be presented the corrosion rate behavior for inhibitor QAC at the same pH like before.

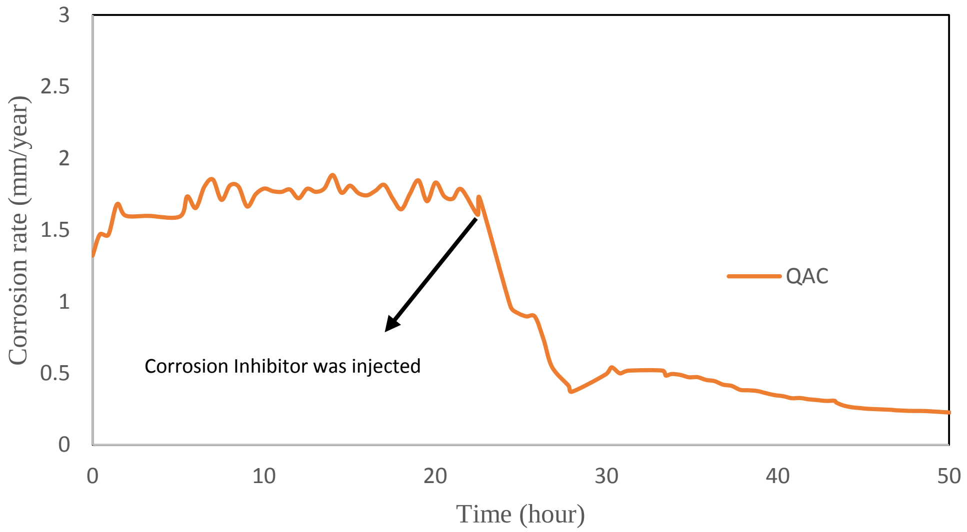


Figure 4.20: Corrosion rate of carbon steel when 100ppm of QAC was injected into the solution at pH 4.0

Interestingly enough, QAC works the same like fatty amine when injected at volume of 100ppm. This phenomena occurred due to effectiveness of inhibitors in forming protective layers on the surface of carbon steel. The initial corrosion estimated was 1.32 mm/year and the final corrosion rate measured was 0.22 mm/year. This results no doubt has empirically proven that the volume of injected inhibitors did effect the corrosion rate very much.

The table below presented E_{corr}, R_p and corrosion rate determined from LPR technique and it was observed from both glass cell, the corrosion rate start to reduce at the period of 24 hour when corrosion inhibitor was injected.

Table 4.15: Fatty amine inhibitor (100ppm) glass cell data at pH 4.0

Pre-Corrosion Period (hour)	**E_{corr} (mV)**	**R_p (ohm.cm2)**	**CR (mm/year)**
2	-686.39	191.69	1.58
24	-618.29	309.92	0.98
Inhibition Period (hour)			
30	-645.48	559.26	0.54
48	-648.64	1281.20	0.24

Table 4.16: QACs inhibitor (100ppm) glass cell data at pH 4.0

Pre-Corrosion Period (hour)	**E_{corr} (mV)**	**R_p (ohm.cm2)**	**CR (mm/year)**
2	-689.14	188.85	1.60
24	-619.45	310.93	0.97
Inhibition Period (hour)			
30	-647.18	557.34	0.53
48	-649.34	1290.3	0.23

4.3.1 Electron Impedance Spectroscopy (EIS)

EIS again was applied to confirm the corrosion rate measurement done in LPR and the following graph will represent the impedance behavior when the volume of corrosion inhibitor was increased to 100ppm.

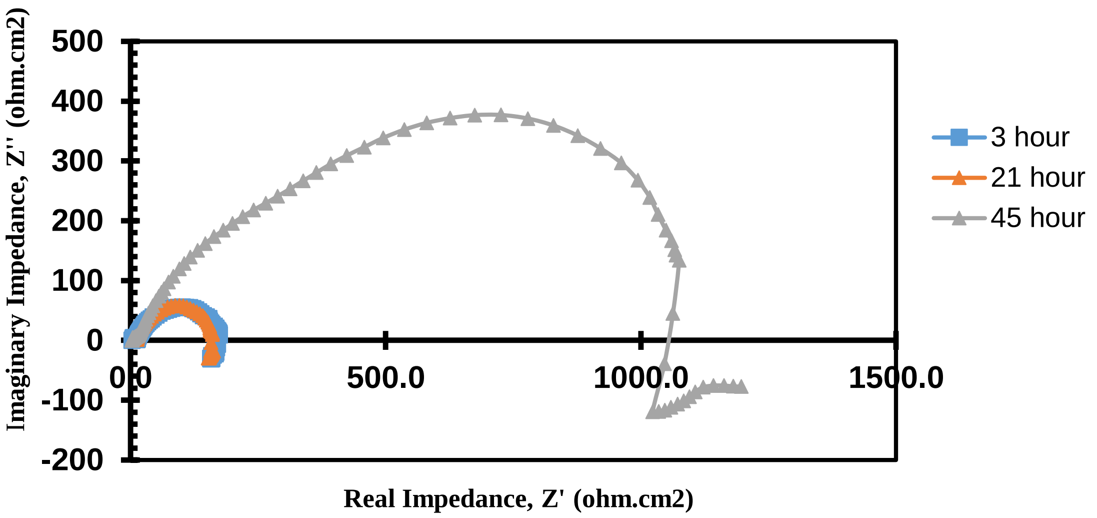


Figure 4.21: Nyquist plot for fatty amine at pH condition 4.0

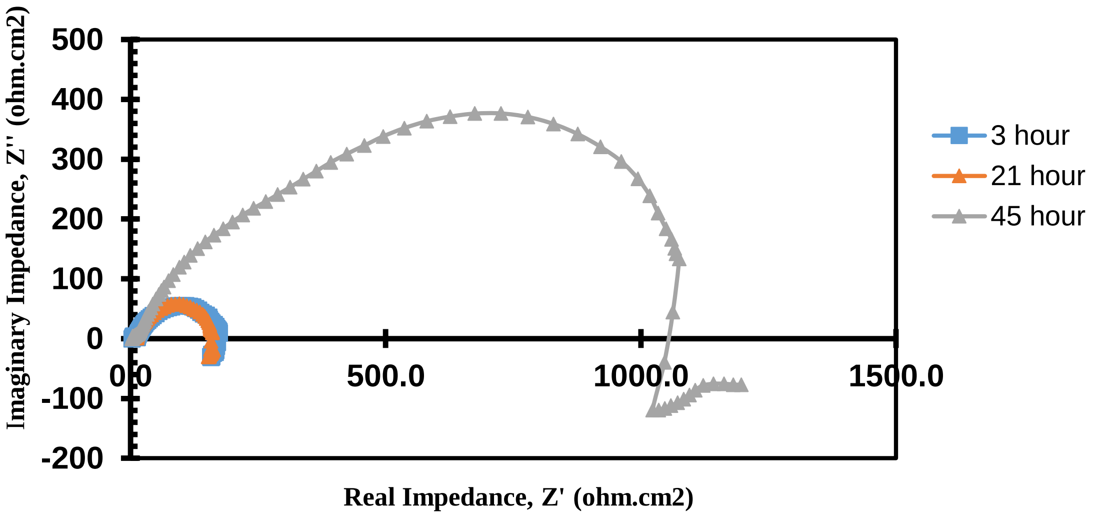


Figure 4.22: Nyquist plot for QACs at pH condition 4.0

Based on the above graph, it was clearly seen that the semicircle at the period of 45 hour was very large for both inhibitors fatty amine and QAC. This magnitude implied that the corrosion rate measure was very small since the polarization resistance, R_p was very big. The EIS data was again processed by Nova 1.11 to get right value of R_p.

Table 4.17: R_p value for fatty amine and QAC (100ppm) at pH 4.0

Type of Corrosion Inhibitors	**Condition**	**Polarization Resistance, Rp (Ohm.cm^2)**
Fatty amine	3 hour	191.69
	21 hour	315.43
	45 hour	1346.34
QAC	3 hour	188.85
	21 hour	313.43
	45 hour	1321.57

The R_p value was then processed by using the stern-geary equation to get the corrosion rate measurement and the following table showed them nicely.

Table 4.18: Corrosion rate calculated for fatty amine and QAC (100ppm) at pH 4.0

Type of Corrosion Inhibitors	**Condition**	**Polarization Resistance, Rp (Ohm.cm^2)**	**icorr (µA/cm2)**	**Corrosion rate (mm/year)**
Fatty amine	3 hour	191.69	130.42	1.52
	21 hour	315.43	79.26	0.93
	45 hour	1346.34	18.57	0.22
QAC	3 hour	188.85	132.38	1.55
	21 hour	313.43	79.76	0.93
	45 hour	1321.57	18.92	0.22

Based on the result from Nova analyzer, the corrosion rate calculated was almost the same like in the LPR technique and this analysis has confirmed that fatty amine and QAC was effectively performed in reducing the corrosion rate of carbon steel.

4.3.2 Custom Sweep

The custom sweep technique was again employed to observe the movement of tafel plot especially when the volume of injected inhibitor has been increased to 100ppm. The tafel plot for the injected CI will usually shifted to the left implying that the corrosion rate is reducing and the it will moved upward since the potential became larger. The following Figure 4.23 showed the tafel plot for baseline and fatty amine CI at pH 4.0.

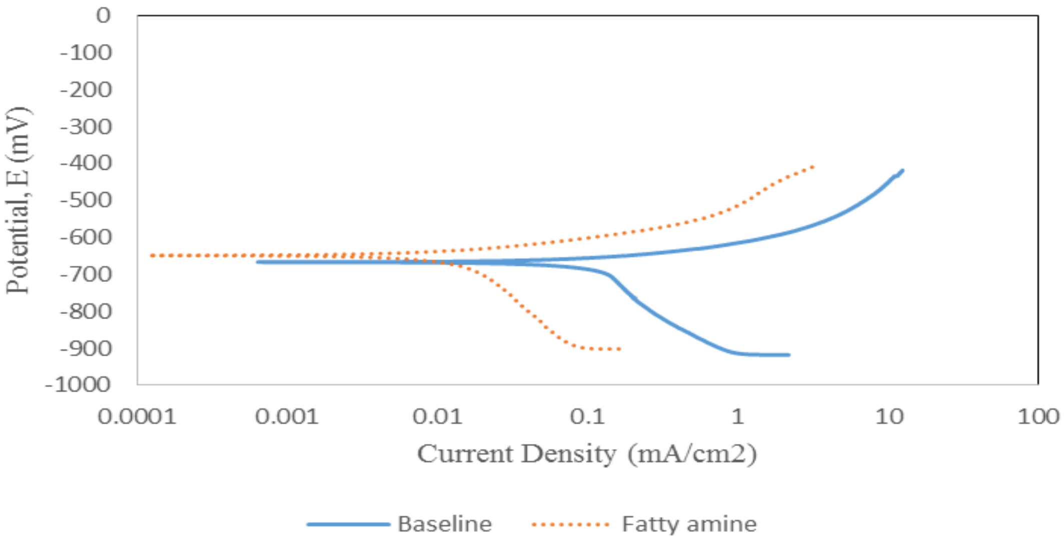


Figure 4.23: Tafel plot for baseline and fatty amine at pH condition 4.0

The results above told that 100ppm of fatty amine affected the CO_2 environment very much by having very low i_{corr} and high E_{corr}.

4.4 Discussion

In the test study 1, it was obvious that the corrosion rate was gradually increasing for both pH 4.0 and 6.6. This was the case because no CI injected to provide protective layers to the surface of carbon steel. However, the corrosion rate at pH 6.6 was smaller compare to the one in pH 4.0 due to the significant reduction of cathodic reaction in producing bicarbonate and carbonate ions. These ions were then reacted with Iron (II) ions to form Iron Carbonate, $FeCO_3$ which then forming protective layers on the steel surface.

As for the test study 2, the first 24 hours of the experiment or known as pre-corrosion time showed the corrosion rate of carbon steel has increased gradually for both glass cell (amine and QAC). However, the corrosion rate was reduced once the CI injected into the solution even though the reduction was not that much. Fatty amine was found out better in reducing the corrosion rate compare to QAC. The inhibition period for 24 hours was seem very long for the corrosion rate to increase back and most probably because CI was not enough to provide long inhibition period. This was the reason when the corrosion rate was observed to increased back at the end of the inhibition period.

The use of corrosion inhibitors in oil and gas industry was to reduce the corrosion rate as mentioned in the previous section of literature review. However, the results of this experiment showed differently in which the corrosion rate has increased after the period of 24 hours although inhibitors have been injected at both glass cell. This problem surely required thorough examination on the surface of the metals to discover type microstructure formed after the experiment. Gulbrandsen et al. observed that the pre-corrosion effect seems to be connected with the formation of cementite. In the other words, the formation of cementite has distorted the performance of inhibitors to reduce the corrosion rate. From the results, fatty amine seemed to be very impaired in providing the helps since the corrosion rate has increased from 0.52 mm/year to 0.73 mm/year. It was found out that both inhibitors provided very short period of inhibition due to the small amount injected into the solution.

The corrosion rate was reduced in the first five hours after the injection but increased back after that. This phenomena indicated that the protective layers formed by CI during the first five hours was not strong enough to protect the surface of carbon steel from corrosive agents.

Therefore, it was decided to further investigated by increasing the amount of injected CI to 100ppm. This study has been very success for both CI since they managed to reduce the corrosion rate efficiently. Strong protective layers were formed on the surface of carbon steel prevented the corrosive environment from affecting the metals. This results indicated the amount of injected CI did effect the corrosion rate very much.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The experimental study that was accomplished has generated several main conclusions such as follows:

1. LPR, EIS and LPR sweep showed that the corrosion rate has increased gradually in the period of 48 hours of the experiment for the baseline at pH 4.0 and 6.6. The reason was due to no protective layers formed on the metal surface to prevent from the attack of the corrosion mechanisms.

2. The application of corrosion inhibitors at volume of 25ppm technically perform really well in reducing the corrosion rate of carbon steel but only for a short period of time. At pH 4, fatty amine seems to better performing that QAC. As for the pH 6.6, both CI were helped by the formation of Iron Carbonate resulted in low corrosion rate at the beginning of the experiment.

3. The increment on injected CI proved that the amount of CI affect the reduction corrosion rate very much. Surprisingly enough, this was the case at the pH 4.0 where production of H^+ ions was significant.

5.2 Recommendations

Some suggestions are encouragingly needed to be included for the future work of this research. Another seven weeks left and surely many things to be finalized in order to have better results. The following are some recommendations that could be done to improve this project:

- Surface characterization of the X65 carbon steel has to be conducted in order to know the microstructure after the corrosion period. It will then help to confirm the main cause that prevent inhibitors from performing very well in this experiment.

- Experiment on varies temperature and volume of injected CI is needed to be conducted to critically examine the effect of environment and the amount of CI in reducing the corrosion rate of carbon steel efficiently.

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